

CHARACTERIZATION OF PHYSICOCHEMICAL PROPERTIES, PHOSPHORUS (P)
FRACTIONS AND P RELEASE OF THE EVERGLADES AGRICULTURAL AREA (EAA)
CANAL SEDIMENTS

By

JAYA DAS

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To my parents

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Jaya Das

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Cochair: George O'Connor
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Nutrient enrichment from the EAA particularly P is thought to be responsible for the ecosystem changes in the Everglades. Reduction of P loads from the EAA farms through the implementation of Best Management Practices (BMP) have been going on since 1995. Nevertheless years of P loading the EAA canal sediments portends that the sediments can act as P sources affecting water quality in downstream ecosystems for years to come.

Sediment physicochemical properties of the EAA farm and main canals were analyzed. The pH of the canal sediments varied from 7.1 to 8.0 and organic matter content ranged from 20 to 70%. Phosphorus fractionation indicated that the majority of P compounds in the sediments exist as Ca and Mg P, which is generally regarded as stable, but that can be released P over time. Unlike the sediments from the downstream ecosystems organic P content was insignificant and comprised about 6-13% of total P. Phosphorus release from Miami canal was greater than both WPB and Ocean canal. Equilibrium Phosphorus Concentration (EPC) measurements were used to identify sediments either as P sources or sinks. Higher P release from Miami canal sediments

resulted in higher EPC values compared to WPB and Ocean canal. The EPC values of Miami canal ranged from 0.07 to 0.15 mg L⁻¹, WPB canal 0.02 to 0.05 mg L⁻¹ and Ocean canal from 0.03 to 0.08 mg L⁻¹. Comparing the EPC_w values with the canal water column SRP concentrations, it was concluded that portions of Miami canal and Ocean canal were functioning as a P source. Thus the EAA main canals are the new P sources in addition to the established P sources to the Everglades including the agricultural farms, water from lake Okeechobee. Attempts to reduce P concentrations in the main canals by management of the farm canals can be compensated by P release from the main canal themselves. Thus maintenance and management of the main canals in at least the portions that were found functioning as P source is critical in order to reduce P loads to the Everglades.

CHAPTER 1 INTRODUCTION AND LITERATURE REVIEW

1.1 Role of Sediments in Eutrophication

Phosphorus (P) releases from sediments including sea (Smith, 1984) streams and lakes (Mortimer, 1941, 1942; Holdren and Armstrong, 1980) can result in nutrient enrichment and is considered an important control for the productivities of these water bodies. Studies on lake sediments in the Netherlands, Lijklema (1980), observed that depending upon hydraulic detention time about 50% to 100% of the total P load can accumulate in the sediments. This accumulated P can cause P release through internal loading and can lead to eutrophication of lakes through increased primary productivity (Lijklema, 1980). The flux of P in these water bodies play a key role in regulating the P concentration in the water column (Filippelli and Delaney, 1992, 1994), thus, understanding the processes that cause P release or P accumulation in sediments is crucial to comprehend P cycling and possible control mechanisms in these water bodies.

1.1.1 Phosphorus Cycling in Marine Sediments

Studies by Ingall and Jahnke (1994) have indicated that sedimentation of P in marine sediments are affected by the water oxygen concentrations and the sedimentation efficiency of oxygen depleted waters is lower than oxygen rich waters. Lower oxygen concentrations are also thought to be important in controlling the accumulation of organic matter in marine sediments (Thiede and van Andel, 1977). The reasons for the development of anoxic conditions and the resultant accumulation of organic matter in bottom waters of marine environments are thought to be due to reduced circulation of oxygen in deep waters accompanied by high productivity and

respiratory oxygen consumption (Herbert and Sarmiento, 1991). Organic matter oxidation and resultant P release in marine sediments can occur through a sequence of different pathways in the order of decreasing free energy yield per mole of carbon oxidized, that occurs sequentially through oxic respiration, denitrification, metal oxide reduction, sulfate reduction and methanogenesis respectively (Froelich et al., 1979). The actual scenario is much more complex since the reactants participating in organic matter decomposition take part simultaneously in other reactions as well. The composition of organic matter is also thought to influence P flux in marine sediments. Studies by Likens et al. (1981) showed that the C/P ratios of marine planktonic organic matter is around 106 whereas terrestrial organic matter has a ratio of 800 to 2050, which suggests that organic matter decomposition in sites containing a high proportion of marine planktonic material would yield higher P flux compared to terrestrial organic matter. Higher P flux from anoxic marine, lake or estuarine sediments relative to oxic sediments, can also result from the reduction and simultaneous P release from iron oxides due to high P sorption capacity of these oxides for phosphates (Lucotte and d'Anglejan, 1988; Buffle et al., 1989). Increased P flux due to reduction of iron oxides are more likely to occur at sites with low oxygen concentrations (Ingall and Jahnke, 1997). It is suggested that in sediments with oxic waters, oxic conditions can develop in the top few centimeters of the sediments that can prevent P release by oxidative precipitation of the iron oxides (Froelich et al., 1988). However, it is considered highly unlikely that the oxic layer will completely prevent P flux, rather it is thought that a steady state condition develops where the quantity of P precipitated is a function of the concentration of oxidized and reduced iron (Ingall and Jahnke, 1997). Working with lake

sediments Mortimer (1942, 1942) demonstrated the presence of an oxic microzone at the sediment water interface that inhibited P release from sediment layers below. Anoxic conditions in the overlying water however were shown to stimulate P release (Mortimer, 1941, 1942). Studies on bacteria and protozoa have shown that, they can store, utilize and release P that is dependent on redox conditions (Van Veen et al., 1993). Thus redox fluctuations can also cause P release from sediment bacterial communities. For example, *Acinetobacter* spp immobilizes or stores P under aerobic conditions and in oxygen depleted conditions uses the stored P as energy source that is subsequently released as dissolved P (Van Veen et al., 1993). During immobilization of dissolved P by bacteria, a fraction of the assimilated P can also be stored as recalcitrant organic P compounds. In marine environments, high fluoride concentrations can cause the precipitation of calcium phosphate phases like carbonate fluorapatite (Ruttenberg and Berner, 1993).

1.1.2 Phosphorus Cycling in Stream and Lake Sediments

Similar to marine sediments, researchers have suggested three important mechanisms for P release from lake sediments that are: P release from sediments under anoxic conditions (Mortimer, 1941, 1942; Holdren and Armstrong, 1980); resuspension of sediments (Reynoldson and Hamilton, 1982) and release of dissolved and particulate P from macrophytes (Landers, 1982). Increased P release under anoxic conditions have been studied in several lake sediments including mud sediments of Denmark (Kamp-Nielsen, 1974), estuarine sediments (Khalid et al., 1978), and near shore/littoral sediments (Bostrom and Pettersson, 1982).

In spite of the fact that anoxic conditions encourage P release, sediments in aerated waters have been shown to substantially release P (Ryding and Forsberg,

1977; Stevens and Gibson, 1977). It has been demonstrated that redox values can decrease to around 200 mV (Bostrom et al., 1982) at a depth of 1 cm in sediments under aerobic water column. The P release due to mineralization of organic matter, (Lee et al., 1977), high sediment pH and increasing temperature (Moller-Andersen, 1974) are considered important factors in affecting P flux from sediments in aerobic waters. Increased bacterial activities in sediment interface with aerobic water at high temperatures can create an anoxic microzone (Kamp-Nielsen, 1974; Holdren and Armstrong, 1980; Bostrom and Pettersson, 1982). Phosphorus release from such temporary or short time anoxic sediments can be affected by all the processes as in anoxic sediments (Kamp-Nielsen, 1974; Holdren and Armstrong, 1980). Increased temperature and resultant increased rates on microbial oxygen consumption in sediments have been universally shown to increase P release, (Holdren and Armstrong, 1980; Kelderman, 1984) although Holdren and Armstrong (1980) found that temperature increase had inconsequential effect on P release from non calcareous Wisconsin lakes. In contrast, it was found that increased temperature caused considerable P release from calcareous lake Wisconsin sediments (Holdren and Armstrong, 1980) and lake Vallentunasjon, Sweden (Bostrom and Pettersson, 1982).

Sediment resuspension in lake Arreso, Denmark, caused 20-30 times greater P release than undisturbed lake sediment (Sondergaard et al., 1992) and about 8-10 times greater P release in lake Taihu, China, (Fan et al., 2001). Interestingly enough bioturbation and resuspension of sediments was found to cause high P flux in calcareous lake Vombsjon, Sweden but inconsequential P releases from non-calcareous lakes Trummen, Sweden and lake Arungen, Norway (Graneli, 1979).

Sediment pH, presence of nitrates, diel variations, seasonal variations, temperature, bioturbation, microbial activity and presence of macrophytes, are other factors identified as factors affecting P release from lake sediments (Bostrom et al., 1982). Nitrate concentrations and pH have been shown to both increase and decrease P release (Andersen, 1982; Bostrom and Pettersson, 1982; Tiren and Pettersson, 1985). The presence of macrophytes and microalgae can considerably influence P flux by photosynthesis and respiration (Carlton and Wetzel, 1987). Photosynthesis of macrophytes and microalgae at low light intensities of as much as $<50 \mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ have been found to be sufficient to affect pH and oxygen concentrations in sediments (Carlton and Wetzel, 1987). Using oxygen sensitive microelectrodes, $^{32}\text{PO}_4^{3-}$ radiotracer and a flow through system using sediment cores collected from Lawrence lake, Michigan, Carlton and Weltzel (1988) demonstrated that consecutive photosynthesis and respiration can result in oxic conditions during day while anoxic conditions at night. This diel variation can result in the daily construction and destruction of oxidized microzone in surficial lake sediments (Mortimer, 1941, 1942) promoting P releases.

In addition to biogeochemical factors, stratification of water layers in lakes have been shown to affect P flux (Larsen et al., 1981; Riley and Prepas, 1984). The relationship between deepwater accumulations of P with the surface water P concentration is subject to study and research has shown a total P increase of about 139-1000% in surface water after P releases from sediments (Larsen et al., 1981). Studies in Nakamun and Halfmoon lakes in Alberta, Canada showed total P increase of 3-43% and 31-52% in the surface water compared to deep water (Riley and Prepas,

1984). The reason of the increase in total P in surface waters is not very clear but was attributed to mixing of resuspended sediments (Riley and Prepas, 1984).

1.1.3 Phosphorus Cycling in Estuarine Sediments

In estuarine environments, tidal flooding and ebbing present a dynamic and complex environment that includes tidal currents, sediment resuspension, settling of particulates, daily variation of water depth, which has been shown to influence P flux (Lillebo et al., 2004; Hakanson and Jansson, 1983). Lillebo et al., 2004 determined P flux in land forms in Mondego estuary, Portugal including seagrass beds, salt marshes, mud and sand flats without vegetation and concluded that P flux from all the estuarine land forms were higher during the first hours of a tidal flood and lowers at high tide. Lillebo et al., 2004 also showed that P release increased with the combination of shallow depth and enhanced temperature.

1.2 Everglades Agricultural Area (EAA)

The original Florida Everglades watershed was a broad, freshwater marsh that extended from what is now the Kissimmee River basin, through lake Okeechobee to the southern tip of the Florida peninsula. The historic flow, arising from a nearly flat land slope, was at very low velocity from north to south. Historically, the Everglades was a contiguous wetland rich in organic soils underlain by marl and limestone. The system was characteristically oligotrophic (Davis and Ogden, 1994) and P limited (McCormick et al., 1996). As a part for the Central and South Florida Project (1953 to 1967) the US Army Corps of Engineers (USCOE) drained and divided the Everglades into the Everglades Agricultural Area (EAA), the Water Conservation Areas (WCA) and the Everglades National Park (ENP). Drainage was accomplished by the construction of

over 2500 canals, levees and hundreds of water control structures (Chimney and Goforth, 2001).

1.2.1 Farming and Water Management in EAA

Agriculture in the Everglades began after drainage development (1906-1927) and expanded with the completion of several water control projects in the early 1950s (Snyder and Davidson, 1994). Today, the EAA consists of approximately of 2,872 km² of organic soils (SFER, 2010a). The main commercially grown crops in EAA are sugarcane, winter vegetables, rice (*Oryza sativa*) and sod (Bottcher and Izuno, 1994).

Water management in the EAA is crucial due to the flat topography of the area, and uneven rainfall distribution makes drainage compulsory (Bottcher and Izuno, 1994). During the wet season, surplus rainfall and runoff has to be pumped out of the EAA. During the dry season, irrigation water is supplied primarily from lake Okeechobee (SFER, 2010a).

1.2.2 Drainage and Concern about Nutrients

The EAA is divided into four agricultural basins, S-8/S3, S-7/S2, S-6, and S-5A, each drained by main canals originating from lake Okeechobee and emptying into the Atlantic Ocean. Drainage in EAA is accomplished using pumps and a network of field ditches and canals operated by pumps and gates. Ditches are on-farm waterways that discharge into the farm canals. Farm canals are controlled by privately owned pump stations and are used to irrigate and drain the farms which drain into the main canals. The S-8/S3 basin is drained by the Miami canal, the S-7/S2 basin by the North New River canal, the S-6 basin by Hillsboro canal and the S-5A basin drained by West Palm Beach and Ocean canal (Tracey, 2006)(see Chapter 2, Figure 2-1). Three connecting canals facilitate runoff and supply irrigation water: Bolles canal, Cross canal, and Ocean

canal (SFER, 2010a). The connecting canals do not originate from lake Okeechobee but connect the main canals.

Nutrient-rich agricultural drainage water generated in the EAA flows from the farm canals to the main canals (Stuck et al., 2002). On average, about $1 \times 10^9 \text{ m}^3$ of drainage water is discharged from the EAA annually (SFER, 2010a) and flows into the Everglades Protection Area (EPA) (Abtew and Khanal, 1994; Abtew and Obeysekera, 1996). The EPA consists of Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), Water Conservation Areas (WCAs), the Everglades National Park (ENP) and the Storm Water Treatment Areas (STAs) (SFER, 2009). The drainage/runoff of the EAA is the main source of surface water inflow into the EPA (SFER, 2009). The nutrient enrichment, specifically phosphorus (P), is cited as one of the causes of ecosystem changes in the WCAs and the ENP (LOTAC., 1990; Whalen et al., 1992).

Agricultural drainage water containing P from the EAA has been linked to several ecosystem changes including reduction in population of wading birds and intrusion of cattails into native sawgrass and slough habitats (Noe et al., 2001). Responses to P enrichment have been documented in several of the ecosystem components, including surface water (Koch and Reddy, 1992; McCormick et al., 1996), periphytons (Pan et al., 2000), soils (Koch and Reddy, 1992; Craft and Richardson 1993), macrophytes (Doren et al., 1997; Miao and Sklar, 1998) and consumers (Rader and Richardson, 1994). Efforts to mediate the environmental changes arising from modified flow include restoration efforts focused on reducing nutrient loading (especially P), and restoring a more natural hydroperiod to sensitive wetland areas (Light and Dineen, 1994).

1.2.3 Best Management Practices (BMPs) and Restoration

Remediation plans were dictated by the Everglades Forever Act (EFA) of 1994 [Section 373.4592, Florida Statutes (F.S.)]. The Restoration Planning and Permitting Program under the EFA is the principal guide in the restoration and protection of the Everglades ecological system. The Plan for Achieving Long-Term Water Quality Goals (Long-Term Plan) in EFA include control of P sources by implementation of BMPs for P reduction, (SFER, 2009).

Categories of BMPs implemented in the EAA to control agricultural drainage water runoff quality include water management, nutrient management and control of particulate matter from farms and canals (SFER, 2002). Practices include modifying pumping practices, protecting canal banks with vegetation, minimizing fertilizer application, using cover crops, and retention of on-farm drainage (SFER, 2002).

The BMP regulatory program requires P loads in drainage water leaving the EAA to be reduced by at least 25% relative to the historic levels (SFER, 2009). The Comprehensive Everglades Restoration Plan (CERP) was authorized in 1999 as part of the Federal Water Resources Development Act to protect the ENP. Under CERP, the South Florida Water Management District (SFWMD) constructed six large wetlands located between the EAA and WCA, to remove excess P from agricultural drainage water before it is discharged into the WCA canals. The wetlands also called the Storm Treatment Areas or STAs range in size from 3500 to 6700 ha are situated along the SFWMD main canals that treat discharges from the Everglades basins (Chimney and Goforth, 2001).

1.2.4 Particulate P in EAA Drainage

The nature and composition of particulate matter from farms can considerably influence the physical and chemical properties of the EAA canal sediments. The predominantly organic particulate matter is light and flocculent that can be easily transported to downstream ecosystems (SFER, 2004; Dierberg and DeBusk, 2008) as suspended particles spread throughout the entire water column (Daroub, 2002a). The P content of particulate materials containing a mixture of detrital waterweeds and planktonic growth can range from 1500-3500 mg kg⁻¹ for waterweeds and from 9000-15000 mg kg⁻¹ for different planktons. The particulate P can increase P storage in EAA canal sediments and in the P limited downstream ecosystems.

Drainage water from EAA consists of dissolved P and particulate P. The source of dissolved P can be fertilizers and mineralized soil organic matter (Daroub et al., 2002a). Izuno and Rice (1999) estimated that particulate P constitutes about 20 to 70% of the total P exported from EAA farms. Particulate P consisting of filamentous algae, plankton, macrophyte particles and soil particles dominate P export of agricultural drainage water from the EAA farms (Stuck, 2001). Apart from EAA farms, particulate P can also arise from erosion of P-enriched canal banks (Andreis, 1993; Hutcheon Engineers, 1995). The biological nature of particulate P and the presence of calcium carbonate bedrock influence the sediment characteristics. The EAA bedrock formed from precipitated calcium carbonate (CaCO₃) (Scott, 1997) can influence sediment properties including pH, mineralogical composition and distribution of different P fractions.

1.3 Physicochemical Properties and P Fractions of EAA Canals

1.3.1 pH

Soils and sediments in Everglades have circum-neutral pH compared to extremely low pH values found in organic and peat soils. The pH values of sediments in WCA-2A are around 7.2 (DeBusk et al., 1994) and, in WCA-3A around 7 (Swift and Nicholas, 1987). The pH values of cultivated soils in EAA, was found to be around 7.3, 7.4 and 6.6 for Dania, Lauderhill and Pahokee soil series respectively (Janardhanan, 2007). Typically rain fed peat lands are low in plant nutrients and have low pH values between 3 and 5.5 (Clymo et al., 1984) but at the same time extremely acidic Histosols with pH values around 3, have also been observed in drained coastal region bogs containing pyrite (FeS_2) (White et al., 1997).

Sediment pH values can influence the distribution of different P fractions. Phosphorus in alkaline wetland sediments tend to be preferentially retained as insoluble Ca-P or Mg-P compounds (Moore and Reddy, 1994; Reddy et al., 1999; Richardson, 1999), whereas Fe and Al-phosphate compounds tend to dominate in wetland systems with low pH values (Khalid et al., 1977).

Several laboratory studies have demonstrated increased P flux from sediments to the overlying water column with increasing pH (Andersen, 1975). High pH values facilitate P release from sediments by competition between hydroxide (OH^-) and phosphate (H_2PO_4^-) ions for sorption sites on iron (Boström, 1984). The proposed release mechanism was supported by a correlation between pH and internal phosphorus loading (Walker, 2001).

1.3.2 Organic Matter

Farm canals in EAA can retain drainage water for long periods during which plant detritus, algae and macrophyte particles accumulate until they are discharged by pumps to the farm canals (Dierberg and DeBusk, 2008). The accumulation of organic matter in farm canals can influence sediment physical properties as well as quality of the overlying water column.

The light and flocculent nature of organic matter accumulated in EAA canals leads to surface layer sediments with lower bulk densities than subsurface layers and affect transport properties. During aerobic decomposition of organic matter, P and other elements associated with organic matter along with carbon are mineralized, releasing P (Qualls and Richardson, 2008). Anoxic conditions prevailing in sediments promote fermentation of organic matter, which can also release P (Goltermann, 2001). Organic acids released during fermentation can reduce the interstitial pH, dissolve carbonate minerals, and release associated P (Marsden, 1989). The organic acids chelate with calcium, iron, manganese and aluminum, thereby promoting P release (Boström et al., 1982; Stauffer and Armstrong, 1986)

1.3.3 Bulk Density

Sediments can affect water quality wherever they are transported, and the transport of sediments in EAA is profoundly affected by the pumping rates. Rates are easily doubled or tripled by running multiple pumps or by switching from small to large capacity pumps (SFER, 2004). Sediment transportability varies with pumping rates, velocity of water in the canals and bulk density of sediments (Lick et al., 2001). Studies in the EAA have shown that lower sediment bulk densities were related to greater transportability (Daroub et al., 2002b). Sediment erosion rates (cm s^{-1}) of river

sediments determined by Jepsen et al. (1997) in laboratory studies were unique functions of bulk density, and decreased as the bulk density increased.

Low bulk densities make sediments susceptible to resuspension that can affect water quality. Resuspension of lake sediments in the wind-exposed lake Arreso, Denmark, resulted in P loading 20-30 times greater than loading from undisturbed lake sediment (Sondergaard et al., 1992). Storm events that resuspend sediments have the potential to enhance P mobilization by increasing sediment surface for P release, as well as by carrying P mass into the water column from sediments (Laenen and LeTourneau, 1996).

1.3.4 Phosphorus Fractions

The general nature of canal sediments in the EAA has been investigated by measuring total P content in suspended solids of drainage water from EAA farms (Stuck, 1996; Stuck et al., 2001; SFER, 2006), but the exact chemical nature of the sediments is not known. The forms in which total P is chemically held is best understood by sequential fractional techniques that extract theoretically discrete forms of P, removing one component after another (Graetz and Nair, 1995; Reddy et al., 1995). The quantification of the different P fractions can be useful in predicting P responses to physicochemical changes and in understanding the internal P cycling (Olila et al., 1994). James et al. (1995) studied sediments of lake Pepin and showed that P could be released under both oxic and anoxic conditions. Release depended on P forms, and P release rates correlated with the labile and Fe and Al associated P.

Phosphorus fractionation schemes divide P into inorganic and organic fractions of different solubility and identify the nature and distribution of the different P fractions, including labile and recalcitrant P fractions. Reddy et al. (1995, 1998) suggested

fractionation schemes consisting of five steps: KCl extractable P (KCl-Pi), NaOH extractable P, HCl extractable P (HCl-Pi), and residual P (Residue-P). The KCl-Pi fraction represents labile Pi that is water soluble and exchangeable (loosely adsorbed); NaOH extractable P represents Fe- and Al- bound P (NaOH-Pi) and humic and fulvic acids (NaOH-Po). The HCl-Pi fraction represent Ca- and Mg- bound P, and residue-P represents recalcitrant organic P compounds and P bound to minerals.

1.4 Nutrient P and Internal Loading

1.4.1 Internal P Loading

The ultimate goal of farm BMPs and constructed wetlands is to deliver water of low P concentration to the downstream ecosystems in South Florida. Historic P loading to main canals, and the resulting P flux from accumulated sediments to the water column, is a potential additional source of P. A reduction in external P load does not always translate in a decrease in total P in the water column because high internal sediment P load can initiate and sustain algal blooms and eutrophication (Welch and Cooke, 1995). The quantity of P stored in the sediments is great compared to P in the water column, so even small amounts of P released from sediments can significantly impact P concentrations in the water column (Boström et al., 1982). Internal loading is the recycling of nutrients from bottom sediments to the overlying water column (Carpenter, 1983). After external load reduction, internal loads of sediments determine the trophic status of a water body and the time for recovery (Petterson, 1998). It is suggested that P stored in surface soils in the EAA can sustain a P load of 170 mt per year for 47 to 118 years to the downstream ecosystems (Reddy et al., 2010).

1.4.2 Equilibrium Phosphorus Concentration (EPC)

Equilibrium Phosphorus Concentration (EPC) values can indicate previous loadings to the sediments (Martin, 2004). The extent of internal loading from the sediments can be determined by the EPC (Martin, 2004). The EPC is the P concentration in the water column at which no net flux, i.e. release or retention, occurs from the sediments to the water and the P in solution is considered to be in equilibrium with P in the solid phase (Reddy et al., 1999). The concept of EPC has been used to understand the quantity and direction of soluble reactive phosphorus (SRP) flux in sediments (House and Denison, 2002). At water column SRP concentrations above the EPC, SRP is retained by the sediments, whereas at SRP concentrations below EPC, the sediments serve as source for SRP (Reddy et al., 1995; Pant and Reddy, 2001; Zhou et al., 2005).

Agricultural input of P into the canals can increase the EPC values of the sediments and reflect P loading (Reddy et al., 1998). Determination of EPC values in the Everglades have been conducted in the Kissimmee River watershed, lake Okeechobee sediments, the dairies and farms north of the lake and the Water Conservation Areas. For example, the EPC values of stream sediments in Lower Kissimmee River Basin, Florida, was around $0.013 \text{ mg P L}^{-1}$ (Martin, 2004). The nutrient-impacted wetland soils in Fisheating Creek and Istokpoga Basins had EPC values of 1.95 and 3.9 mg P L^{-1} respectively (Dunne et al., 2005). Clark et al. (2002) noted the wide spatial and temporal variability of internal P loads and P release potentials within the south Florida canals adjacent to the EAA and the Water Conservation Areas (WCAs). The roles that the canal sediments play in maintaining P levels in EAA canal waters are largely unknown; thus measures of internal loading and

EPC values of the EAA canal sediments are critical to determining the P status and extent of P loading in the sediments.

1.4.3 Mineral Solubility and Internal P Loading

Phosphorus flux from the sediments to the overlying water column can be controlled by mineral solubility (Haggard, 2005). Oxygenated water has a redox potential of around +500 mV, but the potential decreases rapidly below the sediment surface and anoxic and reducing conditions predominate (Boström et al., 1982). At sediment depths > 1 cm, redox potentials < 200 mV and oxygen concentrations ~ 0.1 mg L⁻¹ can develop (Boström et al., 1982). Amorphous Iron (III) oxides and hydroxides are reduced at Eh values around 200mV, thereby releasing phosphate to the water column (Boström et al., 1982).

Mineralogical studies on the presence or absence of mineral P forms in the canal sediments can explain the P dynamics in canal sediments. Non apatitic Ca-P compounds were found in the lake Apopka sediments suggesting that P in the sediments was due to the P coprecipitation with CaCO₃ (Olila and Reddy, 1995). Sediments in lake Okeechobee contained quartz and calcite but no P-associated minerals (Olila et al., 1994). The lack of crystalline forms of Ca-P minerals was attributed to insufficient time for mineral formation or inhibition in mineral formation by humic acids or other ions (Harris et al., 1994).

1.4.4 Organic P and Internal P loading

Organic P can occur in dissolved, particle associated and colloidal forms and can contain a wide variety of compounds including phospholipids, nucleic acids, inositol phosphates, phosphoproteins, sugar phosphates, phosphonic acids, humic associated organic compounds, polyphosphates and pyrophosphates (McKelvie, 2005).

Condensed P compounds, such as polyphosphate and pyrophosphate, are termed biogenic P, i.e., inorganic P compounds derived from organic compounds (Hupfer et al., 2004). Hupfer and Lewandowski (2005) showed that organic P compounds can influence internal loading of P. Ahlgren et al. (2006) studied Baltic sea sediments and concluded that degradation of organic P compounds were involved in the internal loading from the lake sediments. Enzymes like alkaline phosphatases are thought to hydrolyze organic phosphate esters, thereby releasing dissolved P (Boström et al., 1982).

Robinson et al. (1998) conducted ^{31}P NMR spectroscopic studies on the wetland soils of Apopka Marsh, Eustis Muck Farm, and Sunny Hill Farm (SHF) Florida and identified phytate, along with different inorganic ortho P esters and organic mono and diesters. Pant et al. (2002) identified polynucleotides, nucleoside monophosphates, and glycerophosphoethanolamine and phosphoenolpyruvates in inflow sediments of STA-1W. Turner et al. (2006) identified inorganic orthophosphate, phosphate monoesters, DNA and pyrophosphate in sediments from STA-1W. Turner and Newman (2005) found phosphate, phosphate monoesters, DNA, and pyrophosphate in the sediments of WCA-1 and 2A. Confirming the presence or absence of the organic P compounds in the canal sediments should help determine whether the canal sediments are the source of these organic P compounds to the EAA canals and downstream ecosystems.

1.5 Research Objectives

Knowledge about the physical and chemical properties of the EAA canal sediments is important to enhance our understanding of the entire Everglades system. Sediment properties can affect the water quality in the canals as well as downstream ecosystems, owing to the easy transportability of the sediments.

The objectives of this research were to:

- Determine the spatial variability of EAA farm canal sediments with respect to physicochemical properties and P fractions (Study 1, Figure 1-1).
- Determine the spatial variability of EAA main canal sediments with respect to physicochemical properties and P fractions (Study 2, Figure 1-2).
- Determine the P release potential of the EAA canal sediments (Study 3, Figure 1-2).
- Determine the EPC values of the sediments by adsorption isotherm and incubation studies (Study 4, Figure 1-2).

1.6 Dissertation Format

The dissertation consists of four major studies to address objectives in a manuscript format. Chapter 1 includes literature review of factors influencing P releases from marine, lake and stream sediments. Thereafter, the literature review focuses on EAA. Chapter 2 evaluates the physicochemical properties and P fractions of the EAA farm canal sediments. Chapter 3 evaluates the EAA main canal sediments with respect to their physicochemical properties, P fractions and mineralogical properties. Attempts are made to understand the P release potential of main canal sediments using information on sediment physical and chemical properties. A detailed site description of the farm and main canals are provided in Chapter 2 and 3. Sediment P fluxes from main canal sediments were determined using an incubation experiment that is reported in chapter 4. Chapter 5 is on the evaluation of the Equilibrium Phosphorus Concentrations (EPC) of the main canal sediments that was performed using two separated experiments; incubation of sediment cores and adsorption isotherm. Overall summary and conclusions are presented in Chapter 6.

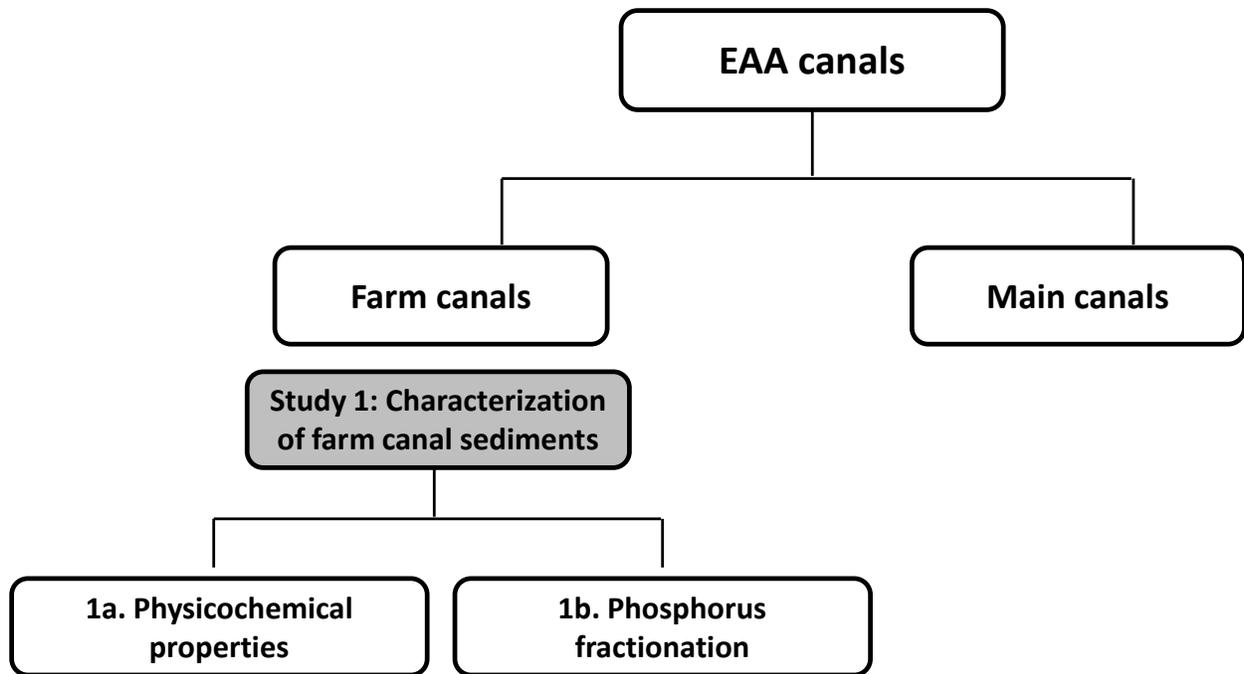


Figure 1-1. Flowchart of the different experimental steps performed upon the EAA farm canal sediments.

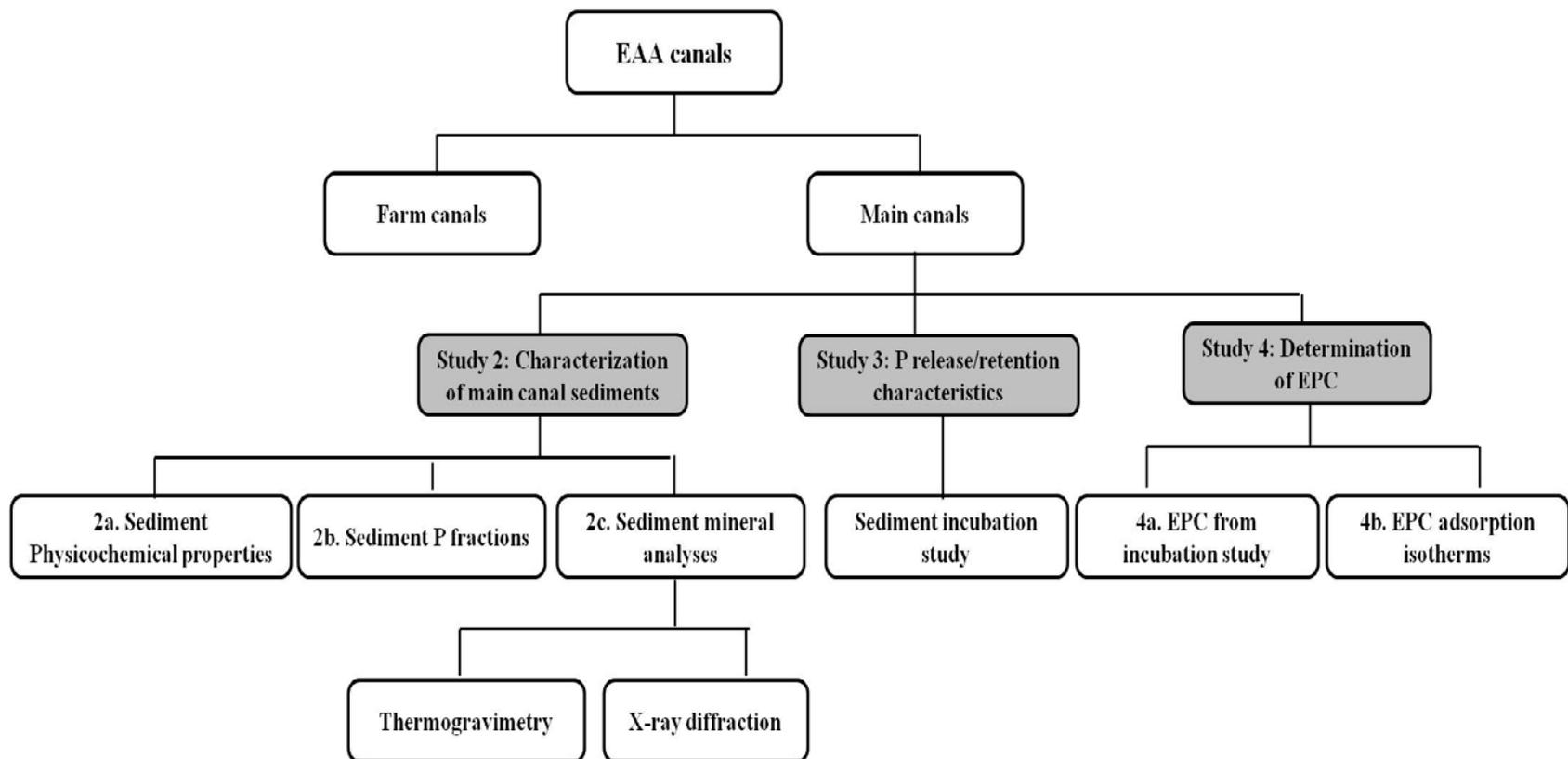


Figure 1-2. Flowchart of the different experimental steps performed upon the EAA main canal sediments.

CHAPTER 2
PHYSICOCHEMICAL CHARACTERISTICS AND PHOSPHORUS FRACTIONS OF
THE EVERGLADES AGRICULTURAL AREA (EAA) FARM CANAL SEDIMENTS.

2.1 Introduction

2.1.1 Historical Background

The original Florida Everglades watershed was a broad, freshwater marsh that extended from what is now the Kissimmee River basin, through lake Okeechobee, to the southern tip of the Florida peninsula consisting of an area of more than 10,000 km² (Light and Dineen, 1994). The historic flow arising from a nearly flat land slope was at very low velocity from north to south. Historically the Everglades was a contiguous wetland rich in organic soils that was drained for agriculture by the construction of over 2500 canals and levees and hundreds of water control structures (Light and Dineen, 1994). Presently the Everglades is fragmented into the Everglades Agricultural Area (EAA), the Water Conservation Areas (WCAs) and the Everglades National Park (ENP). The EAA presently comprises of 2,872 km² of organic soils (SFER, 2010b) drained during 1953 to 1967 by the US Army Corps of Engineers for flood protection and agricultural production (Chimney and Goforth, 2001). The wetland remains of ENP, the WCAs and the Holeyland and Rotenberger Wildlife Management Areas is considered an ecosystem of immense importance because it contains a multitude of habitats that supports unique biotic communities. Everglades National Park, the largest subtropical wilderness in the United States has been declared as a Wetland of International Importance under the 1987 Ramsar Convention, an International Biosphere Reserve and as a United Nations World Heritage site and (Maltby and Dugan, 1994).

Agriculture in EAA is focused on sugarcane but other crops like corn, winter vegetables and sod are also grown (Bottcher and Izuno, 1994). The hydrology of the

EAA is managed by the South Florida Water management District (SFWMD) and the region is drained by network of field ditches and canals. Nutrient rich agricultural drainage water is pumped from the farm canals to the main canals and, the WCAs and finally discharged into the downstream ecosystem including the ENP. The farm canals are used to irrigate and drain the farms which drain into the main canals. The main canals originate from lake Okeechobee and ultimately drain into the Atlantic Ocean (Light and Dineen, 1994).

Native Everglades vegetation including sawgrass and upland pine (*Pinus spp*) is adapted to low nutrient levels and is P limited (Davis and Ogden, 1994). Nutrient enrichment from EAA agricultural drainage, specifically phosphorus (P), has been identified as one of the causes of ecosystem changes in the WCAs and the ENP (LOTAC., 1990; Whalen et al., 1992). About 129 metric tons of total P load with total P concentration of $119 \mu\text{g L}^{-1}$ from the EAA was estimated to have been discharged in 2009 (SFER, 2010a). To mediate the environmental changes, restoration efforts have focused on reducing nutrient loading from EAA and restoration of a more natural hydroperiod to sensitive wetland areas of WCAs and ENP (Light and Dineen, 1994). Current remediation plans require area growers to implement Best Management Practices (BMPs) in EAA. Practices include modifying pumping practices, protecting canal banks with vegetation, minimizing fertilizer application, using cover crops, and retaining of on-farm drainage to reduce P discharge to the canals of the EAA (SFER, 2003; SFER, 2002). To further treat agricultural drainage water, several wetlands called Storm Treatment Areas (STAs) have been constructed in the southern edge of the EAA.

2.1.2 Phosphorus in the EAA

Agricultural farms in EAA are privately owned and managed by growers. The farms are drained by farm canals that discharge into the EAA main canals. Along with the flow of water, canals can carry suspended solids, nutrients and other constituents from the farms can either accumulate or be further transported depending upon the canal management practices. Phosphorus in the EAA farms can be sourced from fertilizer application to agricultural farms, inflow water from lake Okeechobee or the mineralization of the organic soil (Stuck, 1996). Historically before the initiation of farming rainfall was the dominant source of P in the Everglades (Davis, 1994).

Phosphorus sorbed by soil particles and organic materials is termed particulate P and consists of solid phases of P (Diaz et al., 2005). Particulate P constitutes about 20 to 70% of the total P exported from EAA farms (Izuno and Rice, 1999). The P in organic particulate P consists of a mixture of detrital water-weeds, and planktonic growth that can range from 1500-3500 mg kg⁻¹ and 9000-15000 mg kg⁻¹ respectively (Daroub et al., 2002a). Particulate P in agricultural residues in EAA is highly variable and varies with land use and management practices. Farms in EAA grow different crops with different fertilizer requirements and management practices. In a study conducted by the engineering firm CH2M Hill (1978), vegetable farms in EAA were shown to have an annual total P load four times than that of sugarcane farms. Canal management factors like pump velocity, canal depth and canal maintenance can determine particulate P load from canals (SFER, 2004). The pump operated water movement in EAA is characterized by rapid hydrodynamic changes that are different than a natural system thus causing the EAA canal systems to undergo changes from static conditions to very high velocities (Daroub et al., 2002b). Hydraulic quiescence period in canals can

facilitate particulate deposition and increase the concentration of organic particulates (Engle and Melack, 1990) subject to remobilization during flow conditions (Daroub et al., 2002b; Svendsen et al., 1995). Good aquatic weed management program can prevent accretion of particulate P in farm canals, resulting in lower total P and organic matter content than in canals that do not have similar management programs. The light and flocculent nature of the predominantly organic particulate matter is easily transportable to the downstream ecosystems (SFER, 2004; Dierberg and DeBusk, 2008).

Accumulation of particulate matter can lead to higher total P and organic matter content on the surface sediments compared to the subsurface sediments, as has been observed in the Everglades (Newman et al., 1997; White and Reddy, 2001, 2003).

Physicochemical properties of EAA farm canal sediments can be vary with the geological (mineralogical) composition of bedrock at that location. The presence of calcium carbonate bedrock can also influence sediment properties including pH, mineralogical composition and distribution of P fractions. The calcium carbonate bedrock in combination with the biological nature of particulate P can influence the sediment physical and chemical properties in EAA canal sediments. The heterogeneous mixture of organic matter with various levels of P content have variable transport properties (SFER, 2004), which can lead to changes in sediment properties within different locations of a canal. Other factors leading to differential physicochemical properties along canals can be changes in sediment depth, varying degree of incorporation of limestone into sediments, presence of structures obstructing sediment transport.

Due to the underlying limestone bedrock and the accumulation of particulate matter on top, the EAA canal sediments are very different from either organic or mineral soils. The biological nature, the heterogeneity of the suspended solids, varied erosion rates, sedimentation velocities, and rates of disengagement of attached plant growth, result in dynamic changes in the sediments and the overlying water column that may not occur in systems that are predominantly mineral in nature (Daroub et al., 2002a).

The differences in the mobility and reactivity of the P stored in EAA canal sediments are controlled by the chemical composition and forms of P in sediments. The ability of sediments to store or release P has repercussion on water quality as well as on management and restoration strategies. The detailed study of sediment P fractions is critical to a better understanding the P cycle in the EAA canals.

2.1.3 Phosphorus Fractionation

Phosphorus fractionation allows us to distinguish and quantify both inorganic and organic pools of P, and the recalcitrance of these P pools. Phosphorus availability from different P pools can determine the mobility of stored P, which can affect water quality of the canals. Phosphorus fractionation methods are operationally defined and involve selective dissolution of different P forms in different solvents (Ivanoff et al., 1998). Loosely bound P or labile P is extracted using salt solutions like KCl, NH₄Cl and NaCl (Reddy and Delaune, 2008). Following the extraction of loosely bound P, alkali (NaOH) is used to extract Fe and Al bound P. Acid (HCl) is subsequently used to extract Ca and Mg bound P. Other alkali extractants used by researchers to extract Fe and Al bound P, are NaOH with citrate-ditionite-bicarbonate (CDB). Hieltjes and Lijklema, (1980) concluded that NaOH and CDB was unsuitable for the extraction of Fe and Al bound P in calcareous sediments because the strongly complexing citrate solubilizes substantial

quantities of Ca bound P. Residual P is the P fraction left when all other P fractions i.e. labile P, Fe and Al bound P and Ca and Mg bound P are extracted. The residual P is considered to be mostly recalcitrant organic P or P that is occluded into mineral matter.

Phosphorus fractionation procedures have been used to investigate the transformation and P movement in upland soils (Tiessen et al., 1983; Beck and Sanchez, 1996), organic wetland soils (Ivanoff et al., 1998), lake sediments (Hieltjes and Liklema, 1980) and calcareous sediments (Clark and Reddy, 2002). In South Florida, White et al. (2004) performed inorganic P fractionation (KCl-NaOH-HCl) on sediments from STA-1W and found that the Ca phosphates and residual P accounted for more than 75% of total P, with half of all P present as organic P. Phosphorus fractionation on sediment samples of the WCA-1 performed by Newman et al. (1997) showed that almost 70% of the total P was organic in nature. The constructed wetlands in Everglades or the STAs operate as flow-through treatment systems to reduce phosphorus levels entering the Everglades by removing P through emergent aquatic vegetation, submerged aquatic vegetation, periphyton and sediment accretion (Chimney and Goforth, 2010). The WCAs are shallow diked marshes maintained for flood control, water supply, and environmental restoration. The hydrologic regime and vegetation in wetlands promote accumulation of organic matter due to low decomposition rates under flooded conditions (DeBusk and Reddy, 1998) resulting in organic matter accumulation rates in the WCAs in the order of millimeters per year and in the Everglades about cms per year (Craft and Richardson, 1993; Reddy et al., 1993). High organic matter accumulation rates in the Everglades wetlands result in higher organic P than in EAA canal sediments.

The KCl-NaOH-HCl fractionation scheme was applied by Diaz et al. (2006) on the canal sediments within the STAs to evaluate the different inorganic and organic fractions of P. They found that Ca and Mg bound P and residual P were the dominant P forms in these canals. Though successfully performed on the sediments and soils of the STAs and the WCAs, this fractionation scheme has not been used to analyze the canal sediments within EAA.

We hypothesize that the (i) physicochemical properties of EAA farm canal sediments vary with depth (surface and subsurface layers) and between locations in the farm canals, and (ii) sediment P fractions vary with depth (surface and subsurface layers) and between different locations within the farm canals.

The objectives of this study were to (i) characterize physicochemical properties in surface (0-5 cm) and subsurface (5-10 cm) sediments from different locations of three EAA farm canals and (ii) characterize sediment P fractions in surface (0-5 cm) and subsurface (5-10 cm) sediments from different locations of three EAA farm canals.

2.2 Material and Methods

2.2.1 Site Description and Sample Collection

Sediments were collected from three farm canals: UF9209A (09A), situated in the western part of the EAA; UF9200A (00A), situated in the eastern part of EAA; and UF9206AB (06AB), located in the southeastern EAA near STA-1W (Figure 2-1).

Farm 09A is a large (12.4 km²) sugarcane monoculture farm drained by three manually operated pumps (6.31-36.8 m³ min⁻¹ range). Farm 09A is situated within Terra Ceia (Typic Haplosaprists) and Pahokee (Lithic Haplosaprists) soil map units. Depth to bedrock range from 50.8-91.4 cm (West Palm Beach Soil Survey, 1978) at farm 09A, which is situated in the S8 basin (Figure 2-1). Farm canal 09A represents a large farm

with a large canal relative to pump capacity and the farm canal has low velocity (0.13 m s^{-1}) (SFER, 2004). Owing to low pump velocity and moderately large canal depth (0.98 m) (Daroub et al., 2009), farm canal 09A sediments are slow to mobilize or have long response times (SFER, 2004). Particulate P from farm canal 09A averaged about 70% of total P (SFER, 2004). Farm canal 09A drains into the Miami canal.

Farm 00A is located in the eastern part of EAA and is a medium-size (5.18 km^2) sugarcane monoculture farm. It is drained by two high capacity ($9.46\text{-}29.44 \text{ m}^3 \text{ min}^{-1}$ range), and one lower capacity ($5.2\text{-}8.93 \text{ m}^3 \text{ min}^{-1}$ range), single speed electrical pumps with automatic on-off level control. Automatic level controls ensure that the farm canal is drained regularly and that water is not held up for a long time, which prevents the accumulation of particulate P. Farm 00A consists of Terra Ceia (Typic Haplosaprists) and Pahokee (Lithic Haplosaprists) soil series with depths to bedrock $>129.5 \text{ cm}$ and $91.4\text{-}129.5 \text{ cm}$ respectively. Farm 00A is situated within the S5A farm basin and has average sediment dredging program and clean the canals as necessary. Average sediment dredging program consists of cleaning canals when thought necessary by the farm owner in contrast to a periodic program. There was no major canal work conducted on farm canal 00A over a period of four years (SFER, 2004). Farm canal 00A sediments (due to high velocity flow in the canals) responds faster than farm canal 09A sediments, i.e. farm 00A sediments are likely to be transported than 09A canal sediments. Farm 00A receives irrigation water and discharges into the West Palm Beach canal.

Farm 06AB is a medium-size (7.08 km^2) mixed-crop farm located in the S-5A sub-basin in eastern part of EAA. Farm 06AB consists of Terra Ceia (Typic Haplosaprists) and Pahokee (Lithic Haplosaprists) soil series, and depth to bedrock ranges from

>129.5 cm and 91.4-129.5 cm, respectively. Farm 06AB has two pump stations, each with two high capacity diesel pumps. This farm is partitioned into multiple hydraulic units and has a sophisticated hydraulic system with culverts, risers and booster pumps placed strategically throughout the farm. Farm 06AB includes multiple control structures that allow an aggressive water management program that prevents build up of particulate P in the farm canal (SFER, 2004). Farm 06AB has depth 0.88 m (Daroub et al., 2009) lower than both farm canals 09A and 00A. Farm canal 06AB has the highest average velocity 0.27 m s^{-1} which causes particulates in the canal to mobilize faster than both 09A and 00A. Thus canal 06AB is likely to have greater mineral matter content than the deeper 09A (0.98 m) and 00A (1.16 m) canals as the light and flocculent particulates could be transported along the canal (SFER, 2004). Irrigation and drainage in farm 06AB is accomplished through farm canal 06AB which drains into the Ocean canal.

Sediment cores were collected from five transects within each of the three farm canals (Figure 2-1). The first transect (T1) was near the intersection where the farm canals drain into the main canal, i.e., where farm canal 00A drains into the West Palm Beach canal, 09A drains into the Miami canal and the 06AB drains into the Ocean canal. The remaining four transects (T2, T3, T4, and T5) of each canal were taken progressively away from T1 into the central part of the canals. Triplicate sediment cores were collected at each transect within the middle two thirds of the canal cross-sectional area.

All the transect locations (T1 to T5) in each of the canals were geo-referenced by the GPS coordinates using a Trimble Unit Pro-XR DGPS Unit (Trimble Navigation

Limited Mapping and GIS Systems, Sunnyvale, CA). The GPS position and the distance between transects are given in Appendix A (Tables A1, A2 and A3). At each transect location two steel rebars were installed at the edge of the water on each side of the canal. During sediment sampling, a steel cable was attached to the rebars to anchor a boat used during measurements. Sediment cores were collected using a sediment sampler fitted with a polycarbonate core that was inserted on the sediment bed. The sampler along with the core was then quickly pulled up into the boat, stoppered at both ends and transported upright to the laboratory. The sediment cores were stored at 4°C until sectioned, which was done within 24 h of sampling. The water in the columns was removed by vacuum suction and the sediment sectioned at depth increments of 0-5 cm and 5-10 cm. Sediment samples were stored in plastic jars at 4°C until analysis. A total of 3 replicates were taken from each of the 5 transects from each canal leading to 15 sediment cores from each canal, totaling up to 45 cores from the three canals.

2.2.2 Sediment Analyses

All sediment samples were analyzed for total P, bulk density (BD), %Loss on ignition (%LOI) and pH. Loss on ignition was determined by combusting an oven-dried sediment sample at 550°C for 4 h in a muffle furnace, and the weight loss was considered a measure of the organic matter content. (Andersen, 1974). This method was based on the principle that, at the chosen temperature, all organic carbon was converted to CO₂, whereas loss of CO₂ from carbonates and loss of water from clay minerals are negligible. Thermogravimetric studies using standard calcium carbonate by Kasozi, (2007) indicated that the required activation energy needed for decomposition of calcium carbonate necessitates a temperature of at least 600°C. Kasozi, (2007) concluded that the decomposition of calcium carbonate was energy reliant rather than

temperature reliant. Similar results using thermogravimetry were also observed by Singh and Singh (2007). The atmospheric partial pressure of CO₂ is 0.00035 Pa. It is suggested that, in a closed furnace undergoing decomposition of CaCO₃ the partial pressure of CO₂ can increase which necessitates high temperature of decomposition (Lide, 2005). In fact there has been attempts to lower the calcium carbonate decomposition temperature using carboxylic acids primarily to save energy in the cement industry (Kasselouri et al., 1995). The ash from the muffle furnace was digested with 6N HCl and analyzed for total P using the ascorbic acid method (Method 365.4, U.S. Environmental Protection Agency, 1983) using an Alpkem segmented-flow 650 nm analyzer (The limit of detection for the Alpkem analyzer was 0.007 mg L⁻¹). Bulk density was measured by placing 10 g of sediment in glass beaker in an oven at 105°C for 12 h. Sediment pH was determined by weighing 10 g of sediment and adding 20 mL of DI water (mass to volume ratio - 1:2) (Thomas, 1996).

The P fractionation scheme developed by Reddy et al., 1995, 1998 was used in this study. The five step fractionation included of both organic (o) and inorganic (i) fractions of P: KCl extractable P (KCl-Pi), NaOH extractable P, HCl extractable P (HCl-Pi), and residual P (Residue-P). The KCl-Pi fraction represents the labile Pi that is water soluble and exchangeable (loosely adsorbed); NaOH extractable P represents Fe- and Al- bound inorganic P (NaOH-Pi) and organic P associated with humic and fulvic acids (NaOH-Po). The HCl-Pi are the Ca- and Mg- bound P, while Residue-P represents recalcitrant organic P compounds and P bound to minerals.

The fractionation procedure involves sequential extraction of 0.3 g dry sediment equivalent of wet sediments with 1 M KCl, 0.1 M NaOH, and 0.5 M HCl solutions in that

order. Residual P fraction was determined in the residues left after solution extractions and involved ashing followed by dissolution with 6N HCl acid. Details of the fractionation are given in Reddy et al. (1998). Concentrations of P in the filtrates of each sequential extraction and the acid digestion were determined by colorimetry using Spectronic 20 Genesys spectrophotometer and Lachat Quickchem FIA 8000 series (Murphy and Riley, 1962). Quality assurance/quality control was strictly followed with calibration, standards, spikes, and blanks routinely included in the analysis. A check standard was included every 10 samples and a duplicate after every 10 samples. A spike was included for every 20 samples. The limit of detection for the Lachat Quickchem was 0.001 mg L⁻¹.

2.2.3 Statistical Data Analysis

Descriptive statistics of means, standard deviation and standard errors (proc MEANS), were performed on data collected from the sediment sample analysis using SAS statistical program (SAS Institute, 2003). Normality and goodness-of-fit tests were conducted to check the distribution patterns of the physico-chemical properties and P fractions data. Where the data were not normally distributed, log-transformations were used to stabilize the variance, and make the residuals Gaussian distributed for parametric analysis. Analysis of variance (ANOVA) was used to compare sediment physico-chemical properties and P fractions between canal transects (USEPA., 1989). Summary statistics were conducted and Tukey test were used (SAS Institute, 2003) to assess significant differences between physicochemical properties, P fractions between transects within each farm canal and between the canals.

2.3 Results and Discussion

2.3.1 Physicochemical Properties

Sediment physicochemical properties varied between transects, canals, and canal depths, (Table 2-1, Table 2-2 and Table 2-3 and Table 2-4, respectively). The sediment total P values of farm canal 09A in the 0-5 cm layer varied from 571 mg kg⁻¹ at T4 to 1110 mg kg⁻¹ at T1. In canal 00A, total P varied from 928 mg kg⁻¹ at T5 to 2460 mg kg⁻¹ at T3. For canal 00A at depth 5-10 cm, total P values varied from 480 mg kg⁻¹ at T1 to 2210 at T3. Canal 06AB total P values at 0-5 cm varied from 344 mg kg⁻¹ at T1 to 742 mg kg⁻¹ at T4. The total P content for the 5-10 cm layer did not vary significantly among the five transects of farm canals 09A and 06AB and averaged 636 mg kg⁻¹ and 569 mg kg⁻¹, respectively. Both at the 0-5 and 5-10 cm depths the average total P values followed the trend 00A>09A>06AB i.e. canal 00A had greater total P values while 06AB had smaller total P values. Total P of sediments decreased with depth for farm canal 09A and 00A. High total P at 0-5 cm layer could be due to higher P content of accumulated detrital matter. Similar trends of decreasing total P with depth have been found by researchers in sediments of the Everglades region (Reddy et al., 1993; Newman et al., 1997; White and Reddy, 2001, 2003). There was no change in total P values with depth for 06AB canal sediments. Aggressive aquatic weed control and canal cleanup operations possibly have prevented accumulation of high P content detrital matter on the surface resulting in no change in total P content at depths 0-5 and 5-10 cm layers.

Bulk density values of farm canal 09A did not vary significantly among transects and averaged 0.19 g cm⁻³ at 0-5 cm. Bulk density values varied from 0.08-0.16 g cm⁻³ and 0.24-0.54 g cm⁻³ at depth 0-5 cm for farm canal 00A and 06AB respectively. At 5-10

cm layer the bulk density values varied from 0.19-0.56 g cm⁻³, 0.10-0.50 g cm⁻³ and 0.29-0.50 g cm⁻³ for farm canals 09A, 00A and 06AB respectively. Similar bulk density values ranging from 0.10-0.60 g cm⁻³ were found by Diaz et al. (2006) in the canal sediments of the STAs and the WCAs of the Everglades. Studies performed by Reddy et al. (1998) on the EAA soils yielded average bulk density value of 0.42 g cm⁻³. Bulk density values in the sediments of the farm canals are lower than typical bulk density values of mineral soils. These low bulk density sediments thus are susceptible to be transported in the EAA drainage waters as suspended load distributed throughout the water column (Daroub et al., 2002b). Mineral soil bulk density values range from 1.0-1.6 g cm⁻³ in fine textured soils and 1.2-1.8 g cm⁻³ in coarse-textured soils (Brady et al., 2002). Bulk density values at 5-10 cm layer were higher than that at 0-5 cm layer in all farm canals. This increase in bulk density with depth can be due to increased incorporation of limestone into sediments and compaction. Lower bulk density values at 0-5 cm layer were possibly the consequence of deposition of detrital matter. Bulk density values in the surface sediments of WCA-2A were found to be 0.049, 0.050, 0.052, 0.070 g cm⁻³ at the surface 0-10 cm depth compared to 0.086, 0.104, 0.094 and 0.092 g cm⁻³ at subsurface 10-30 cm depth (White and Reddy, 2000). Average bulk density values determined in STA-1W by at surface 0-5 cm and 5-30 cm layer were 0.306 g cm⁻³ and 0.369 g cm⁻³ (White et al., 2006). The narrow range of difference between the surface and subsurface bulk density values at the STA-1W is attributed to the incorporation of limestone in the surface layers of the soil. The smallest bulk density values among the three farm canals were observed in sediments of 00A canal in both

surface and subsurface sediments, whereas the greatest bulk density values were observed in farm canals 06AB and 09A at depth 5-10 cm.

The %LOI values of farm canal 09A did not vary significantly among transects at both depths, and averaged 31.8% at both 0-5 cm and 5-10 cm layers (std dev 5.18 and 5.27). For farm canals 00A and 06AB at 0-5 cm depth %LOI values varied from 41.9-57.4% and 13.9-41.6% respectively. At 5-10 cm depth for farm canal 00A %LOI values varied from 16.4-73.6% while for farm canal 06AB, %LOI values did not vary significantly among transects and averaged 30.1%. Among all the three farm canals, canal 00A had the high %LOI values (74.2 and 73.6%) at both 0-5 and 5-10 cm depths. Both canals 00A and 06AB have smaller %LOI at T1 which is probably due to the close proximity of pumps that effectively mobilize the light and flocculent sediment surface layer. The canal %LOI values followed the trend 00A>09A, 06AB both at the surface and subsurface layers. The %LOI values decreased with depth for 00A canal, but the values were not significantly different at either depth for 09A and 06AB canals.

Sediment pH values between different transects were not significantly different at the 0-5 cm layers of 09A and 00A canals and 5-10 cm layer of 09A canal. The average pH values of canal 09A, 00A at 0-5 cm sediment layer and 09A at 5-10 cm sediment layer were 7.5, 7.1 and 7.5 respectively. Both at surface and subsurface layer farm canal 00A had smallest pH values at both the surface and subsurface layers (7.1 and 7.2), while 06AB had the greatest pH values of 7.7 at both the layers. The circum neutral values of the sediments are most likely due to incorporation of limestone from the limestone bedrock. Similar pH values have been found in the sediments of the

Everglades region including WCA-2 (7.2), WCA-3 (6.7) and Holey Land Wildlife Management Area (7.5) (Reddy et al., 1998).

2.3.2 Phosphorus Fractions of EAA Farm Canals

Sediment KCl-Pi comprised an average of 1 to 2% of total P at the 0-5 and 5-10 cm layer (Figure 2-2 and Figure 2-3), and the values were not significantly different between transects of farm canal 09A, 00A and 06AB (Table 2-5). Farm canal 00A had the greatest KCl-Pi value at the 0-5 cm layer while at 5-10 cm layer there were no significant differences in KCl-Pi values between the three farm canals (Table 2-6). Phosphorus stored in KCl-Pi is of concern because it represents the readily available P pool. However, the low KCl-Pi values in the farm canal sediments were in accordance to those reported by various researchers in South Florida, 0.1-2.3% of total P in stream sediments of lake Okeechobee watershed (Reddy et al., 1995), 0.3-3% in the organic soils of Everglades (Reddy et al., 1998), <1% in the canal sediments of the Everglades (Diaz et al., 2006), 0.01% of total P in the mesocosm of STA-1W (White et al., 2006). White et al. (2004) found an average KCl-Pi value of 2.99 mg kg⁻¹ in the mesocosms of the Everglades Nutrient Removal (ENR) Project (STA-1W). In contrast the concentrations of readily available P measured by 1M NH₄Cl varied between 10 to 24% in the surface sediments in lake Apopka and 10-17% of total P in the littoral and peat sediments of lake Okeechobee (Olila et al., 1995). The authors concluded that this fraction could act as a source of P to the overlying water and may be important in internal P cycling (Olila et al., 1995). The variations in the ionic strength and water to soil ratio can cause variation in P desorbed. Both procedures using (KCl and NH₄Cl) used the same soil to solution ratio, same concentrations of the extractant (1 M) and the same shaking time (2 h) for extracting labile P. Since both KCl and NH₄Cl are ionic salts

and dissociate completely in aqueous solutions, the resulting ionic strength of the aqueous solutions can affect the quantity of P desorbed thus changing the labile P estimates. P desorption experiments conducted on soil consecutively with reverse osmosis water, a 50:50 mix of reverse osmosis water and well water, and 0.01 M CaCl₂ yielded progressively lower dissolved P concentrations (Turner et al., 2002). Similar results were obtained by McDowell and Sharpley (2001) using water and 0.01 M CaCl₂. Thus increasing the ionic strength of the solutions yielded progressively lower dissolved P concentrations. Since the ionic strength ($I = 1/2 \sum_{i=1}^n c_i z_i^2$ where c_i =concentration and z_i =charge) are both same for the extractants I would expect no significant differences in labile P estimates by 1M KCl and 1M NH₄Cl.

The NaOH-Pi fraction comprised 4-7% of total P in the 0-5 cm layer and 5-7% of total P in the 5-10 cm layer of the canal sediments and did not vary significantly between transects except 5-10 cm layer of 00A canal. Average NaOH-Pi values at 09A canal at 0-5 and 5-10 cm layers were 68.9 and 43.3 mg kg⁻¹, at 00A canal 74.4 and 62.4 mg kg⁻¹ while at 06AB canal the values were 15.2 and 9.32 mg kg⁻¹. Mean NaOH-Pi values of 09A canal and 00A were significantly higher than for 06AB at both 0-5 cm and 5-10 cm layers. The NaOH-Pi fraction consists of P associated with amorphous and crystalline Fe and Al oxides and oxyhydroxides that can act as a potential long term source of P to the water column under fluctuating redox conditions (Hietjes and Lijklema, 1980; Olila et al., 1995). Phosphorus fractionation studies by Diaz et al. (2006) on the canal sediments of the STA and the WCA canals found that the NaOH-Pi fraction varied from 1-13% of total P. The Fe and Al bound P is usually relatively stable, but is subject to changes in sediment physicochemical properties like changes in redox

potential (Moore and Reddy, 1994) whereby it can get reduced. The reduced form of Fe being more soluble can be released from the sediments to the water column (Mortimer, 1941; Holdren and Armstrong, 1980). Drastic decreases in dissolved oxygen concentrations can occur during summer when high primary productivity and subsequent degradation can result in high sediment oxygen demand (Moore and Reddy, 1994). Redox fluctuations are more likely in sediments with high organic matter, high primary productivity or low flow velocities or pulse flow (Diaz et al., 2006). This is particularly important as water flow in EAA farm canals are not continuous but are regulated by pumps. Such conditions result in pulsed flow, including quiescent no-flow periods between pumping events that favor accumulation of detrital material in the canals (Daroub et al., 2002a).

The NaOH-Po values did not vary significantly between transects in farm canal 09A and 00A. The average NaOH-Po values in canal 09A at 0-5 and 5-10 cm layers were 121 and 82.3 mg kg⁻¹ respectively. In canal 00A the average NaOH-Po values at depth 0-5 and 5-10 cm were 38.0 and 17.7 mg kg⁻¹. Farm canal 06AB, NaOH-Po values ranged from 18.4-39.4 mg kg⁻¹ at the 0-5 cm and 15.3-31.6 mg kg⁻¹ at the 5-10 cm layer. Canal 09A had significantly higher NaOH-Po values than 00A and 06AB canals. The NaOH-Po fraction represented about 3-14% of total P in the surface sediments of all three farm canals. The NaOH-Po fraction represents P bound to humic and fulvic acids and is susceptible to hydrolysis and subsequent release (Bowman and Cole, 1978; Ivanoff et al., 1998). Qualls and Richardson (1995) and Reddy et al. (1998) suggested that the deposition of NaOH-Po in the Everglades was due to vegetative uptake and detrital deposition. The decomposition of the NaOH-Po pool depends on the

availability of oxygen and this P pool is relatively stable under hypoxic conditions.

Ivanoff et al. (1998) found that NaOH-P_o values in a drained agricultural farm, pasture in EAA and flooded soils (ENR project) comprised of 74%, 68% and 54% of total P and concluded that the soils of the three Histosols were highly humified. In the EAA canals, the deposition of detrital matter is not favored due to canal hydrology and management practices. In the Everglades as a result of hydrology and accumulation of nutrients the organic P forms are dominant forms of P storage. The hydrology in EAA canals is very different than that in the rest of Everglades governed primarily by canal management practices that includes use of pumps resulting in rapid changes in water velocity, canal management practices including removal of canal aquatic weeds that does not promote accumulation of organic P. Thus the NaOH-P_o content is lower than the sediments in Everglades.

Phosphorus bound to Ca and Mg minerals (HCl-P_i) was the dominant fraction at both depth 0-5 cm and 5-10 cm at all the three farm canals and at all the transects. The HCl-P_i fraction at the three farm canals accounted for 51-59% of the total P in the 0-5 cm level and 56-61% of total P at the 5-10 cm depth. High levels of HCl-P_i were also found in other parts of the Everglades. Sediments from WCA-1 were found to have HCl-P ranging from 32-47% and 9-16% of total P in the cattail dominated areas and interior marshes respectively (Reddy et al., 1998). The values of HCL-P_i in WCA-2A, WCA-3A, Holey Land Wildlife Management Area varied as 35-46%, 80% and 53% and 44% of total P respectively. The HCl-P_i (Ca-bound P fraction) also dominated (64% of total P) in the canal sediments of North Miami canal and South Miami canal (Diaz et al., 2006). White et al., 2004 found that HCl-P_i fraction and the residue comprised more than 75%

of the total P in the ENR project. The Ca and Mg bound P represented about 64% of total P in the mud sediments of lake Okeechobee (Olila et al., 1995). The greatest concentrations of HCl-Pi (1210 mg kg^{-1}) were measured in sediments from the 00A canal at depth 0-5 cm and the smallest concentrations (245 mg kg^{-1}) in sediments of 06AB canal (Table 2-7). Mean HCl-Pi values of the three farm canals followed the order 00A>09A>06AB at both 0-5 and 5-10 cm layers (Table 2-8). The HCl-Pi is relatively stable and P release from this fraction should be comparatively slow (Sonzogni et al., 1982). The region extending from lake Okeechobee to Florida Bay is underlain, by a series of alternating porous layers of limestone, shell, sand and marl (Jones, 1948) that allows the interaction of ground and surface water resulting in high pH and Ca concentrations (Noe et al., 2001). Drainage water from the EAA is also high in Ca and Mg concentrations (Diaz et al., 1994). Precipitation of the Ca and soluble P as phosphate minerals has been reported by Diaz et al., 1994 in the EAA drainage waters with high Ca concentration and pH values. In addition to precipitation of calcium phosphates, deposition of Ca bound P in EAA canals can result from coprecipitation with calcium carbonate or adsorption/precipitation of phosphates on calcium carbonate surfaces. Richardson and Vaithiayanathan (1995); Reddy et al. (1998) have shown extractable Ca and Mg to be significantly correlated with extractable HCl-Pi in the WCAs. However the determination of the nature of the association of the P with the Ca is subject to mineralogical analyses of the sediments.

Residue P was the second greatest P fraction in all the three farm canal sediments and comprised of 24.9-40.9% and 25.4-38.9% of total P at the 0-5 and 5-10 cm layers respectively. Similar residual P values were found by Diaz et al. (2006) in the canal

sediments of North and South Miami canal (21-35%). Residue-P in canal 09A was not significantly different between transects and averaged 225 mg kg^{-1} at 0-5 and 166 mg kg^{-1} at the 5-10 cm layer. Residue P values varied from (49.4-305) mg kg^{-1} in farm canal 00A and (111-247) mg kg^{-1} in farm canal 06AB at the 0-5 cm. Both at 0-5 and 5-10 cm layers farm canal 00A had higher residue P values than 09A and 06AB canals. Residual P fraction is considered to be highly resistant and biologically unavailable (Hieltjes and Lijklema, 1980). The residual P pool can consist of stable lignin and organo-metallic complexes (Ivanoff et al., 1998).

2.4 Conclusions

Differences in total P, bulk density, %LOI and pH of sediments taken from the five transects within each farm canal show wide variability in physicochemical properties of EAA farm canals sediments. Total P and %LOI of the canal sediments both at the surface and subsurface layers were in the order of 00A>09A>06AB. Sediment %LOI and BD values were inversely related at 0.0001 probability related (Table 2-6) and the BD values of the canal sediments followed the opposite trend of %LOI, 00A<09A<06AB at the 0-5 cm layer. The total P values of canal sediments were positively correlated to %LOI content at the 0.0001 probability level, i.e. well managed canals having less detrital deposition will have low total P and low %LOI and vice versa. The bulk density values were inversely related to total P content i.e. sediments with high mineral matter due to the presence of carbonates had low total P values. The low total P concentration of sediments with higher mineral materials could possibly be due to the lack of P containing minerals in the limestone bedrock, but this is subject to further mineralogical studies.

The pH values of sediments followed the trend 06AB and 09A>00A at the surface layer and 06AB>09A>00A at the subsurface layer. The high pH values of canal 06AB at both layers suggest that 06AB canal sediments have higher mineral matter content than 09A or 00A canal. A sophisticated hydraulic system, in combination with an aggressive water management program and shallow canal depth likely promote transport of low bulk density particulate matter in canal 06AB and result in low total P, low %LOI and high bulk density values. Low bulk density and high %LOI values of the surface sediments of farm canal 00A make them susceptible to sediment resuspension and transport to downstream movement especially during high velocity pumping events.

There were differences in sediment physicochemical properties in the surface and subsurface layers of the canals. Aggressive canal management of 06AB prevented accretion of detrital matter thus the total P values for surface and subsurface sediments were not different in farm canal 06AB. In contrast farm canals 09A and 00A surface sediments had higher total P than subsurface sediments. Sediment bulk density increased with depth at all the canals which can be due to compaction as well as increased mineral content in the subsurface layer.

Several decades of nutrient loading from the EAA have resulted in the storage of P in the canal sediments. This P reserve can lead to P flux in to the water column than can be crucial as this water eventually flows into downstream ecosystems including the WCAs and the Everglades National Park. Lower P content in 06AB canal may lead to lower P flux than that of 00A and 09A canals. Higher NaOH-Pi values in sediments of farm canal 00A and 09A can lead to slow and prolonged P release to the overlying water column. The high HCl-Pi (>50 % of total P) in the farm canal sediments suggests

that this pool can be an important long term storage for P. Calcitic minerals can also be very important in storing P in EAA canal sediments thereby preventing their release into the water column. In contrast to the downstream Everglades ecosystem, organic P in the EAA farm canals ranged from 3-13% of total P compared to about 70% of total P in the Everglades essentially due to Everglades hydrological conditions promoting organic P retention.

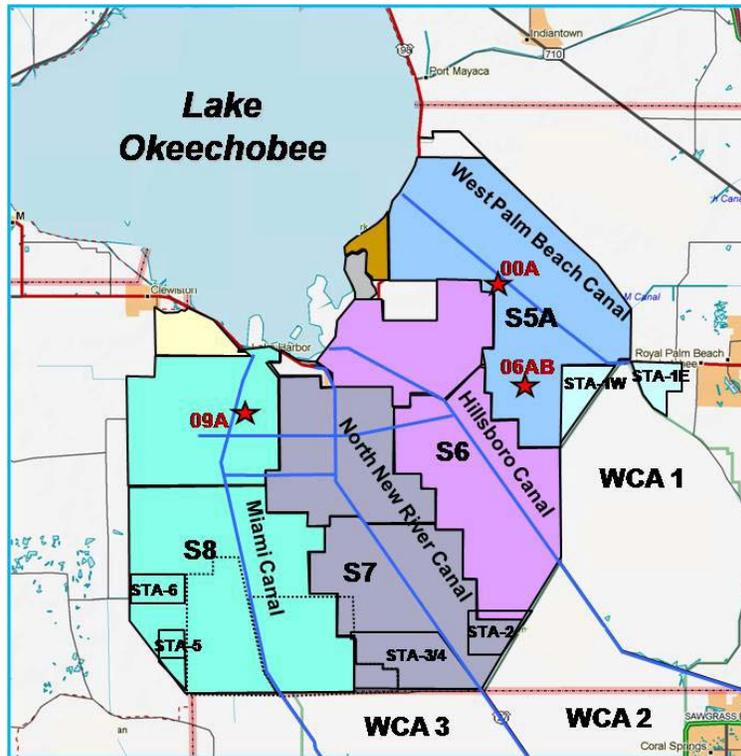


Figure 2-1. Farm basins and positions of farm canals 00A, 09A and 06AB in EAA.

Table 2-1. Total P and bulk density values of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) and depths 0-5 cm and 5-10 cm.

Transect	Total P (mg kg^{-1})			BD (g cm^{-3})		
	09A	00A	06AB	09A	00A	06AB
-----0-5 cm -----						
T1	1110 a†	1120 b	344 c	0.12 ns	0.12 ab	0.54 a
T2	870 ab	1510 ab	519 b	0.16	0.13 ab	0.36 abc
T3	757 ab	2460 a	559 ab	0.19	0.16 a	0.44 ab
T4	571 c	1590 ab	742 a	0.23	0.11 bc	0.27 bc
T5	668 b	928 b	716 a	0.22	0.08 c	0.24 c
-----5-10 cm -----						
T1	748 ns	480 c	494 ns	0.36 ab	0.50 a	0.44 a
T2	643	917 b	572	0.33 ab	0.21 b	0.50 a
T3	586	2210 a	516	0.56 a	0.20 b	0.47 a
T4	550	1170 b	608	0.36 ab	0.14 bc	0.37 ab
T5	653	870 b	653	0.19 b	0.10 c	0.29 b

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal and depth.

P = 0.05.

ns - not significant.

Table 2-2. Percent LOI and pH values of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) and depths 0-5 cm and 5-10 cm.

Transect	%LOI			pH		
	09A	00A	06AB	09A	00A	06AB
-----0-5 cm -----						
T1	37.8 ns	41.9 c	13.9 c	7.5 ns	6.8 ns	7.8 a
T2	36.9	42.0 c	24.3 abc	7.5	7.3	7.6 b
T3	29.4	74.2 a	24.4 bc	7.5	7.0	7.6 ab
T4	25.4	50.1 b	39.5 ab	7.5	7.3	7.6 b
T5	32.4	57.4 b	41.6 a	7.6	7.3	7.7 ab
-----5-10 cm -----						
T1	21.7 ns	16.4 c	20.6 ns	7.4 ns	7.2 ab	7.8 a
T2	27.9	41.3 b	25.1	7.6	7.4 a	7.7 ab
T3	22.3	73.6 a	24.4	7.7	7.0 b	7.7 ab
T4	20.8	44.3 b	38.1	7.6	7.4 a	7.7 b
T5	33.2	52.3 ab	40.1	7.5	7.4 a	7.7 ab

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal and depth.

P = 0.05.

ns - not significant.

Table 2-3. Mean total P, bulk density(BD), %LOI and pH values of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) and depths 0-5 cm and 5-10 cm.

Canal	Total P mg kg ⁻¹	BD g cm ⁻³	%LOI	pH
-----0-5 cm -----				
09A	794±206 b†	0.19±0.05 b	31.8±5.18 b	7.5±0.01 a
00A	1520±592 a	0.12±0.03 c	53.7±13.4 a	7.1±0.25 b
06AB	575±162 c	0.37±0.12 a	28.8±11.6 b	7.7±0.06 a
-----5-10 cm -----				
09A	636±86.5 b	0.40±0.08 a	31.8±4.67 b	7.5±0.06 b
00A	1130±861 a	0.20±0.19 b	45.6±24.3 a	7.3±0.17 c
06AB	569±120 b	0.40±0.11 a	30.1±10.6 b	7.7±0.09 a

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals for each depth.

P = 0.05.

ns - not significant.

Table 2-4. Mean total P, bulk density(BD), %LOI and pH values of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) and depth 0-5 cm and 5-10 cm depth.

Canal	Depth cm	Total P mg kg ⁻¹	BD g cm ⁻³	%LOI	pH
09A	0-5	794 a†	0.19 b	31.8 ns	7.5 ns
09A	5-10	636 b	0.40 a	31.8	7.5
00A	0-5	1520 a	0.12 b	53.7 a	7.1 ns
00A	5-10	1130 b	0.20 a	45.6 b	7.3
06AB	0-5	575 ns	0.37 b	28.8 ns	7.7 ns
06AB	5-10	569	0.40 a	30.1	7.7

† Treatment means within the same column followed by the same letter are not different by Tukey's test between depths for each canal.

P = 0.05.

ns - not significant.

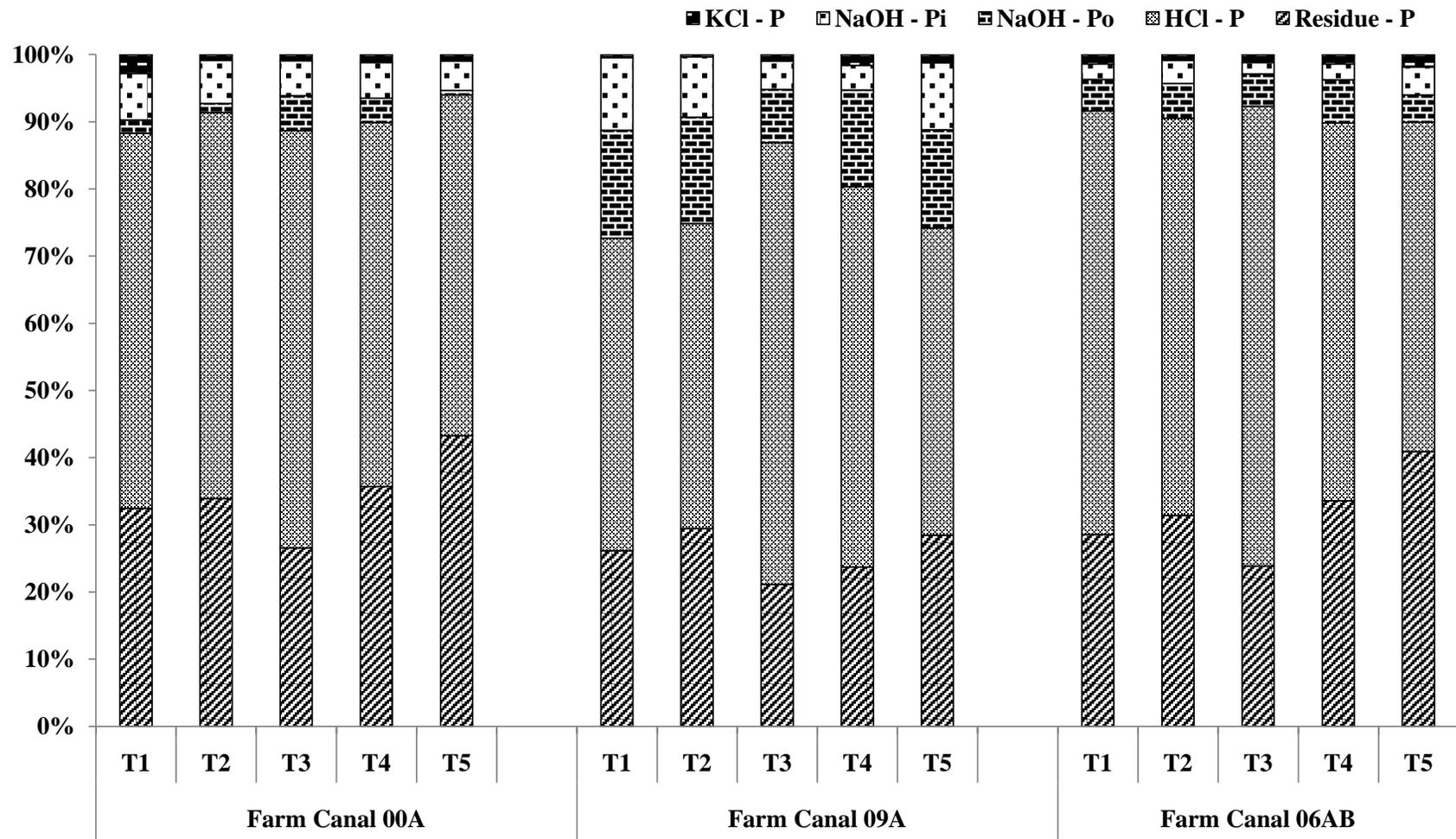


Figure 2-2. Percent comparison of KCl-P, NaOH-Pi, NaOH-Po, HCl-P and Residue P fractions at five transects (T1-T5) at depth 0-5 cm in farm canal 00A, 09A and 06AB.

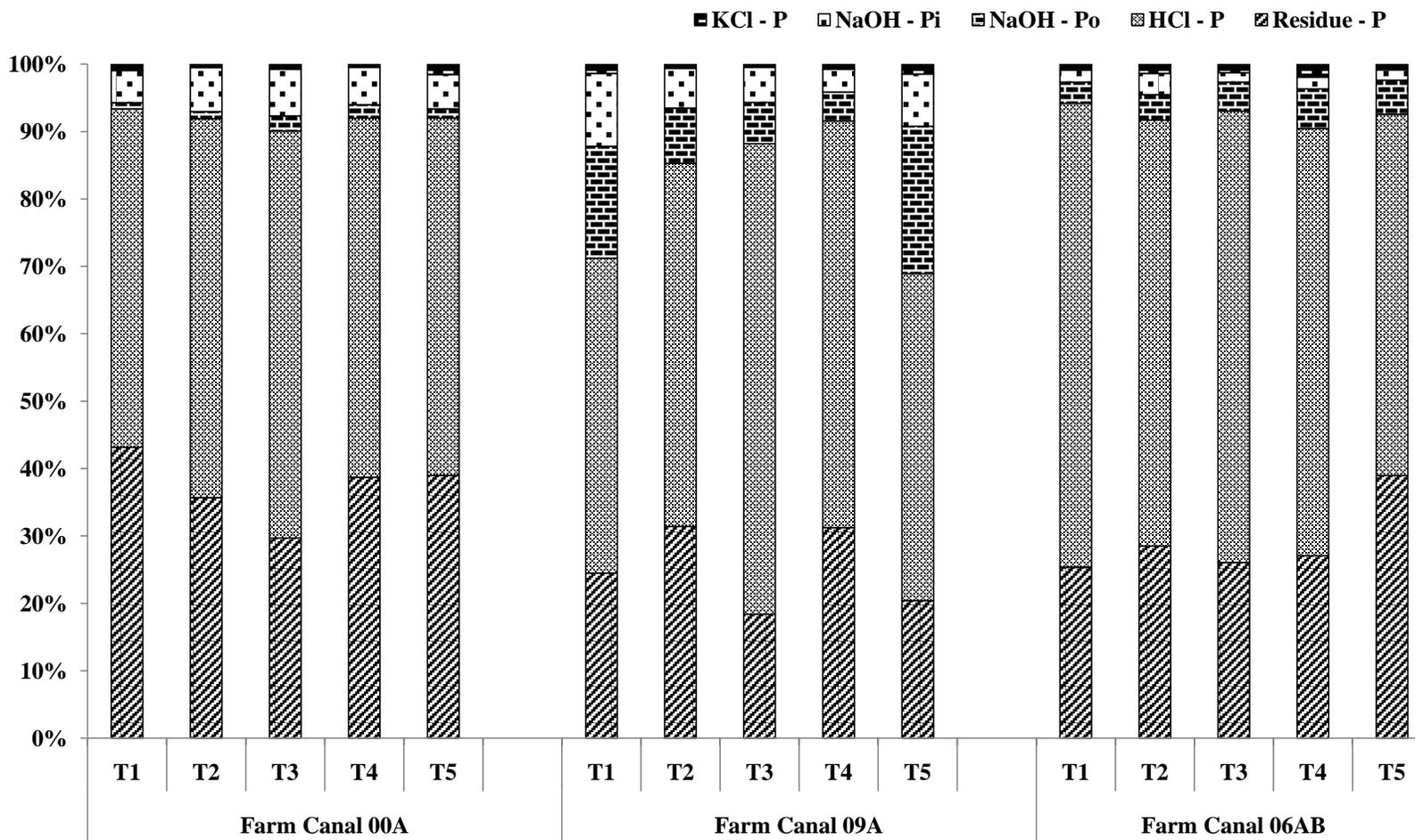


Figure 2-3. Percent comparison of KCl-P, NaOH-Pi, NaOH-Po, HCl-P and Residue P fractions at five transects (T1-T5) at depth 5-10 cm in farm canal 00A, 09A and 06AB.

Table 2-5. KCl-P, NaOH-Pi and NaOH-Po fractions of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) at depths 0-5 cm and 5-10 cm.

Transect	KCl-P (mg kg ⁻¹)			NaOH-Pi (mg kg ⁻¹)			NaOH-Po (mg kg ⁻¹)		
	09A	00A	06AB	09A	00A	06AB	09A	00A	06AB
	----- 0-5 cm -----								
T1	5.40 ns	29.9 ns	5.40 ns	121 ns	73.4 ns	9.00 ns	180 ns	20.6 ns	18.4 b
T2	3.60	11.2	4.60	83.3	80.8	17.7	150	16.5	26.8 ab
T3	7.80	18.4	7.00	32.1	101	9.90	61.6	101	28.3 ab
T4	11.0	14.6	8.70	24.3	64.7	14.0	96.4	43.9	39.4 a
T5	10.4	11.5	11.2	56.0	52.3	25.2	123	8.14	24.7 ab
	----- 5-10 cm -----								
T1	11.7 ns	4.30 ns	4.60 ns	93.2 ns	22.1 c	9.20 ns	140 ns	4.30 ns	16.3 bc
T2	3.90	4.60	5.40	35.9	58.7 b	13.0	50.1	9.40	15.3 c
T3	2.60	14.7	5.90	31.0	129 a	6.60	36.1	42.0	20.2 abc
T4	4.20	4.80	7.60	17.9	56.9 b	8.00	23.1	20.5	28.1 ab
T5	11.0	14.2	5.60	38.2	45.4 bc	9.80	162	12.4	31.6 a

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal and depth.

P = 0.05.

ns - not significant.

Table 2-6. KCl-P, NaOH-Pi, NaOH-Po, of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) at depths 0-5 cm and 5-10 cm.

Canal	KCl-P mg kg ⁻¹	NaOH-Pi mg kg ⁻¹	NaOH-Po mg kg ⁻¹
----- 0-5 cm -----			
09A	7.64±3.17 b†	63.3±39.6 a	120±45.9 a
00A	17.1±7.71 a	74.4±18.2 a	38.0±37.6 b
06AB	7.38±2.65 b	15.2±6.60 b	27.5±7.64 b
----- 5-10 cm -----			
09A	6.68±4.31 ns	43.2±29.0 a	82.3±63.9 a
00A	8.52±5.42	62.4±40.0 a	17.7±14.7 b
06AB	5.82±1.11	9.32±2.39 b	22.3±7.24 ab

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals for each depth.

P = 0.05.

ns - not significant.

Table 2-7. Mean HCl-P and Residue-P of farm canals 00A, 09A and 06AB from transect 1(T1) to transect 5(T5) at depths 0-5 cm and 5-10 cm.

Transect	HCl-P (mg kg ⁻¹)			Residue-P(mg kg ⁻¹)		
	09A	00A	06AB	09A	00A	06AB
----- 0-5 cm -----						
T1	521 ns	589 ab	245 ns	293 ns	342 ns	111 c
T2	422	723 ab	305	273	426	162 abc
T3	504	1210 a	401	162	515	140 bc
T4	379	658 ab	344	158	433	205 ab
T5	385	603 b	296	239	514	247 a
----- 5-10 cm -----						
T1	402 ns	232 c	355 ns	211 ns	200 b	131 b
T2	328	506 b	308	192	321 ab	121 b
T3	412	1130 a	315	108	556 a	122 b
T4	322	544 ab	309	167	395 a	182 ab
T5	359	477 bc	332	151	351 ab	257 a

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal and depth.

P = 0.05.

ns - not significant.

Table 2-8. HCl-P and Residue-P of farm canals 00A, 09A and 06AB from transect1(T1) to transect 5(T5) at depths 0-5 cm and 5-10 cm.

Canal	HCl-P mg kg ⁻¹	Residue-P mg kg ⁻¹
----- 0-5 cm -----		
09A	442±66.6 b	225±62.6 b
00A	756±257 a	446±72.1 a
06AB	318±58.2 c	173±53.8 b
----- 5-10 cm -----		
09A	365±41.3 b	166±39.5 b
00A	578±332 a	365±129 a
06AB	324±20.3 b	163±58.4 b

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals for each depth.

P = 0.05.

ns - not significant.

Table 2-9. Correlation between sediment BD, %LOI, pH and Total P.

	BD gm cm ⁻³	%LOI	pH	Total P mg kg ⁻¹
BD	1.00*	-0.74*	0.42*	-0.62*
LOI	-0.74*	1.00*	-0.44*	0.78*
pH	0.42*	-0.44*	1.00*	-0.56*
Total P	-0.62*	0.78*	-0.56*	1.00*

* Significant at the 0.0001 probability level.

CHAPTER 3
PHYSICOCHEMICAL CHARACTERISTICS AND PHOSPHORUS FRACTIONATION
OF THE EVERGLADES AGRICULTURAL AREA (EAA) MAIN CANAL SEDIMENTS

3.1 Introduction

3.1.1 Historical Background.

The Everglades Agricultural Area (EAA) in South Florida, is situated south of the fresh water lake Okeechobee and north of the Water Conservation Areas (WCAs). Soils in EAA are mostly Histosols (SFER, 2010; Rice et al., 2002). Flat topography in the EAA (Bottcher and Izuno, 1994) and uneven distribution of rainfall (SFER, 2010) makes drainage essential, which is accomplished through a network of canals and pumps. Agricultural drainage water is routed from field ditches through the farm canals into the main canals. Farm canals are individually owned and managed by growers, whereas main canals are operated and maintained by South Florida Water Management District (SFWMD). Four major main canals were originally dug in the early 1900's to drain part of the Everglades: Miami canal, North New River canal, Hillsboro canal and the West Palm Beach canal (Light and Dineen, 1994). These canals were constructed by digging through the EAA limestone bedrock (Gleason and Spackman, 1974). Pumping stations in EAA main canals help direct water from the main canals into the WCAs. Pumps used in EAA farm canals are operated by farm growers and can be either manually driven or with automatic on-off level. Low capacity pumps in EAA farm canals can range from 18.9-32.3 m³ min⁻¹ while high capacity pumps can range between 22.7-132.5 m³ min⁻¹ (SFER, 2004). Pumps used in EAA main canals are managed by SFWMD and have higher discharge capacity. For example the S-3 pump station located at lake Harbor on the southern lake Okeechobee has three diesel powered pumps with a maximum discharge capacity of 4383.4 m³ min⁻¹. The S-135 pump station located northeast of

lake Okeechobee, has a discharge capacity of $849.5 \text{ m}^3 \text{ min}^{-1}$, and pump station G-370 situated on North New River canal has a discharge capacity of $4714 \text{ m}^3 \text{ min}^{-1}$.

Drainage/runoff of the EAA is the main source of surface water inflow into the Everglades Protection Area (EPA), consisting of Arthur R. Marshall Loxahatchee National Wildlife Refuge, Water Conservation Areas (WCAs), and the Everglades National Park (ENP) (SFER, 2010). This phosphorus (P) enriched drainage water from the EAA has been cited as one of the main reasons of ecosystem changes in the WCAs and the ENP (LOTAC., 1990; Whalen et al., 1992).

The Everglades, once a contiguous wetland, was drained for flood control and agriculture through the construction of canals, levees and water control structures (Light and Dineen, 1994). Agriculture in EAA caused runoff enriched with nutrients (Snyder and Davidson, 1994). Due to years of agricultural practices, P has been accumulating in EAA canal sediments. Phosphorus accumulated in sediments can play a pivotal role in P cycling between sediment solid phase pools, and dissolved P (Mortimer, 1941; Stumm and Leckie, 1970). The P storage in canal sediments is much greater than that in canal water. As a consequence, small amounts of P released from sediments can significantly impact water column P concentrations (Bostrom et al., 1982) thereby influencing water quality of the canals as well as the downstream ecosystems. Hence, to evaluate the potential impact of the EAA canal sediments on water quality it is essential to understand the mobility and reactivity of P stored in these sediments. Sediment P mobility and reactivity was assessed through the analysis of physicochemical properties, P fractionation, and sediment mineralogy.

3.1.2 Factors Affecting Sediment Properties in EAA

Sediment transport and P distribution can be controlled by physicochemical properties such as, pH, total P, bulk density and organic matter content. Sediment P can be present in different forms that have different mobility and bioavailability. Thus to assess the potential of P mobility, internal P cycling, it is necessary to know the distribution of P among different sediment phases including reactive and recalcitrant forms (Olila et al., 1994). The mobility and reactivity of P in sediments is determined not only by different P forms but also by sediment mineral phases (Mortimer, 1941). Sediment P can be adsorbed onto Fe and Al oxyhydroxides, carbonates or can undergo precipitation or co-precipitation with Ca, Fe, and Al minerals (Mortimer, 1941; Stumm and Leckie, 1970; Jensen and Thamdrup, 1993). Predominance of a biogeochemical process in sediment P cycling is dependent on sediment mineralogy (Koch et al., 2001). Sediments dominated by mineral forms of calcium carbonates can be influenced by carbonate chemical equilibria in contrast to redox. Thus sediment mineralogy can also reveal important information about the predominant chemical process of these sediments. According to Hupfer and Lewandowski (2005), and Ahlgren et al. (2006), in addition to inorganic P, the mobility and reactivity of organic P compounds can also influence the water quality of aquatic ecosystems. Organic P compounds can include a wide variety of compounds including phospholipids, nucleic acids, inositol phosphates, phosphoproteins, sugar phosphates, phosphonic acids, humic associated organic compounds, polyphosphates and pyrophosphates (McKelvie, 2005). These organic P compounds can differ in their degree of reactivity and degradability. High molecular weight organic phosphates like inositol phosphates or phytic acid are resistant (Bowman and Cole, 1978; Islam and Ahmed, 1973) and can be strongly adsorbed to the surfaces

of ferric oxides (De Groot and Golterman, 1993). Under anaerobic conditions organic monoesters can degrade to orthophosphate (Suzumura and Kamatani, 1995) and under alkaline environment, diesters can degrade to orthophosphate monoesters in as little as 24 h (Turner et al., 2003).

³¹P Nuclear Magnetic Resonance (NMR) spectroscopy has been used to identify organic P compounds in sediments (Sundareshwar et al., 2001; Hupfer et al., 2004; Ahlgren et al., 2006). Soil P fractionation, in contrast to ³¹P NMR spectroscopy, does not provide structural information of P compounds present in soil extracts (Turner et al., 2003). The composition of P forms stored in the different EAA canals can differ from each other depending on the composition of particulate P from EAA drainage and geological factors affecting the mineralogy of sediments.

The Everglades is underlain by a central relatively impermeable limestone bedrock (Gleason and Stone, 1994) composed of deposits of calcium carbonate (CaCO₃) (Scott, 1997). As ancient sea levels receded, the CaCO₃ bedrock was formed as unconsolidated sand grains (Obeysekera et al., 1999). Carbonatic minerals could hence be an important part of EAA canal sediment mineralogy and can affect the physicochemical properties of sediments including pH, bulk density, total P and distribution of P fractions. The majority of the EAA bedrock is composed of the Fort Thompson Formation (USGS, Figure 3.1), except in the eastern part, where bedrock Anastasia Formation overlies the Fort Thompson Formation. The Fort Thompson Formation is composed of interposed layers of muddy sand with beds of shells in a quartz and sand matrix (Petuch and Roberts, 2007). The Anastasia formation is composed of seashell fragments, quartz and sand, calcium carbonate and iron oxide

(Monk et al., 1968). The configuration of the EAA bedrock is irregular. The western part of the EAA is topographically higher known as the West Everglades High, while the eastern part is the relatively low-lying Loxahatchee Channel (Gleason et al., 1974). The high bedrock topography in southwest EAA and in the lower eastern part of EAA may lead to dominant mineral properties in sediments.

We hypothesized that (i) physicochemical properties of EAA main canal sediments would vary within a canal and between the canals and, (ii) canal sediments would differ with respect to different P fractions and mineralogical composition.

The objectives of this study were to determine:

(i) the sediment physicochemical properties (ii) the P fractions and mineralogical composition within EAA main canals. The results were compared within different transects in canals as well as between the canals.

3.2 Materials and Methods

3.2.1 Description of Main Canals

Sediments were collected from three different main/district canals: Miami canal situated in the western part of EAA; West Palm Beach canal (WPB), situated in the eastern EAA; and the Ocean canal, situated in the southeastern EAA. The main canals are managed by the SFWMD, thus they are also called the district canals. The EAA main canals facilitate runoff removal and also supply irrigation water to the farms (SFER, 2009). The EAA main canals have their origin in lake Okeechobee and drain through several farms before ultimately flowing into Atlantic Ocean. Drainage water in EAA farms is routed through farm canals into main canals with gated control structures. The flow of agricultural drainage water is from the farm canals, to the main canals, the Storm

Treatment Areas (STAs), Water Conservation Areas (WCAs) and Everglades National Park (ENP).

Miami canal also known as the C-6 canal has its source at S-3 pump station on lake Okeechobee ranges about 85 miles (13600 m) to Miami River that ultimately drains into Biscayne Bay to the south (SDAMP, 2001). This canal passes through Palm Beach, Broward and Dade counties, the EAA, WCA-3, the Everglades and overlies the Fort Thomson formation. The Miami canal carries EAA runoff to Holeyland Wildlife Management Area and WCA-3. Gated water control structures, S-339 and S-340, transmit water from the canal into WCAs.

The West Palm Beach canal, also known as C-51 canal, overlies the Fort Thomson formation and stretches 42 miles (67600 m) from canal point, lake Okeechobee and flows southeast to "Twenty Mile Bend" (SDAMP, 1999). The stretch of WPB canal, until Twenty Mile Bend, provides drainage in EAA. Subsequently it flows to the northern boundary of Arthur R. Marshal Loxahatchee National Wildlife Refuge. Thereafter the L-8, L-40 and L-7 canals drain into the WPB canal. Further eastward WPB canal receives stormwater runoff from the coastal urban area from the cities of Royal Palm Beach, Haverhill, Wellington and Palm Springs, the Acme Drainage District, Indian Trail Improvement District, and the lake Worth Drainage District. After passing through the south side of the Palm Beach International Airport, the WPB canal first turns south and then to the east into the lake Worth Lagoon.

The Ocean canal is about 21000 m long, and is a connecting canal that connects main canals Hillsboro canal and WPB canals, both of which originate from lake Okeechobee (SFER, 2009). At Twenty Mile Bend the Ocean canal joins the WPB canal

(SDAMP, 1999). Ocean canal stretches east-west and overlies the Fort Thomson and the Anastasia bedrock formation.

3.2.2 Sediment Sampling

Sediment cores were collected from four different transects from the three main canals (Figures 3-2, 3-3, 3-4). The first transect (T1) for Miami and West Palm Beach canal was closest to the lake while the other transects (T2-T4) were taken progressively southward into the EAA. For Ocean canal T1 was closest to WPB canal. Triplicate sediment cores were collected at each transect within the middle two thirds of the canal cross-sectional area.

Transect locations at each study site were marked by GPS coordinates using a Trimble Unit Pro-XR DGPS Unit (Trimble Navigation Limited Mapping and GIS Systems, Sunnyvale, CA). At each transect two steel rebars were installed at the edge of the water on each side of the canal. During sediment sampling, a steel cable was attached to the anchor rebars to anchor a boat used during measurements. Triplicate sediment cores were collected at each transect within the middle two thirds of the canal cross-sectional area. The sediment cores were transported upright to the laboratory, stored at 4°C and sectioned within 24 h. The water in the columns was removed by vacuum suction, and the sediment sectioned at depth 0 to 5 cm. Sediment samples were stored in plastic jars and stored at 4°C until analysis.

3.2.3 Sediment Analysis

3.2.3.1 Physicochemical properties

All samples were analyzed for moisture content, bulk density, organic matter, and total P. Organic matter content was determined by igniting an oven-dried sediment sample at 550°C for 4 h in a muffle furnace (Andersen, 1974). The residue following

digestion of the ash was analyzed for total P using the ascorbic acid method (Method 365.4, U.S. Environmental Protection Agency, 1983).

3.2.3.2 Phosphorus fractions

The distribution of P in the canal sediments of the EAA were determined by the sequential chemical fractionation procedure followed by Reddy et al. (1995 and 1998). The operationally defined scheme was composed of five steps: (i) KCl extractable P: This fraction represents the labile P_i that is water soluble and exchangeable (loosely adsorbed); (ii) NaOH extractable P: This fraction is considered to represent the Fe- and Al- bound P and humic and fulvic acids (P bound to Al, Fe oxides and hydroxides); (iii) HCl extractable P: This fraction represents the Ca- and Mg- bound P; (iv) alkali extractable organic P (fulvic- and humic-bound P); and (v) residual P: This fraction is thought to represent recalcitrant organic P compounds and P bound to minerals.

Field wet samples (0.3 g dry weight equivalent, were sequentially extracted with 1 M KCl (labile P), 0.1 M NaOH (Fe- and Al- bound P, and alkali extractable P_o), and 0.5 M HCl (Ca and Mg-bound P). The data for each P fraction from each canal were evaluated transect wise averaging the replicates of each transect. (The details of the fractionation procedure are provided in the Appendix A).

3.2.3.3 Thermogravimetry

Organic matter content was determined by igniting sediment sample at 550°C for 4 h in a muffle furnace (Andersen, 1974). This method is based on the principle that, at the chosen temperature, all organic carbon is converted to CO_2 , where loss of CO_2 from carbonates and loss of water from clay minerals are negligible. For calcareous EAA sediments this assumption can lead to erroneous results which can be avoided by thermogravimetry (TG). In a thermogravimetric analysis, a substance is subjected to a

controlled temperature while the change in mass of the substance is recorded as a function of temperature (Earnest, 1988). Thermogravimetric measurements are carried out in air or in inert gas atmosphere, such as helium (He) or argon (Ar) using a computer-controlled thermal analysis system. In addition, TG can also provide information on the quantity of the minerals, for example calcite and dolomite present in the sediments.

Estimates of organic matter content by TG method can be drawn by the weight loss between approximately 200 and 600°C depending upon the TG curve inflections (Harris et al., 2007). Minerals like 1:1 layer silicates Kaolinite and Halloysite have weight losses from 400°C to 600°C (Jackson, 1975) while 2:1 layer silicates like Mg-smectite have weight losses at 25-250°C (Karathanasis and Hajek, 1982) and at 600-900°C (Jackson, 1975). 2:2 layer silicates like chlorite have weight losses in the range 540-800°C (Jackson, 1975).

3.2.3.4 X-ray-diffraction (XRD)

The canal sediments were mixed thoroughly with a spatula and a portion of it was transferred in to a sieve (mesh size #270) placed on a funnel over a 1000 mL beaker. The contents were stirred using a rubber policeman and distilled water. The silt and clay size portions (<50 μ) were collected into the glass beaker while the sand fraction was left on the sieve. This process was continued until the leachate was colorless. About 50 mL of the silt and clay solution was filtered by vacuum suction using 0.45 μ filter paper. The contents collected on the filter paper were first rinsed with distilled water followed by magnesium chloride ($MgCl_2$) solution for magnesium saturation. The layers were cation saturated (Mg) to aid in identification of phyllosilicates (Whittig and Allardice, 1986). Distilled water was used to get rid of excess $MgCl_2$. Excess moisture was

removed and the thin layer of silt and clay was mounted onto a labeled glass slide and stored in water desiccators for X-ray analysis. The X-ray diffractometer was equipped with graphite-crystal monochromator. X-ray analyses of the samples were done at a scan rate of $2^\circ 2\theta$ per minute using Cu anode and $K\alpha$ radiation.

3.2.3.5 ^{31}P NMR

Extracts for ^{31}P NMR analysis were prepared by shaking 5 g of wet sediment containing 0.25 M NaOH and 0.05 M EDTA for 4 h at 20°C (Cade-Menun and Preston, 1996) and centrifuging the contents at 10,000 rpm for 30 min. Equal volumes of the replicate extracts were combined and frozen immediately at 80°C . The frozen extracts were lyophilized, ground and stored in the refrigerator. Lyophilization or freeze-drying works by freezing the material and reducing the surrounding pressure to allow the frozen water in the material to sublimate directly from the solid phase to gas. Prior to analysis the freeze-dried samples were redissolved in 0.9 mL solution of 1 M NaOH and 0.1 M EDTA. About 0.1 mL of deuterium oxide was added to the mixture and transferred to a 5-mm NMR-tube. The deuterium oxide acts as an NMR signal lock by providing temporally constant and homogenous magnetic field necessary to produce a high resolution NMR spectrum. Solution ^{31}P NMR spectra was obtained using a Mercury 300 MHz spectrometer using a 6- μs pulse (45°), a delay time of 1.0 s, an acquisition time of 0.2 s, and between 48,000 and 69,000 scans. Chemical shifts of signals were expressed in parts per million (ppm), relative to an external standard of 85% H_3PO_4 and Methylene DiPhosphonic Acid (MDPA) as the internal standard.

3.2.4 Statistical Data Analysis

Descriptive statistics of means, standard deviation, and standard errors (proc MEANS), were performed on data collected from the sediment sample analysis using

SAS statistical program (SAS Institute, 2003). Normality and goodness-of-fit tests were conducted to check the distribution patterns of the physicochemical properties and P fractions. Where the data were not normally distributed, log-transformations were used to stabilize the variance, and make the residuals Gaussian distributed for parametric analysis. Analysis of variance (ANOVA) was used to compare sediment physicochemical properties and P fractions between canal transects (USEPA., 1983, 1989). Summary statistics were conducted and Tukey test were used (SAS Institute, 1999) to assess significant differences between P forms, transects, and canals.

3.3 Results and Discussion

3.3.1 Physicochemical Properties

Sediment total P varied from 914 mg kg⁻¹ at T3 to 1938 mg kg⁻¹ at T4 in Miami canal (Table 3-1). Miami canal T4 had the greatest total P value among all the canals. Studies of six EAA canal sediments by Anderson and Hutcheon (1992) also showed that total P of Miami canal was the greatest. Total P values for WPB canal did not vary significantly along transects and average total P for WPB canal was 1134 mg kg⁻¹. Total P values for Ocean canal varied from 432 mg kg⁻¹ at T1 to 932 mg kg⁻¹ at T4. Miami and WPB canal had higher total P values than Ocean canal (Table 3-2). Ocean canal is a connecting canal that drains lesser area than either West Palm Beach canal or Miami canal (Figure 2-2) that can lead to lower drainage from farm canals and thus low total P values.

Bulk density values for Miami canal sediments varied from 0.14 g cm⁻³ at T3 to 0.54 g cm⁻³ at T4 (Table 3-1). Miami canal T4 had the greatest bulk density among all transects and all main canals. Bulk densities of WPB canal varied from 0.12 g cm⁻³ at T3 to 0.29 g cm⁻³ at T2. Bulk density values of Ocean canal did not vary significantly

between the different transects and averaged around 0.35 g cm^{-3} . Ocean canal sediments had higher bulk density values than either Miami or WPB canal (Table 3-2).

Sediment %LOI values in Miami canal ranged from 7.19% at T4 to 42.9% at T2 (Table 3-3). Miami canal T4 had the smaller %LOI value at all the transects and all the canals than WPB and Ocean canal. The %LOI values for WPB canal did not vary significantly between the transects and averaged about 26.7%. For Ocean canal sediments the %LOI varied from 17.4% at T3 to 37.6% at T4. The %LOI values did not vary significantly among Miami, WPB and Ocean canals (Table 3-4).

The pH values of Miami canal ranged from 7.2 at T2 to 7.7 at T4 (Table 3-3). The pH value at T4 was the greatest among the transects of Miami canal, while there was no statistical difference between the pH values of the rest of three transects. The pH values of WPB canal did not change significantly between the transects and averaged about 7.4. Ocean canal sediment pH values varied from 7.8 at T4 to 7.9 at T2 and T3. Among the canals Ocean canal sediments had higher pH values than both Miami and Ocean canal (Table 3-4).

Everglades Agricultural Area main canals were constructed by dredging down to the limestone bedrock (Stuck, 1996). Sediment trapping experiments by Hutcheon engineers (1995) showed that sedimentation at canal bottom occurs at the rate of $42.7\text{-}54.9 \text{ cm yr}^{-1}$. Therefore EAA canal sediment properties are influenced both by limestone bedrock properties and particulate materials deposited. The source of particulates in canals can be soil mobilized from farms (Stuck, 1996) or from in canal biological growth (Daroub, 2002a). High total P values of Miami and WPB canal could be due to high total P of materials deposited. Higher bedrock topography at Ocean canal has possibly

influenced the sediment physicochemical properties which results in lower total P, higher bulk density, lower %LOI and higher pH. The shallow depth of Ocean canal has possibly further facilitated the transport of flocculent particulate matter leaving behind materials that is highly mineral in nature.

3.3.2 Phosphorus Fractions of EAA Main Canal Sediments

The KCl-Pi fraction represented 0.2-2% of the total P in surface sediments at all the transects in the main canals (Figure 3-3). The KCl-Pi fraction did not vary significantly between the different transects of Miami and WPB canal and averaged around 7.78 and 14.2 mg kg⁻¹. Ocean canal KCl-Pi (Table 3-5) values ranged from 4.52-7.91 mg kg⁻¹. KCl-Pi values did not vary significantly between the canals (Table 3-6).

Inorganic NaOH-Pi ranged from 3-8% of the total P in all main canal sediments. The values of NaOH-Pi did not vary significantly among the different transects of the main canals and averaged 105 mg kg⁻¹, 93.2 mg kg⁻¹ and 18.1 mg kg⁻¹ for Miami, WPB and Ocean canal respectively (Table 3-6). The significance of NaOH-Pi fraction is its susceptibility to changes with redox potential that can result in possible long-term P release to the water column. Phosphorus stored as Al bound P is relatively stable, but Fe-bound P is strongly affected by sediment physicochemical properties such as changes in redox potential. The reduced form of Fe is more soluble than its oxidized counterpart, thus, P release from sediments is normally greater under anaerobic conditions (Hieltjes and Lijklema, 1980; Olila et al., 1995). NaOH-Pi values of Miami canal and WPB canal were higher than Ocean canal.

The NaOH-Po fraction represented 1-6% of total P in all canal sediments. The NaOH-Po values did not vary significantly between the different transects of the Miami, WPB and Ocean canals and averaged 88.2, 49.4 and 4.18 mg kg⁻¹ (Table 3-6). Under

oxygen deficient conditions, NaOH-Po pool is relatively stable as the rate of organic matter decomposition is regulated by the availability of oxygen. Sediment NaOH-Po values of Miami and WPB canal were higher than Ocean canal sediments (Table 3-6).

The HCl-Pi fraction at all canals accounted for 60-73% of total P in the surface layer sediments of the main canals, and was the largest P fraction at all the transects of all canals. The HCl-Pi values for Miami canal ranged from 653 mg kg⁻¹ at T1 to 1530 mg kg⁻¹ at T4. Sediment HCl-Pi values did not vary significantly between transects of WPB canal and average HCl-Pi value was 649 mg kg⁻¹ (Table 3-7). Ocean canal HCl-Pi values ranged from 316 at T2 to 735 mg kg⁻¹ at T4. Ocean canal T4 had the greatest HCl-P while the values did not vary significantly between the rest of the transects. The HCl-P values of Miami and WPB canal were greater than Ocean canal (Table 3-8).

Residue P fraction was the second largest storage pool, after the HCl-Pi pool. Sediment residue P at all transects represented about 17-26% of total P. Residue P values for WPB canal varied from 187 mg kg⁻¹ at T2 to 389 mg kg⁻¹ at T3 (Table 3-7). The values of residue-P did not vary significantly among transects of Miami and Ocean canal and averaged 234 and 127 mg kg⁻¹ respectively. Miami and WPB canal sediments had higher residue P values than Ocean canal sediments (Table 3-8).

3.3.3 Thermogravimetry and X-Ray-Diffraction

The mineralogical composition of the EAA canal sediments was studied by TG and XRD. Thermogravimetric studies on sediment samples of Miami canal T1-T3 indicated four inflections corresponding to weight loss due to moisture, organic matter, dolomite and calcite (Figure 3-4). Temperature range for weight loss due to organic matter was approximately between 300 and 600°C depending on the inflection of the curve. Thermogravimetric analysis for sediments from T4 of Miami canal resulted in 3

inflections corresponding to weight loss due to moisture, organic matter and calcite. The %Wt loss due to OM in T4 of Miami canal was smallest in all transects and canals (Figure 3-4), this was also observed in the %LOI values.

Thermogravimetric curves of sediment samples from WPB canal showed four inflection points corresponding to weight loss due to moisture, organic matter, dolomite and calcite. Similar to Miami canal T1, T2 and T3 and WPB canal sediments, Ocean canal sediments showed four inflections signifying weight loss due to moisture, organic matter, dolomite (DO) and calcite (CO). Sediment weight loss in all the transects and canals followed the trend %Wt loss-OM > %Wt loss-CA > %Wt loss-DO. The %Wt loss-OM for Miami and WPB canal higher than Ocean canal sediments as observed in the %LOI values from the analysis of physicochemical properties. Along with having smaller %Wt loss-OM values than other Miami and WPB canal, the %Wt loss-CA for Ocean canal sediments is greatest (except for Miami canal T4) among all the three canals which suggest that Ocean canal sediments are more mineral in nature than either Miami canal and WPB canal sediments.

The presence of dolomite $[(CaMg(CO_3)_2)]$ was confirmed by XRD studies in sediment samples from T1-T3, but dolomite was not found in T4 (Figure 3-5). Miami canal sediment samples from T1-T3 had similar mineralogical composition. Other minerals identified by XRD in Miami canal samples were sepiolite (Mg silicate), quartz, calcite ($CaCO_3$), and aragonite (polymorph of calcite). The heights of the peaks of calcite and aragonite from Miami canal T4 suggested that this transect contained higher concentration of calcite and aragonite than the other transects. Mineralogical compositions of sediment samples from Miami canal T1-T3 were very similar to those of

lake Okeechobee mud sediments determined by Harris et al. (2007). Obeysekera et al. (1999) indicated that mineral matter from lake Okeechobee could be washed into the canals, which explains the similarity in mineralogical composition between Okeechobee and EAA canal sediments. X-ray-diffraction studies after oxidation of organic matter and removal of carbonates from clay suspensions from Miami canal sediments indicate the presence of smectite and kaolinite in these sediments (Table 3-9). Mineralogical composition determined by XRD on WPB canal verified the presence of dolomite, calcite along with sepiolite and quartz in the sediments (Figure 3-6). In contrast to Miami canal, the four transects of WPB canal were mineralogically similar. X-ray-diffraction studies after removal of organic matter and carbonates determined the presence of smectite, palygorskite (magnesium aluminum phyllosilicate) and kaolinite in the sediment samples of WPB canal (Table 3-10). The XRD data of Ocean canal sediments indicated the presence of palygorskite in addition to sepiolite, calcite, dolomite, quartz and aragonite (Figure 3-7). The presence of phyllosilicates like smectite and kaolinite was verified after removal of organic matter and carbonates from sediment clay suspensions (Table 3-11). Minerals like smectite, sepiolite, and palygorskite found in the EAA canal sediments lose water in the temperature range of 105 and 550°C. Thus weight loss due to organic matter determined by TG in the 300-600°C range cannot be solely attributed to organic matter in these sediments.

Mineralogical studies of EAA canal sediments are lacking but the nature of Florida Bay sediments were studied by Scholl (1966) whereby he concluded that these sediments consisted mostly of calcium carbonate. The major components of Florida Bay sediments were found to be mollusk shells (Ginsburg, 1956), aragonite, sponge

spicules (Stockman et al., 1967). X-ray-diffraction studies on the clay fraction of lake Okeechobee indicated the presence of smectite, sepiolite, quartz, calcite and dolomite while the fine silt fraction of lake Okeechobee indicated the presence of quartz along with calcite and dolomite (Harris et al., 2007). The current study in the EAA main canal sediments revealed that all three canals were dominated by carbonate minerals which is consistent with the geology of the area. The Fort Thomson bedrock formation that underlies Miami and WPB canal, and Anastasia formation that underlies Ocean canal is composed of sand, shells and quartz. Visual assessment of the sediments, particularly Ocean canal sediments revealed an abundance of intact and broken seashells. The higher quantity of calcite in T4 of Miami canal could be attributed to higher bedrock topography in southwestern EAA. All the three main canals indicated the presence of sepiolite, quartz, calcite and dolomite. In addition aragonite was found in Miami canal and palygorskite in WPB and Ocean canal. Sepiolite and palygorskite found in EAA main canals, owing to small particle size, low density and fibrous nature could be easily resuspended in the water column of the canals (Harris et al., 2007). This is important as flow conditions in EAA main canals are regularly managed, and the turbulence can cause these minerals to resuspend and flow to the downstream ecosystems.

The lack of crystalline forms of Ca-P minerals was probably due to the inhibition in mineral formation by the presence of carbonates (Stumm and Leckie, 1970), organic acids (Inskeep and Silvertooth, 1988), absence of seed crystals (Griffin and Jurinak, 1973). Phosphate has been shown to be adsorbed on calcite and aragonite surfaces (Griffin and Jurinak, 1973; Kitano et al., 1978; Millero et al., 2001). Thus it is likely that P in Miami, WPB and Ocean canals do not exist as discrete phosphatic minerals but exist

as adsorbed phosphate on carbonate minerals. This is supported by the fact that deposits of P minerals occur in central and northern Florida but have not been found in south Florida (Porter and Porter, 1997). Consequently, it was suggested by Noe et al. 2001 that P from weathering of mineral rock is not available in the Everglades.

3.3.4 ^{31}P NMR Analysis

^{31}P NMR analysis was performed on the sediments of the main canals to determine the nature of organic P compounds present in the sediments. The analyses were performed on 0.25 M NaOH and 0.05 M EDTA (ethylene diamine tetra acetate) extracts of the sediments, using MDPA (methyl di phosphonic acid) as the internal standard. The NaOH-EDTA extraction has been applied to samples from the Florida Everglades (Robinson et al., 1998; Pant et al., 2002; Turner et al., 2006; Turner et al., 2007). Robinson et al. (1998) identified inorganic ortho P, ortho P monoester, and ortho P diester in the organic soils of Apopka marsh, Eustis Much Farm and Sunny Hill Farm. Pant and Reddy (2001) analyzed the detrital matter as part of the Everglades Nutrient Removal Project (ENRP) and identified P compounds like sugar phosphate, glycerophosphates, polynucleotides and phospholipids. Turner and Newman (2005) identified the presence of inorganic phosphate, phosphate monoesters, DNA and pyrophosphates in sites dominated by cattail and sawgrass in WCA-1 and 2.

The NMR study on the canal sediments yielded orthophosphate as the only detectable P compound, apart from the internal standard MDPA. The inability to find organic P forms may be due to the low organic P (NaOH-Po) concentrations in the main canal sediments suggested by the P fractionation study. Phosphorus sequestration and litter decomposition in the WCAs have been thought to be responsible for the

identification of organic P compounds like phosphodiester and pyrophosphates (Cheesman et al., 2010).

3.4 Conclusions

The physicochemical properties, P fractions and mineralogy of the sediments varied with transect and canals. The physicochemical properties of Miami, WPB canal sediments were similar in terms of total P, bulk density, %LOI and pH. In addition to high total P, both Miami and WPB canal sediments had low bulk densities which make them susceptible to resuspension and downstream transport. This is a cause of concern due to the high total P content of these sediments. Miami canal T4 was very different compared to the three other transects in terms of very high total P, high bulk density, high pH and very low %LOI.

Physicochemical properties of Ocean canal sediments were very different from Miami and WPB canal sediments. Ocean canal sediments had lower total P, higher bulk density and higher pH values than Miami and Ocean canal. Ocean canal sediments were more mineral in nature compared to both Miami and WPB canal. This could be due to the different bedrock formation underlying Ocean canal and the shallow canal depth. Shallow canal depth can mobilize sediments in lesser time than at deeper canals. This ease of mobilization prevents accumulation of particulate matter contributing to increased mineral nature of Ocean canal. Phosphorus fractionation of main canal sediments indicated that HCl-P or P associated with Ca and Mg was the dominant P fraction in all canals and transects. Mineralogical analyses did not indicate the presence of apatite minerals which suggests that P is probably associated as adsorbed complexes on minerals phases.

The second largest P fraction was residue P in all the canals and transects. Phosphorus from HCl-P and residue is relatively unavailable under canal conditions. The combined labile P, NaOH-Pi and NaOH-Po for Miami and WPB canal was higher than Ocean canal. This indicates that P release from Miami and WPB canal sediments would possibly be greater than Ocean canal sediments.

X-Ray Diffraction studies indicated that the dominant crystalline phase in all the main canals was calcite and polymorphs of calcite. Other minerals identified in the canal sediments were quartz, smectite, kaolinite, sepiolite and palygorskite. Sepiolite and palygorskite due to their fibrous nature and light weight can be easily suspended in the canal water column and be transported as suspended load.

Canals with higher bedrock topography in EAA are likely to have lower canal depth where particulates more likely to be transported downstream resulting in dominant mineral properties in sediments including higher BD, higher pH, lower %LOI, lower total P, higher Ca-Mg P and vice versa. The origin of particulate P in canals can be from in canal biological growth or due to soil erosion from EAA farms. Similarity of minerals found in EAA canals with lake sediments suggests that particulate materials are transported down from the lake to these canals. The EAA canal P fractions indicate that P can be released from these sediments and thus it is necessary to perform research to determine the P release potential from these sediments which can affect water quality in the canals as well as in the downstream ecosystems.

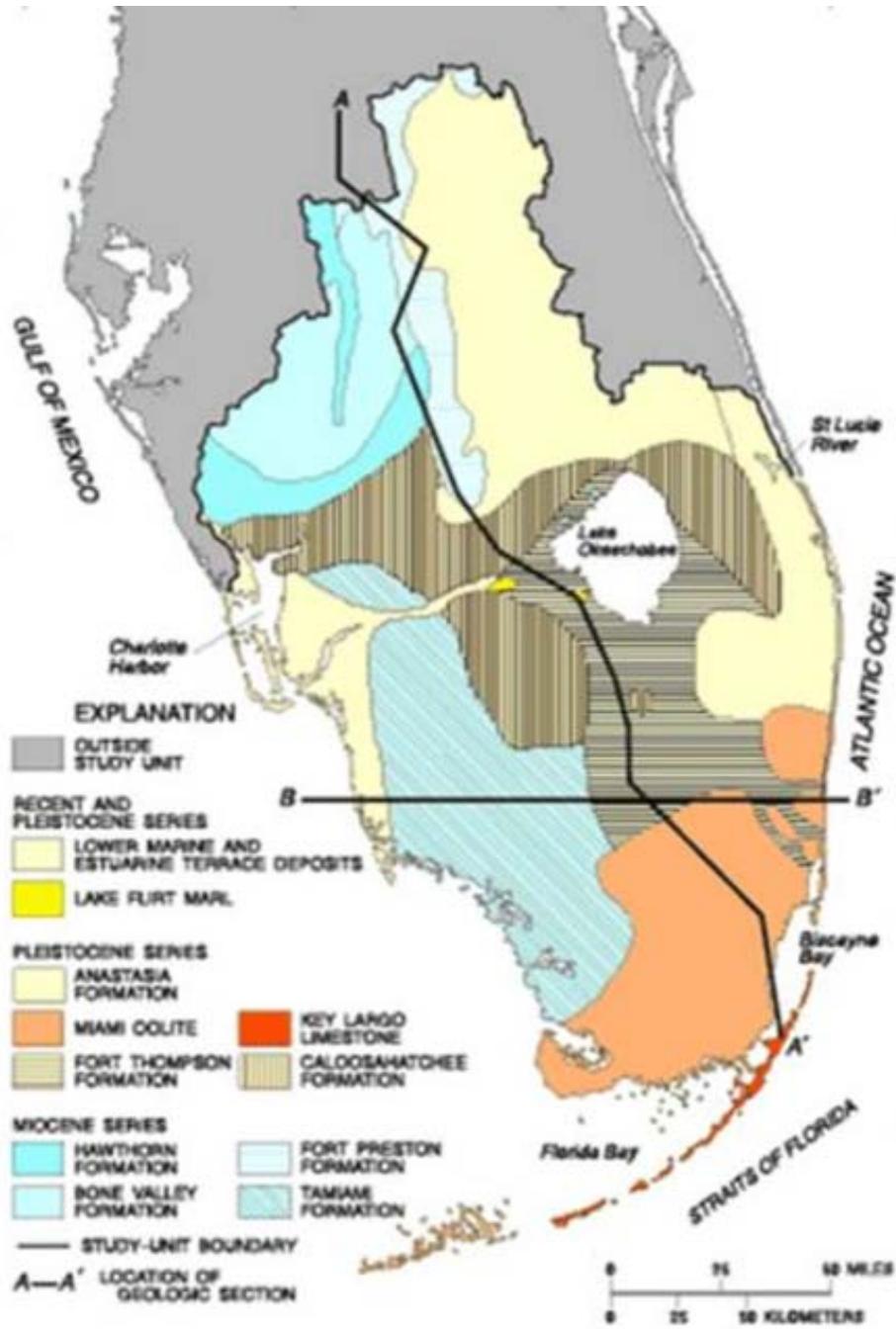


Figure 3-1. Different bedrock layers underlying EAA soils (USGS maps).

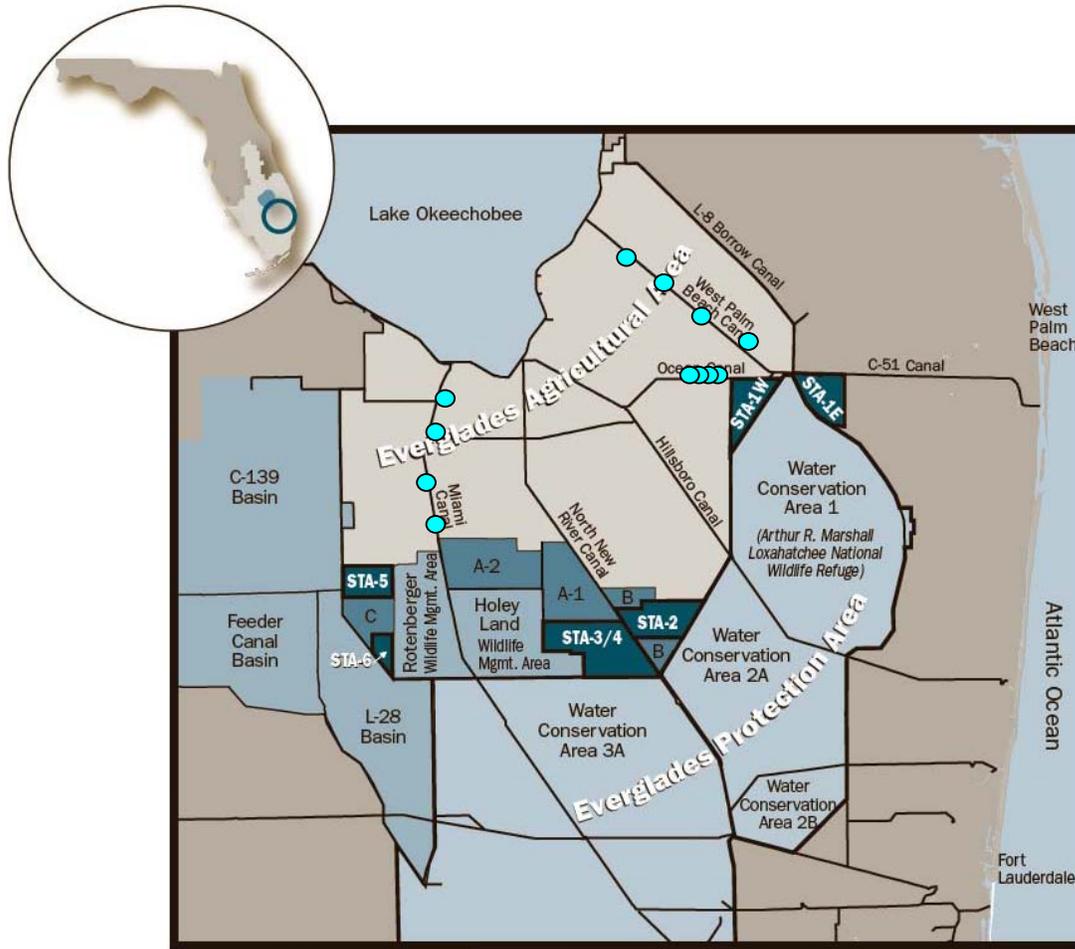


Figure 3-2. Position of EAA main canals and the sampling transects within the main canals.

Table 3-1. Mean total P and bulk density of Miami, WPB and Ocean canal sediments from T1 to T4.

Transect	Total P (mg kg ⁻¹)			Bulk Density (g cm ⁻³)		
	Miami	WPB	Ocean	Miami	WPB	Ocean
	----- 0-5 cm -----					
T1	1140 bc†	1300 ns	481 ab	0.18 b	0.22 a	0.37 ns
T2	914 c	1190	432 b	0.18 b	0.12 b	0.36
T3	1730 ab	1010	514 ab	0.14 b	0.29 a	0.40
T4	1940 a	1050	932 a	0.54 a	0.26 a	0.26
	----- 5-10 cm -----					
T1	1240 a	953 ns	393 ns	0.18 b	0.30 ab	0.45 a
T2	868 b	931	445	0.21 b	0.38 a	0.53 a
T3	2050 a	1070	355	0.19 b	0.23 b	0.37 ab
T4	886 b	1010	445	0.50 a	0.25 ab	0.20 b

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal.

P = 0.05.

ns - not significant.

Table 3-2. Mean total P and bulk density (BD) of Miami, WPB and Ocean canal sediments.

Canal	Total P mg kg ⁻¹	BD g cm ⁻³
----- 0-5 cm -----		
Miami	1430 a†	0.26 b
WPB	1130 a	0.22 b
Ocean	590 b	0.35 a
----- 5-10 cm -----		
Miami	1260 a	0.27 b
WPB	990 a	0.29 b
Ocean	409 b	0.39 a

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals.

P = 0.05.

ns - not significant.

Table 3-3. Mean %LOI and pH values of Miami, WPB and Ocean canal sediments from T1 to T4.

Transect	%LOI			pH		
	Miami	WPB	Ocean	Miami	WPB	Ocean
----- 0-5 cm -----						
T1	30.1 a	28.9 ns	23.1 ab	7.2 b	7.3 ns	7.9 a
T2	42.9 a	33.4	19.9 ab	7.3 b	7.4	7.9 a
T3	24.3 a	18.4	17.4 b	7.4 b	7.4	7.9 a
T4	7.19 b	26.1	37.6 a	7.7 a	7.4	7.8 b
----- 5-10 cm -----						
T1	26.7 a	41.0 ns	28.9 ns	7.3 b	7.4 ns	8.0 a
T2	37.2 a	24.4	17.4	7.4 b	7.5	8.0 a
T3	26.7 a	25.1	43.0	7.5 b	7.3	7.9 a
T4	7.20 b	29.4	54.0	7.9 a	7.5	7.8 b

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal.

P = 0.05.

ns - not significant.

Table 3-4. Mean %LOI and pH of Miami, WPB and Ocean canal sediments.

Canal	%LOI	pH
----- 0-5 cm -----		
Miami	26.1 ns	7.4 b
WPB	26.7	7.4 b
Ocean	24.5	7.9 a
----- 5-10 cm -----		
Miami	24.4 b	7.5 b
WPB	30.0 a	7.4 b
Ocean	35.8 a	7.9 a

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals.

P = 0.05.

ns - not significant.

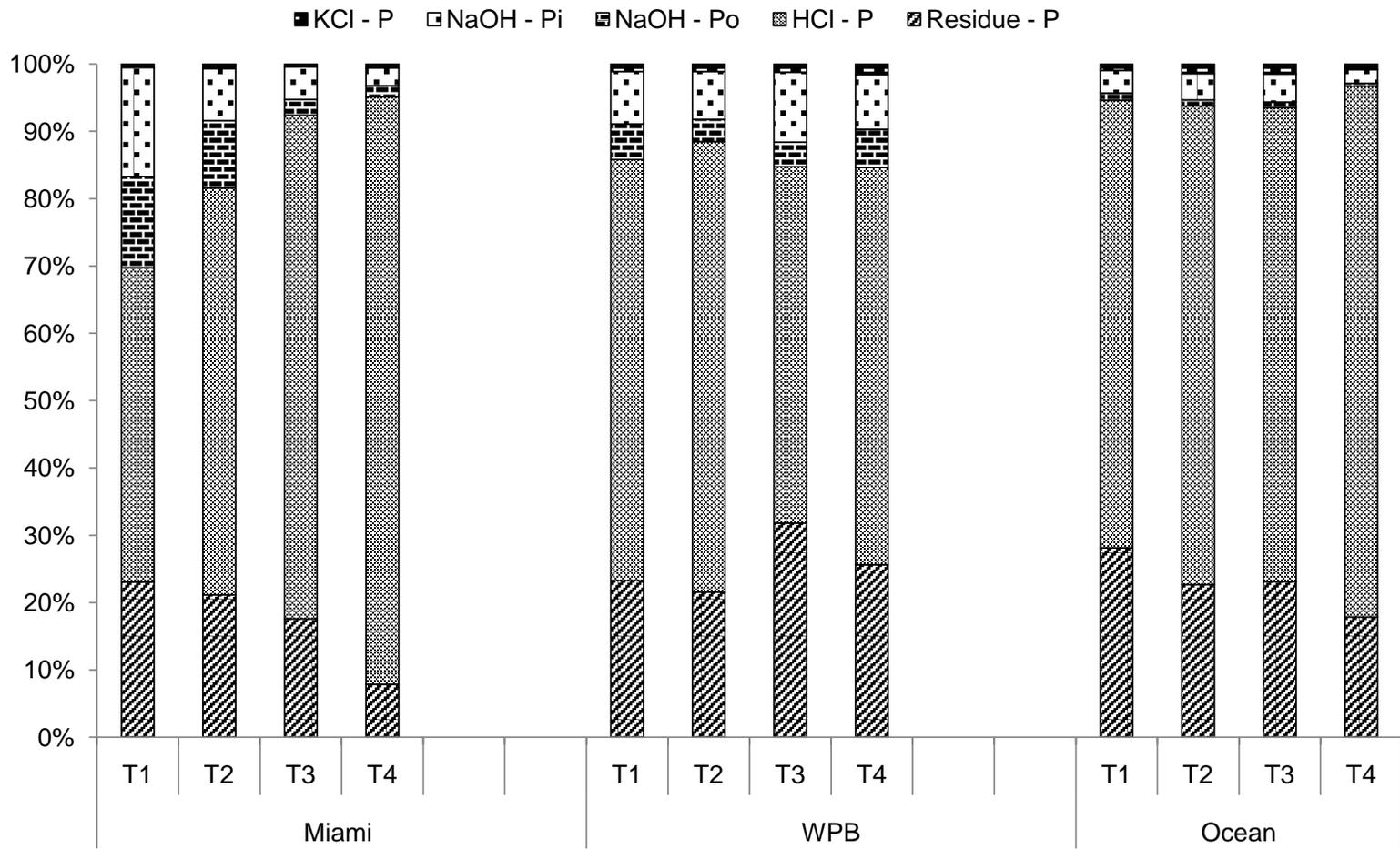


Figure 3-3. Percent comparison of different P fractions from T1 to T4 in Miami, WPB and Ocean canal at depth 0-5 cm.

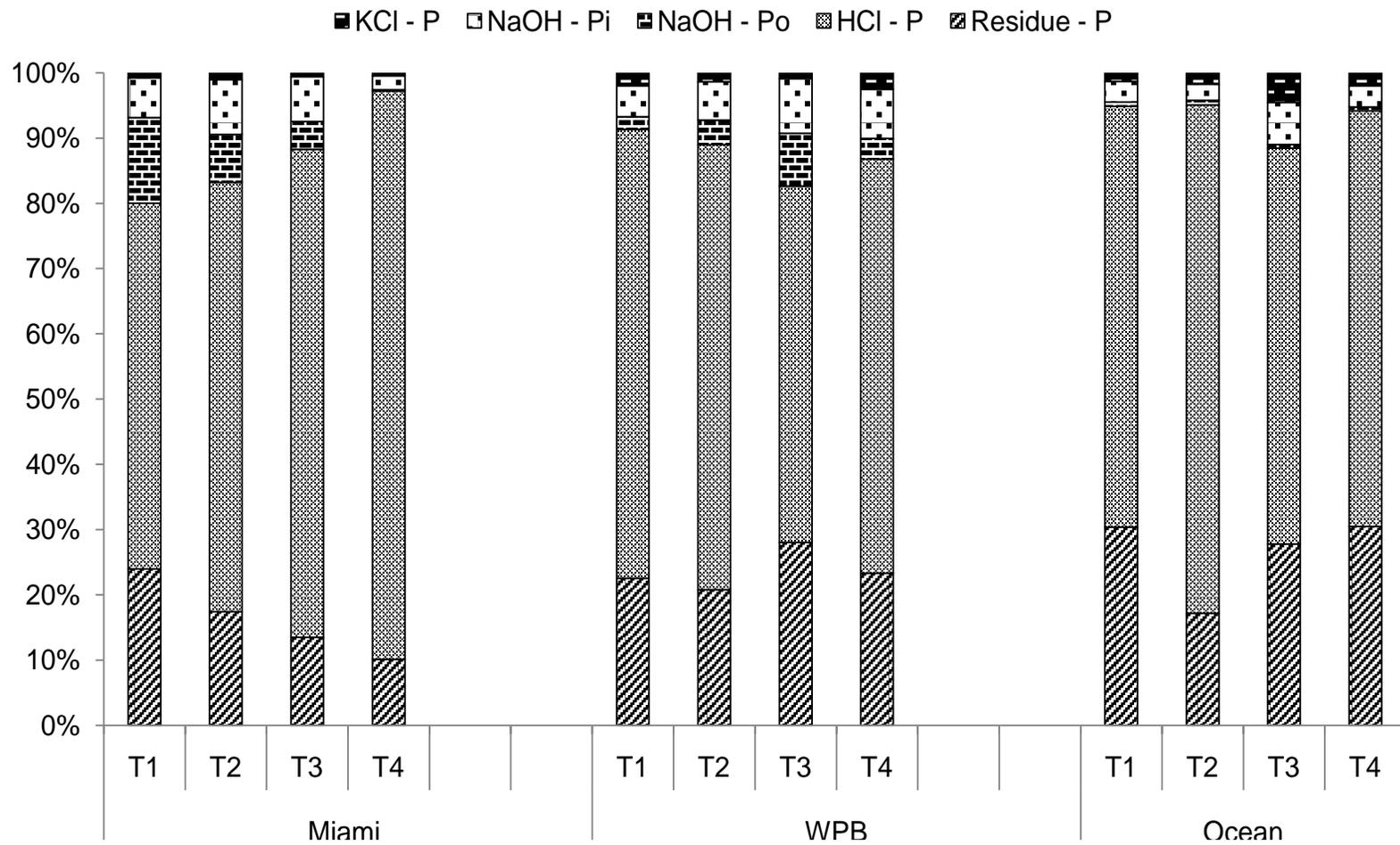


Figure 3-4. Percent comparison of different P fractions from T1 to T4 in Miami, WPB and Ocean canal at depth 5-10 cm.

Table 3-5. Mean labile P, NaOH-Pi and NaOH-Po fractions of Miami, WPB and Ocean canal sediments from T1 to T4.

Transect	KCl-P (mg kg ⁻¹)			NaOH-Pi (mg kg ⁻¹)			NaOH-Po (mg kg ⁻¹)		
	Miami	WPB	Ocean	Miami	WPB	Ocean	Miami	WPB	Ocean
----- 0-5 cm -----									
T1	7.27 ns	21.1 ns	4.52 ns	226 ns	109 ns	16.5 ns	190 ns	75.9 ns	5.08 ns
T2	6.82	15.1	6.41	75.4	130	17.4	97.4	44.4	3.95
T3	6.41	9.90	6.90	74.2	60.6	19.2	36.2	28.2	3.81
T4	10.6	10.5	7.91	46.3	73.1	19.2	29.3	49.2	3.89
----- 5-10 cm -----									
T1	12.9 ab	11.3 ns	5.00 ns	30.7 b	84.8 ns	12.2 ns	12.6 ns	180 a	2.57
T2	11.6 b	9.41	6.10	51.0ab	74.7	9.07	32.6	65.4 a	1.57
T3	10.8 b	10.2	12.7	110 a	120	18.0	102	73.2 a	1.69
T4	25.5 a	4.10	9.70	77.0 ab	19.4	16.1	32.4	17.1 b	2.84

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal.

P = 0.05.

ns - not significant.

Table 3-6. Mean KCl-P, NaOH-Pi and NaOH-Po of Miami, WPB and Ocean canal sediments.

Canal	KCl-P mg kg ⁻¹	NaOH-Pi mg kg ⁻¹	NaOH-Po mg kg ⁻¹
----- 0-5 cm -----			
Miami	7.78 ns†	105 a	88.2 a
WPB	14.2	93.2 a	49.4 a
Ocean	6.44	18.1 b	4.18 b
----- 5-10 cm -----			
Miami	15.2 a	67.2 a	44.9 a
WPB	8.75 b	74.7 a	83.9 a
Ocean	8.37 b	13.8 b	2.16 b

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals.

P = 0.05.

ns - not significant.

Table 3-7. Mean HCl-P and Residue P fractions of Miami, WPB and Ocean canal from T1 to T4.

Transect	HCl-P (mg kg ⁻¹)			Residue-P (mg kg ⁻¹)		
	Miami	WPB	Ocean	Miami	WPB	Ocean
----- 0-5 cm -----						
T1	653 b	790 ns	323 b	323 ns	137 ab	133 ns
T2	589 b	649	316 b	206	389 a	101
T3	1140 a	571	323 b	269	187 b	106
T4	1530 a	585	735 a	138	217 ab	167
----- 5-10 cm -----						
T1	447 ns	785 ab	250 ns	147 c	336 a	117 ns
T2	590	587 b	288	180 bc	155 bc	56.9
T3	685	1280 a	170	351 a	233 ab	77.8
T4	648	794 ab	291	238 ab	92.5 c	128

† Treatment means within the same column followed by the same letter are not different by Tukey's test between transects for each canal.

P = 0.05.

ns - not significant.

Table 3-8. Mean HCl-P and Residue-P of Miami, WPB and Ocean canal sediments.

Canal	HCl-P mg kg ⁻¹	Residue-P mg kg ⁻¹
----- 0-5 cm -----		
Miami	973 a	234 a
WPB	649 a	232 a
Ocean	424 b	127 b
----- 5-10 cm -----		
Miami	593 b	229 a
WPB	863 a	204 a
Ocean	249 c	95.0 b

† Treatment means within the same column followed by the same letter are not different by Tukey's test between canals.

P = 0.05.

ns - not significant.

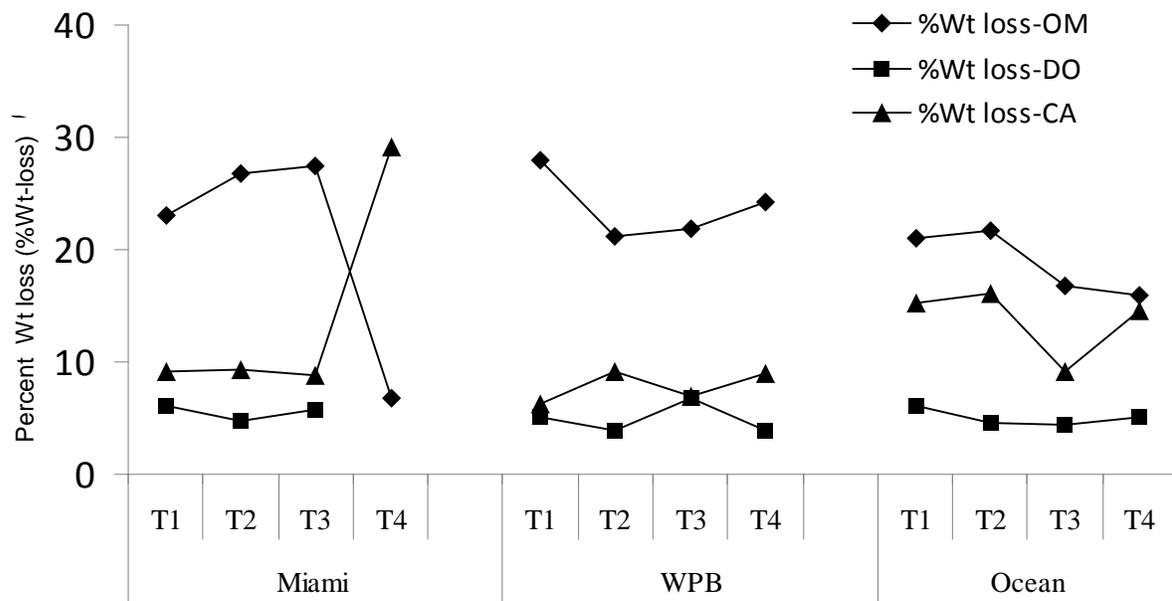


Figure 3-5. Weight loss due to OM, Dolomite and Calcite of Miami, WPB and Ocean canal sediments from T1 to T4.

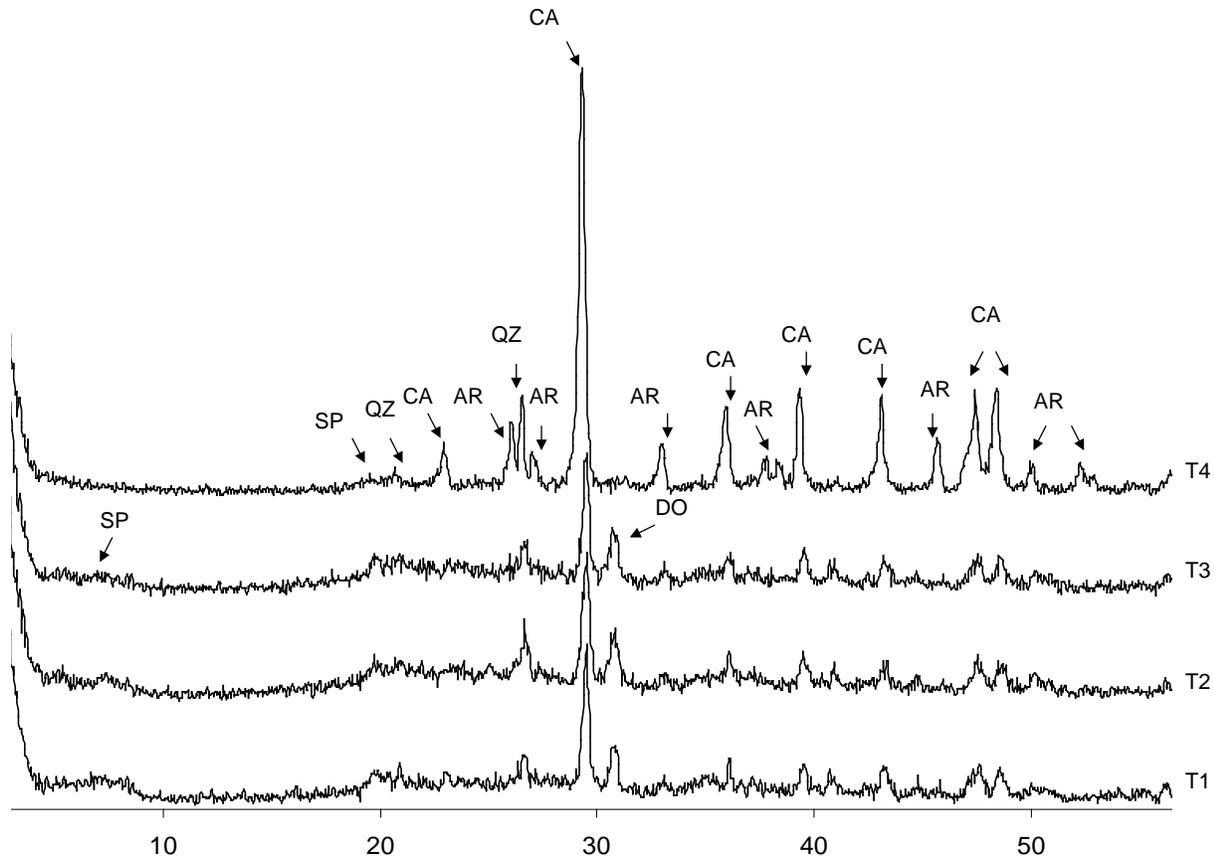


Figure 3-6. X-ray diffraction patterns from Miami canal sediments from T1 to T4.

Table 3-9. Minerals identified in sediments of Miami canal sediments from T1 to T4.

Canal	Transect	Minerals							
		SP	QZ	CA	DO	AR	SM	KL	PL
Miami	T1	✓	✓	✓	✓	✓			
	T2	✓	✓	✓	✓	✓			
	T3	✓	✓	✓	✓	✓			
	T4	✓	✓	✓	...	✓	✓	✓	...

SP-Sepiolite-Magnesium Silicate [$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$].

QZ-Quartz-Silicon dioxide (SiO_2).

CA-Calcite-Calcium carbonate ($CaCO_3$).

DO-Dolomite-Calcium magnesium carbonate, [$CaMg(CO_3)_2$].

AR-Aragonite-Polymorph of calcium carbonate, ($CaCO_3$).

SM-Smectite (determined by removing carbonate and organic matter).

KL-Kaolinite (determined by removing carbonate and organic matter).

PL-Palygorskite-Magnesium Aluminium Phyllosilicate ($Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$ (determined by removing carbonate and organic matter).

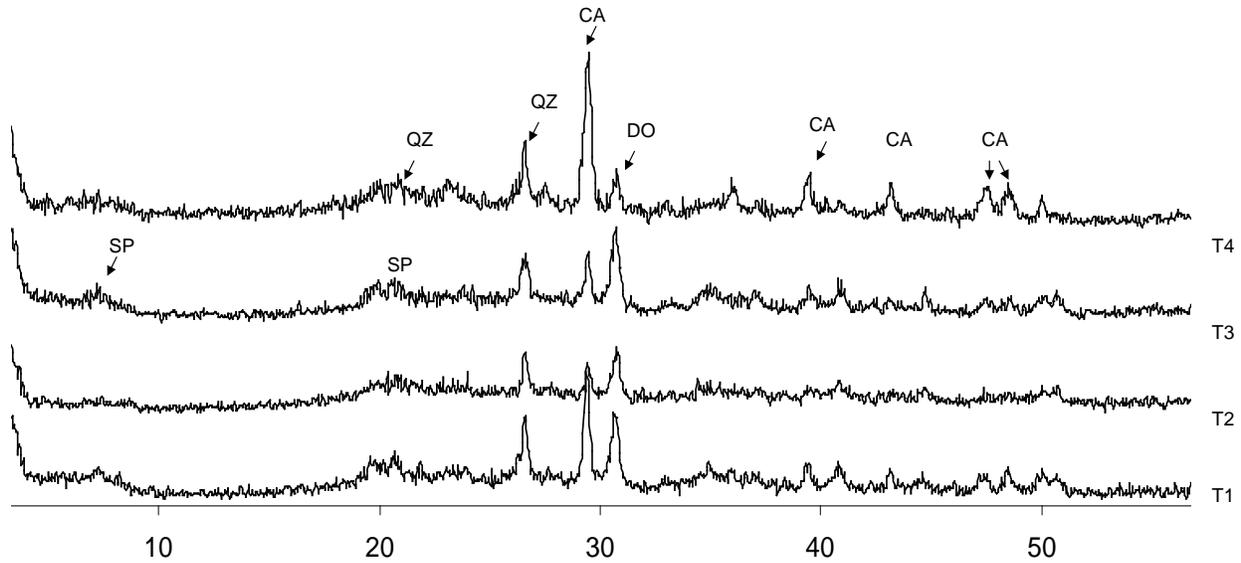


Figure 3-7. X-ray diffraction patterns from WPB canal sediments T1 to T4.

Table 3-10. Minerals identified in sediments of WPB canal sediments from T1 to T4.

Canal	Transect	Minerals							
		SP	QZ	CA	DO	AR	SM	KL	PL
WPB	T1	✓	✓	✓	✓	...			
	T2	✓	✓	✓	✓	...			
	T3	✓	✓	✓	✓	...	✓	✓	✓
	T4	✓	✓	✓	✓	...			

SP-Sepiolite-Magnesium Silicate [$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$].

QZ-Quartz-Silicon dioxide (SiO_2).

CA-Calcite-Calcium carbonate ($CaCO_3$).

DO-Dolomite-Calcium magnesium carbonate, [$CaMg(CO_3)_2$].

AR-Aragonite-Polymorph of calcium carbonate, ($CaCO_3$).

SM-Smectite (determined by removing carbonate and organic matter).

KL-Kaolinite (determined by removing carbonate and organic matter).

PL-Palygorskite-Magnesium Aluminium Phyllosilicate ($Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$ (determined by removing carbonate and organic matter).

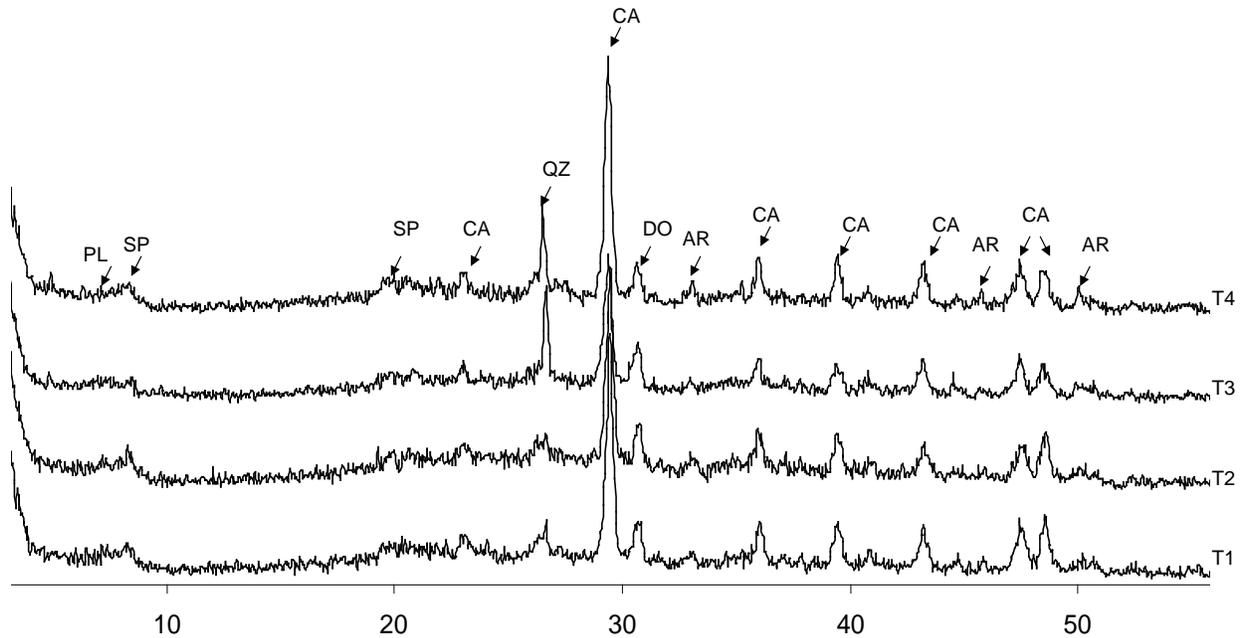


Figure 3-8. X-ray diffraction patterns from Ocean canal sediments T1 to T4.

Table 3-11. Minerals identified in sediments of Miami, WPB and Ocean canal sediments from T1 to T4.

Canal	Transect	Minerals							
		SP	QZ	CA	DO	AR	SM	KL	PL
Ocean	T1	✓	✓	✓	✓	✓	✓	✓	✓
	T2	✓	✓	✓	✓	✓			
	T3	✓	✓	✓	✓	✓			
	T4	✓	✓	✓	✓	✓			

SP-Sepiolite-Magnesium Silicate [$Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$].

QZ-Quartz-Silicon dioxide (SiO_2).

CA-Calcite-Calcium carbonate ($CaCO_3$).

DO-Dolomite-Calcium magnesium carbonate, [$CaMg(CO_3)_2$].

AR-Aragonite-Polymorph of calcium carbonate, ($CaCO_3$).

SM-Smectite (determined by removing carbonate and organic matter).

KL-Kaolinite (determined by removing carbonate and organic matter).

PL-Palygorskite-Magnesium Aluminium Phyllosilicate ($(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$) (determined by removing carbonate and organic matter).

CHAPTER 4
PHOSPHORUS RELEASE FROM THE MAIN CANAL SEDIMENTS OF THE
EVERGLADES AGRICULTURAL AREA (EAA)

4.1 Introduction

Phosphorus (P) in water bodies can have both external and internal sources. External sources of P can be agriculture or point sources like industrial or domestic effluents. Sediments can also release P, acting as an internal source of P to the overlying waters at levels comparable to external sources (Welch and Cooke, 1995; Steinman and Reddy, 2004). Internal loading is the recycling of nutrients from bottom sediments to the overlying water column (Bostrom et al., 1982; Carpenter, 1983; Marsden, 1989). After the external load reduction, the internal loads of sediments determine the trophic status of a water body and the time for recovery (Pettersson, 1998).

The release of P is controlled by a number of physical, chemical and biological processes (Bostrom et al., 1982). The various physicochemical factors affecting P sorption and release from sediments are redox potential (Eh), pH, temperature, and bioturbation/mixing (Andersen, 1975; Holden and Armstrong, 1980; Bostrom et al., 1982; Sondergaard, 1989). Various compounds can bind phosphorus efficiently like iron (III) and aluminum (III) hydroxides, clays, calcium, and humic substances (Bostrom et al., 1982). Phosphorus release from sediments can occur through hydrolysis of Fe/Al bound P; dissolution of Ca bound P, and mineralization of organic P (Pant and Reddy, 2001).

4.1.1 Influence of Redox on P Release

Inorganic P can be held as Fe and Al phosphates in wetland systems (Khalid et al., 1977). According to Mortimer (1941, 1942), P flux at the sediment-water interface is

primarily controlled by the ferric (Fe, III) iron, to which phosphate adsorbs forming FeOOH-PO₄ complexes. Below a redox potential of 80 mV at pH 7 insoluble iron (III) is reduced to iron (II) and dissolved P is fluxed into the water column (Reddy and DeLaune, 2008). The reduction of iron (III) can be induced by organic acids and sulfides (Bostrom et al., 1982). While P associated with the amorphous Fe and Al oxides readily desorb the crystalline forms are desorbed only under extended water logged conditions (Reddy et al., 1995). Moore et al. (1998) indicated that the P flux from the sediments of lake Okeechobee was sensitive to changes in redox reactions and oxygen status of the overlying water. However it was found that redox had greater influence on non-calcareous than calcareous sediments (Holdren and Armstrong, 1980).

4.1.2 Influence of Sediment pH on P release

Inorganic P can be retained as insoluble Ca-P or Mg-P compounds in alkaline wetland sediments (Moore and Reddy, 1994; Reddy et al., 1999; Richardson, 1999). Acid fermentation products released due to microbial degradation of organic matter can lower the interstitial pH that can cause dissolution of carbonate minerals mobilizing calcium, and magnesium associated P (Marsden, 1989). In addition, competition between hydroxyl and phosphate ions at high pH conditions can cause P release from clays, oxides and hydroxides of Fe and Al (Lijklema, 1980; Stauffer and Armstrong, 1986).

4.1.3 Phosphorus Flux from Sediments

Phosphorus flux to the overlying water column can be controlled by mineral solubility (Haggard, 2005) within the sediments. Using equilibrium calculations (Moore et al., 1991, 1998) showed that P solubility can be controlled by Ca mineral and Fe mineral precipitation. Oxygenated water has a redox potential of around +500 mV that

decreases rapidly and at sediment depth of 1-cm the redox potential and oxygen concentration can be about 200 mV and 0.1 mg L^{-1} respectively (Bostrom et al., 1982). Anoxic conditions can lead to a decrease in pH which can dissolve apatite (Stumm and Morgan, 1970; Golterman, 1998, 2001). Iron and P may not exist as apatites but may exist as different as ferrosferric hydroxyphosphates and strengite under oxidized conditions and vivianite under reducing conditions (Nriagu and Dell, 1974; Patrick et al., 1973). The lack of crystalline forms of Ca-P minerals can be due to several factors including inhibition in mineral formation due to presence of carbonates (Stumm and Leckie, 1970), organic acids (Inskeep and Silvertooth, 1988) and absence of seed crystals (Griffin and Jurinak, 1973).

4.1.4 Influence of Organic Matter on P release

P release from organic matter under oxic conditions has been reported by Boers and Van Hese (1988), Boers and De Bles (1991), and Sinke et al. (1990). Mineralization of organic material can occur rapidly under aerobic conditions thus potentially releasing P into the water column (Marsden, 1989). But organic matter mineralization can generate P flux in anaerobic conditions as well (Golterman, 2001). Under anoxic conditions bacterial populations turn to anaerobic fermentation and in order to acquire the same energy as aerobic respiration they decompose a large part of organic matter thus releasing P (Golterman, 2001).

Apart from releasing P through mineralization, organic matter functions as electron donor thereby affecting redox and subsequently (Golterman, 1975) influencing P flux from sediments. Organic acids can also act as chelating agents by sorbing calcium, iron, manganese and aluminum (Bostrom et al., 1982; Lijklema, 1985). This competitive exclusion can reduce P adsorption thus giving rise to P flux to the water column

(Stauffer and Armstrong, 1986). Complexation of organic acids with iron particles can ultimately hinder the precipitation of iron phosphates, and in the process leaves dissolved P in the water column (Pizarro et al., 1995).

Organic P can occur in a wide variety of compounds including phospholipids, nucleic acids, inositol phosphates, phosphoproteins, sugar phosphates and phosphonic acids (McKelvie, 2005). Different organic P compounds including diester P, polynucleotides, nucleosides, monophosphosphates, glycerophosphoethanolamine, phosphoenolpyruvates and pyrophosphates have been identified by researchers in the Everglades including STA-1W (Pant et al., 2002; Turner et al., 2006), WCA-1 and WCA 2 (Turner and Newman, 2005). Investigations by Ahlgren et al. (2006) and Hupfer and Lewandowski (2005) in twenty two lakes in Europe with different trophic conditions showed that organic P compounds especially polyphosphates can also undergo internal loading and can contribute significantly to P release. Due to the deposition of detrital matter in canal sediments and the presence of readily degradable phosphate diesters (Turner et al., 2006) organic P compounds can play an important role in internal P loading to the water column in EAA canals.

4.1.5 Other Factors Influencing P Release

Adsorption of phosphates can occur on clay minerals like kaolinite involving chemical binding to positively charged Al^{3+} edges of clay plates (Stumm and Morgan, 1970). The formation of ferrous sulfides can also reduce P sorption (Marsden, 1989) and liberate P to the water column. Water movement and turbulence within the sediment water column can significantly increase the P flux and maintain a high P concentration gradient thus increasing P diffusion from the sediments (Marsden, 1989).

The Everglades Agricultural Area (EAA) in South Florida is situated between Lake Okeechobee and the Water Conservation Areas (WCAs) comprising 2,872 km² of (SFER, 2010) of cultivated Histosols. Agriculture in EAA is focused on sugarcane but other crops like corn, winter vegetables and sod are also grown (Bottcher and Izuno, 1994). The EAA is distinguished by flat topography, shallow soils and seasonally high water tables underlain by limestone bedrock. Owing to flat topography in EAA, drainage is accomplished through a network of pumps and canals. Drainage from farms are pumped into farm canals that are managed by farm owners. The farm canals drain into the main canals. Main canals originate from the lake Okeechobee and are operated by the SFWMD. During the dry season irrigation water is pumped into the fields while in the wet season excess precipitation is pumped off the farms into the canals. Drainage water is routed from the farm canals to the main canals and into the Stormwater Treatment Areas (STAs). The STAs are constructed wetlands for P removal through biological removal and subsequent sequestration by sedimentation. Phosphorus fertilization, soil organic matter oxidation (subsidence) and inflow water from lake Okeechobee are the main sources of P exported to the EAA main canals (Sanchez and Porter, 1994; Stuck, 1996). It is estimated that nearly 2.5×10^{12} m³ (SFER, 2010) of water, and nearly 129 metric tons P per year (SFER, 2010) is discharged annually from the EAA into the Everglades Protection Area. Water pumped out of the EAA contains P in the dissolved (orthophosphate and soluble organics) and in the particulate form (minerals and particulate organics) (Daroub et al., 2002a). Phosphorus transported to the main canals accumulate in the sediments and the capacity of sediments to retain or release P can affect water quality. Everglades Agricultural Area canal sediments can act as potential P

source and generate an internal load of P to the overlying water column which is delivered to the rest of Everglades. In addition the main canal sediments are subject to transport and these sediments can act as a P source when transported to the downstream ecosystems.

Sediment core incubation studies have been performed in the Everglades and elsewhere to determine P flux in the sediments in wetlands in lake Okeechobee basin, the WCAs, lake Apopka and the Lower St Johns River (Dunne et.al., 2006; Fisher and Reddy, 2001; Moore et al., 1991; Malecki et.al., 2004). Sediment incubation studies were also performed in the canals of the STAs by Clark and Reddy (2002) but have not been used to date to determine the P flux from the main canals in the EAA. Thus P release capabilities of the EAA main canals are not known and our goal was to use intact sediment columns to determine P release and understand the P release characteristics associated with internal loading.

We hypothesized that, sediments with high organic matter content and high NaOH extractable P will have higher P release compared to sediments with low organic matter and low NaOH extractable P; also sediments with high HCl extractable P will have low P release.

Our objectives were to: (i) study P release characteristics of three main canals in EAA: Miami canal, West Palm Beach canal and Ocean canal sediments based on incubation experiments, and (ii) evaluate factors such as bulk density (BD), pH, P-fractions, amorphous Fe and Al oxides, and Ca and Mg carbonates that may affect sediment P release within the canals.

4.2 Materials and Methods

4.2.1 Study Site Description

Sediments for the study were collected from Miami canal situated in western EAA, West Palm Beach canal (WPB) situated in eastern EAA, and Ocean canal situated in south-east EAA. Water used in the incubation study was collected from Arthur R. Marshall Loxahatchee National Wildlife Refuge. Pumping in these canals is managed by the South Florida Water Management District (SFWMD) and thus these canals are also called district canals.

4.2.2 Sediment Sampling

Intact sediment cores were collected from four different transects from Miami, WPB and Ocean canal. Thus we have four different transects (T1, T2, T3 and T4) in each of the canals (Figure 4-1). The first transect (T1) for Miami and West Palm Beach canal was closest to the lake while the other transects (T2, T3 and T4) were taken progressively southward into EAA. The average distance between the transects in Miami and WPB canals were 10.7 km (Table 3-8). The first transect (T1) in Ocean canal was closest to the WPB canal and the fourth transect (T4) was closest to the Hillsboro canal. The average distance between the transects in Ocean canal was 2 km.

Three cores from each of the four transects and from each of the three main canals were collected leading to a total of $3(\text{cores}) \times 4(\text{transects}) \times 3(\text{canals}) = 36$ cores. Thus 36 intact sediment cores along with 2 blank cores (no sediment) were used for the incubation experiment. Details about sediment sampling and description of Miami, WPB and Ocean canals have been provided in Chapter 3.

4.2.3 Sediment Core Incubation

Canal water from the sediment cores was carefully siphoned off and the cores were refilled with 275 mL water collected from Arthur Raymond Marshall Loxahatchee wild life refuge. Before each of the three exchanges, water was collected from the Arthur Raymond Marshall Loxahatchee wild life refuge and stocked. The SRP concentration of water collected from the refuge during the first, second and third exchanges were 0.008, 0.004 and 0.007 mg L⁻¹ respectively. A 20 cm water column was maintained above the sediment layer in the cores (Malecki et al., 2004). The water columns in the cores were maintained under aerobic conditions by bubbling air using aquarium pumps via tubing inserted into the water columns. The floodwater dissolved O₂ concentrations were maintained between 5 and 8 mg L⁻¹. Bubbling air through the water column ensured aerobic conditions in the water columns (Gale et al., 1994). The interior of the incubation box was lined with black polythene to exclude light and prevent algal growth. The sediment cores were incubated in water bath to maintain a constant temperature (21±2°C).

Three floodwater exchanges were performed at the interval of 28 days. During exchanges water from the sediment cores were suctioned using a syringe fitted with tubing and with minimum disturbance to the sediment column. The cores were then refilled with stock 275 mL, 0.008, 0.004 and 0.007 mg L⁻¹ water during the first, second and third exchange respectively and incubated for another 28 days.

4.2.3.1 Collection of water samples

Prior to sampling, the aerator was turned off to minimize disturbance. Water column pH (Fisher scientific, accumet AP-85) and dissolved oxygen (Fisher scientific oxygen meter 06-662-66) of the water column from each core was measured before

sampling. A 20 mL sample was pipetted from the water column, filtered through a 0.45 µm membrane filter, and analyzed for soluble reactive phosphors (SRP) using ascorbic acid colorimetric method (EPA 1993, Method 365.1). Each time during sampling, water taken out was replenished with equal volume (20 mL) of stock P solution. The loss of water due to evaporation was replenished everyday by double distilled water.

4.2.3.2 Estimation of P flux

The estimation of P released/retained was calculated by the product of the volume of the water column multiplied by the difference in concentrations of the water column as shown below (Steinman and Reddy, 2004):

C_t = SRP concentration (mg L^{-1}) of the overlying water at time t days

C_{t-1} = SRP concentration (mg L^{-1}) of the overlying water at time t-1 days

V_T = The total volume (L) of the water column overlying the sediment

A = The inner cross sectional area of the sediment cores (m^2)

Thus P released/retained = $(C_t - C_{t-1}) * V_T$

Phosphorus flux from sediment to the water column was estimated by plotting cumulative SRP release/retention (Malecki et al., 2004) per unit surface area of the sediment column. Sediment P fluxes were calculated as linear changes in P mass in the overlying water after correction for sampling volume divided by the internal area of the sediment cores. Flux calculations were based on the increase/decrease of the amount of P in the water column. Phosphorus flux is calculated as SRP released/retained per unit surface area as:

$$\text{Flux} = (C_t - C_{t-1}) * V_T / A \quad \text{equation (1)}$$

The amount of P removed during sampling was also accounted for as the product of the sampling volume and the difference between the concentration of the water taken and the concentration of the water added.

C_s = concentration (mg L^{-1}) of the water replaced after sampling

V_s = volume of water (L) taken for sampling.

C_t = SRP concentration (mg L^{-1}) of the overlying water at time t days

Thus P removed (mg) due to sampling = $(C_t - C_s) * V_s$ equation (2)

Hence the total change in P (mg) = the sum of P released/retained and P removed during sampling. i.e. equation (1) + equation (2)

$P = \sum [(C_t - C_{t-1}) * V_T + (C_t - C_s) * V_s]$ equation (3)

Total flux of P (mg m^{-2}) (Reddy et al., 2007) = $\sum [(C_t - C_{t-1}) * V_T + (C_t - C_s) * V_s] / A$
equation (4)

To determine release and retention on a daily rate basis release and retention data were divided by number of sampling days per sampling period. Phosphorus mass release/retention at each sampling event was then converted to a rate ($\text{mg m}^{-2} \text{d}^{-1}$) by dividing by time or the number of sampling days per sampling event (Clark and Reddy, 2002).

4.2.4 Sediment Analysis

Sediment P release can occur due to a combination of chemical factors including sediment physicochemical properties (Andersen, 1975; Holden and Armstrong, 1980; Bostrom et al., 1982; Sondergaard, 1989), different P fractions (Pant and Reddy, 2001; Moore and Reddy, 1994; Reddy et al., 1999; Richardson, 1999) and the presence of amorphous Fe and Al oxides and Ca and Mg carbonates (Mortimer, 1941, 1942;

Bostrom et al., 1982; Reddy et al., 1995). The dependence of P release from the EAA sediments on these factors is not well established. Our investigation considered the effects of these factors affecting P release from the EAA canal sediments.

4.2.4.1 Sediment physicochemical properties

Sediment samples were analyzed for %Loss on ignition (%LOI), total P, BD, and pH. The details of the methods are provided in chapter 3.

4.2.4.2 Phosphorus fractionation

Sequential extraction was performed according to the method of Chang and Jackson (1957) modified for wetland soils (Qualls and Richardson, 1995; Reddy et al., 1998; Reddy et al., 2007). The detailed procedure of P fractionation is provided in Appendix A.

4.2.4.3 Extractable Fe and Al

Active amorphous Fe and Al oxide was extracted using 0.2 M ammonium oxalate and 0.2 M Oxalic acid at pH 3.0 (Loeppert and Inskeep, 1996; McKeague and Day, 1966) after pre-treating the samples with ammonium acetate for calcium carbonate (CaCO_3) (Loeppert and Inskeep, 1996).

4.2.4.4 Extractable Ca and Mg

Extractable Ca and Mg were determined by 0.5 N acetic acid extracting solution (Sanchez, 1990). The extracts were analyzed for Ca and Mg by Atomic Absorption Spectrometry (AAS).

4.2.5 Statistical Analysis

Calculation of P flux from intact cores was done by simple linear regression of the concentration versus time curve for the initial period of P flux. The mean and standard deviation of each parameter used for %LOI, total P, BD, pH and P fractions, and P

fluxes were calculated with Excel (Microsoft, 2000). Determination of the relationship between P flux, soil physicochemical properties, P fractions and extractable Fe, Al, Ca and Mg were performed using SAS statistical program (proc CORR) (SAS Institute, 2003).

4.3 Results and Discussion

4.3.1 Phosphorus Release from Canal Sediments

4.3.1.1 Miami canal

The P release values from Miami, WPB and Ocean canal sediments varied extensively between the transects, canals and floodwater exchanges. In exchange 1 (Figure 4-2), sediments from Miami canal T1 and T4 had lower cumulative P release rates (31.9 and 37.0 mg m⁻² respectively) than T2 and T3 (107 and 86.9 mg m⁻² respectively). During exchange 2, the cumulative P release values of all transects decreased and the same P release trend as exchange 1 was observed i.e. T2 and T3 had higher cumulative P release rates (70.5 and 77.1 mg m⁻² respectively) than T1 and T4 (35.6 and 18.8 mg m⁻² respectively). During exchange 3, the cumulative P release rates of all four transects decreased from exchange 1 and exchange 2. During exchange 3, T1, T2 and T3 had comparable cumulative P release values of 18.9, 16.7, 18.7 mg m⁻² respectively. Transect 4 at exchange 3 had the lower P release value among all the exchanges and transects in Miami canal. Total P released from Miami canal sediments over all the three exchanges were about 600 mg m⁻² for T2 and T3 (Figure 4-3). For T1 and T4 the total P released over all the three exchanges were about 300 and 200 mg m⁻² respectively. Similar to cumulative P release values, P flux from Miami canal sediments T1 and T4 (1.1 and 1.3 mg m⁻² d⁻¹) were lower than T2 and T3 (Figure 4-4). Similar P flux values (1 mg P m⁻² d⁻¹) were calculated for lake

Okeechobee sediments by Moore et al., 1998. The Miami canal is located in the S8 basin of the EAA. The S8 basin had a P load of 16300 kg yr⁻¹ in water year 2008 (SFER, 2009.) Multiplying cumulative P release by Miami canal area gives P load that can range from 30.1 to 101.6 kg month⁻¹ or 361.7 to 1218.8 kg yr⁻¹. Phosphorus release from Miami canal roughly estimated was about 2-7% of the total P load of the entire S8 basin.

4.3.1.2 West Palm Beach canal

The P release values from WPB canal sediments were lower than that of Miami canal at all transects and exchanges (Figure 4-5). Within WPB canal, T4 had least cumulative P release values at all the three exchanges, (6.9, 3.0 and 2.9 mg m⁻² for exchange 1, 2 and 3 respectively). During exchange 1, cumulative P release values of T1, T2 and T3 were 31.2, 28.1 and 26.5 mg m⁻². Similar to Miami canal, P release values decreased at all transects at WPB canal for exchange 2 and 3. Total P released from WPB canal sediments over all three exchanges were about 100 mg m⁻² for T1, T2 and T3 (Figure 4-6). For T4, total P released over the three exchanges was about 50 mg m⁻². The P flux values of WPB canal T1, T2 and T3 were greater than T4 during all exchanges (Figure 4-7). Both cumulative P release values and daily P release values of WPB canal sediments were lower than Miami canal sediments. The WPB canal is located in EAA S5A basin. The S5A basin had a total P load of 50000 kg yr⁻¹ in water year 2008 (SFER, 2009.). Multiplying cumulative P release by WPB canal area gives P load that can range from 14.0 to 63.5 kg month⁻¹ or 168 to 762 kg yr⁻¹, corresponding to approximately less than 0.1% of the total P load for the entire S5A sub-basin.

4.3.1.3 Ocean canal

Ocean canal P release values were comparable to P release values of WPB canal sediments (Figure 4-8). Within the transects of Ocean canal, the highest cumulative P release was observed at T2 43.1, 25.1 and 9.3 mg m⁻² during exchange 1, 2 and 3 (Figure 4-8). Cumulative P release of T1, T3 and T4 were 24.2, 21.9 and 20.6 mg m⁻² during exchange 1. Similar to Miami canal and WPB canal sediments, cumulative P release decreased at all transects during subsequent exchanges. Total P released from Ocean canal sediments over all three exchanges was about 65 mg m⁻² for T1, 200 mg m⁻² for T2, 150 mg m⁻² for T3 and 140 mg m⁻² for T4 (Figure 4-9). The P flux values decreased during subsequent exchanges at all transects in Ocean canal (Figure 4-10). Ocean canal is located in the S5A basin. Multiplying cumulative P release by Ocean canal area gives P load that ranges from 14.2 to 29.7 kg month⁻¹ or 170 to 356 kg yr⁻¹. West Palm Beach and Ocean canals have a total P load ranging from 339 to 1120 kg yr⁻¹. Combined P release from WPB and Ocean canal comprise about 0.07 to 2% of the total P load of the S5A basin.

4.3.2 Sediment Physicochemical Properties

Everglades Agricultural Area, main canal sediment physicochemical properties are provided in chapter 3, section 3.3.1.

4.3.3 Sediment P Fractions

Information in EAA main canal sediment P fractions are provided in chapter 3, section 3.3.2.

4.3.4 Extractable Fe, Al, Ca and Mg

Extractable Fe concentration varied from 62.6 to 906 mg kg⁻¹ in Miami, WPB and ocean canal sediments while Al concentration varied from 23 to 195 mg kg⁻¹ (Table 4-1).

The Fe and Al concentrations measured in the Histosols of EAA by Janardhanan and Daroub (2010) were much higher and averaged 7355 g kg^{-1} and 1715 g kg^{-1} . It is possible that Fe(III) in canal sediments were reduced to soluble Fe(II) that was released in canal water thus leading to low Fe concentrations in the sediments. The Ca concentrations were higher than Fe and Al concentrations and varied from 1816 to 32400 mg kg^{-1} in Miami, WPB and Ocean canal sediments. Magnesium concentrations were lower than the Ca concentrations and varied from 213 to 1285 mg kg^{-1} in Miami, WPB and Ocean canal sediments.

4.3.5 Factors Affecting P Release

Sediment total P release from Miami, WPB and Ocean canals were significantly correlated with both amorphous Fe and Al concentrations but were not significantly correlated with Ca and Mg concentrations (Table 4-1). This signifies that even though present in lower concentrations than Ca and Mg, amorphous Fe and Al concentrations significantly affect P flux in EAA canals. Similarly Janardhanan and Daroub (2010) found that P sorption capacities of the EAA Histosols were affected by the amorphous Fe and Al concentrations than the CaCO_3 concentrations. Hayes (1964), Lijklema (1977) found that sorption efficiencies for iron oxides and hydroxides are greatest around pH 6 and decrease with increase in pH. The EAA canal sediment pHs were circumneutral which may have lead to reduced sorption capacity leading to P release which explains the dependence of P release with extractable amorphous Fe. Though present in lower concentrations than Fe the dependence of P release with Al signifies the sensitivity of Al-phosphate complexes to undergo release in EAA canal sediments. Though present in large quantities P release in calcareous EAA canal sediments were not significantly related the Ca and Mg concentrations. Calcium in EAA canal sediments

can exist as calcium carbonates/calcites (as verified by mineralogical analysis of the main canal sediments in chapter 3, section 3.3.3) or as dissolved Ca^{2+} ions.

Phosphorus associated with Ca can be released by the dissolution of carbonate minerals by acid fermentation products (Marsden, 1989) or by competing hydroxyl ions substituting phosphates at high pH values (Lijklema, 1980; Stauffer and Armstrong, 1986). Most probably there were not enough of the acid fermentation products produced to dissolve carbonates to release P as well as the pH values were not high enough to substitute phosphates with hydroxyls.

Phosphorus released from EAA main canal sediments was not significantly correlated with sediment physicochemical properties including BD, %LOI and pH (Table 4-1). Low bulk density values can be a very important factor in the EAA canals causing increased P flux to the water column by sediment resuspension and by maintaining a concentration gradient owing to the action of pumps. High P release rates due wind induced turbulence and flushing in lakes were reported by Andersen (1974), Ryding and Forsberg (1977), Ahlgren (1980) and Poon (1977). The sediment layers in the intact sediment columns in the laboratory did not undergo any disturbance to affect P release which may explain the non dependence of P release with BD values. Organic matter cannot bind phosphate by itself and is dependent on associated metals such as Fe and Al (Bostrom et al., 1982). Organic materials have strong tendency to chelate iron which is diminished in presence of high concentrations of Ca^{2+} (Williams, 1970; Shukla et al., 1971). It is possible that high concentrations of Ca^{2+} ions in EAA sediments was hindering the association of organic matter with phosphates thus leading to no relationship with P release in these sediments. The significant correlation of P release

with sediment Fe concentration suggests that P release should be correlated with sediment pH values too. The sediment pH values recorded in the experiment were not the sediment core pH values during the course of experiment but were sediment pH values recorded at the beginning of the experiment which does not reflect the pH change that occurs during the course of the incubation period. Perhaps this is why we do not observe any correlation of P release with sediment pH.

Sediment total P release from Miami, WPB and Ocean canals was significantly correlated total P (Table 4-2) but not with individual P fractions. The dependence of P release on total P is indicated by the very low P release from Ocean canal sediments that had the smaller sediment total P values and high P release from Miami canal sediments that had greater total P values (Table 3-2). The lack of significant correlation of individual P fractions with P release indicates that several factors are likely controlling P release in these canal sediments. Furthermore the lack of correlation of P fractions with P release could mean that P mobilization by the different fractions does not necessarily result in P release but in many cases can result in transfer from one fraction to another (Bostrom, 1982). For example subsequent hydrolysis of organic phosphates may not result in P release but can be sorbed onto Fe(III) complexes or P released from Fe/Al or Ca/Mg can be taken up by microorganisms (Bostrom, 1982).

Apart from sediment properties, other factors may have influenced P release, like the presence of shells and the distribution of carbonate layers in canals. Ocean canal sediments had a layer of sea shells on the sediment surface and sea shells distributed throughout the sediment column (Figure 4-12). The presence of shells on the sediment surface possibly decreased the effective surface area which also could have contributed

to the low P release from Ocean canal sediments. The low P release from WPB canal sediments in spite of having comparable total P, BD, %LOI and pH values (Table 3-2 and 3-3) with Miami canal, could be due to alternating carbonate layers distributed throughout the sediment column inhibiting P release from sediments (Figure 4-13, 4-14, 4-15). Alternating climatic conditions favoring peat and calcite formation have been documented by Gleason and Spackman (1974) leading to inter-bedding of peat and carbonate layers in parts of EAA.

4.4 Conclusions

Phosphorus releases from EAA main canal sediments have been found vary among the three main canals in this study. Based on sediment physicochemical properties and P release characteristics Miami canal and Ocean are two very different canals. Miami canal sediments had high organic matter and high total P. Ocean canal sediments on the other hand were very mineral in nature with lower organic matter and lower total P. Phosphorus release from Miami canal sediments was much higher than Ocean canal sediments which support the correlation of P release with total P. The function of organic matter in P release is not clear as there was no correlation of P release with organic matter in the EAA canals. Organic matter can play an important role in facilitating P release by either masking adsorption sites or by acting as organic ligands and promoting P release. Support for this suggestion also stems from the fact that the fourth transect in Miami canal that was very mineral in nature had P release similar to Ocean canal sediments. Similar low P release was observed in EAA agricultural ditches by Collins (2005) where he estimated greater P release in ditches with organic sediments compared to mineral sediments. West Palm Beach canal which is similar to Miami canal in physicochemical properties and total P content had P

releases comparable to Ocean canal sediments. We suspect that though WPB canal sediments have the potential to release P, the alternating distributions of carbonate layers may have reduced P release to water column. Thus not only sediment properties but also the distributions of the sediment layers influence P release in EAA. The presence of a surface shell layer was also thought to inhibit P release by reducing the effective surface area in Ocean canal. Therefore P release in organic matter rich sediments in EAA which are expected to have high P release can behave in the opposite way if sediment bed is not completely in contact with the water column due to presence of shells. Phosphorus release from Miami canal ranged from 2-7% of the total P load from Miami canal basin (S8), while WPB-Ocean canal combined contributed approximately 0.07-2% of the total P load in the WPB-Ocean (S5A) sub-basin respectively. Based on the incubation experiments we conclude that the EAA canals do release P. The incubation experiments showed that, the canal sediments can act as a P source for at least a period of 84 days. This P release was conducted in the laboratory under controlled conditions and only diffusive fluxes from the sediments were considered. In canals, factors like canal flow conditions, resuspension and continuous addition of P can increase the magnitude as well as prolong the time of the P release. Future studies should focus on the evaluation of the extent and dependence of this P release on external P concentrations. Future research should also investigate the chemical characteristics of organic matter facilitated P release and mineral P release in EAA canals from different basins and topographical regions.

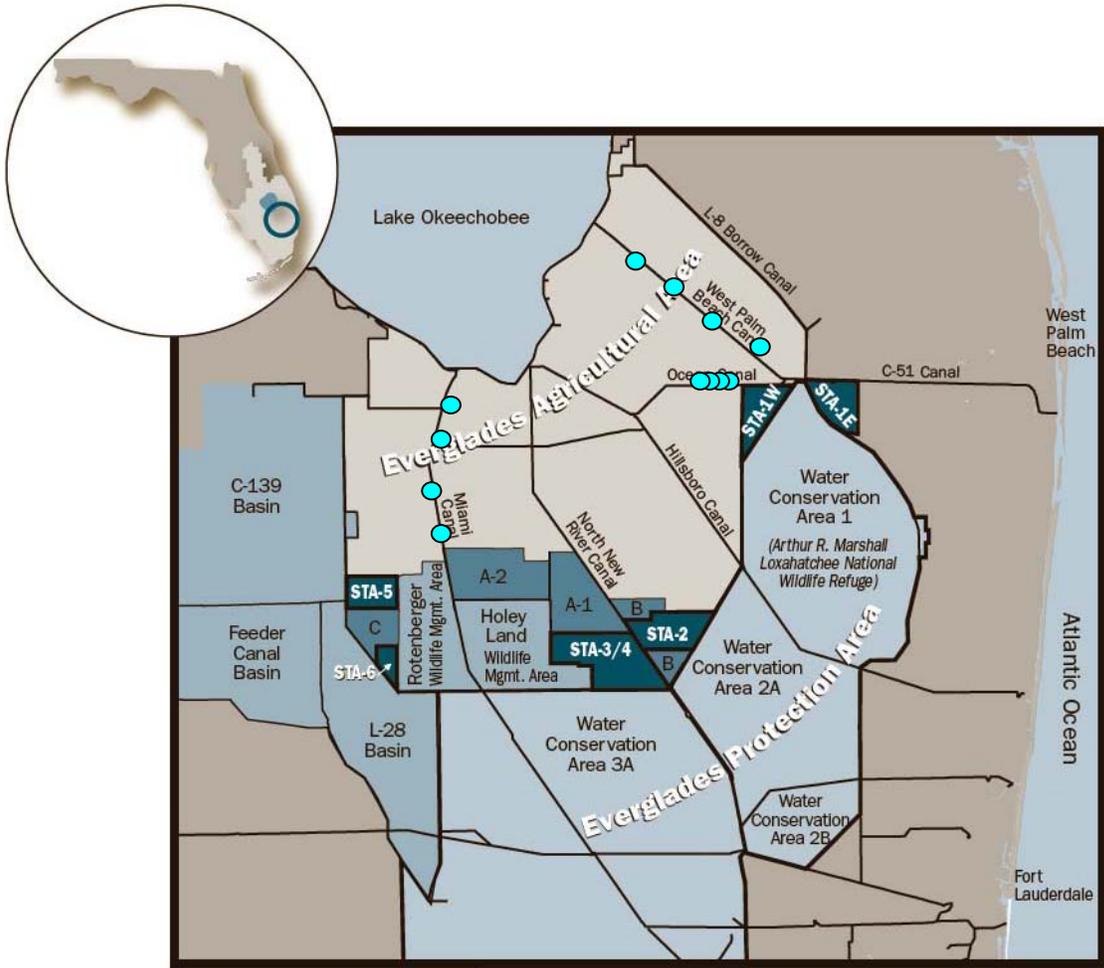


Figure 4-1. Transect locations T1 to T4 of Miami canal, WPB canal and Ocean canal in Everglades Agricultural Area.

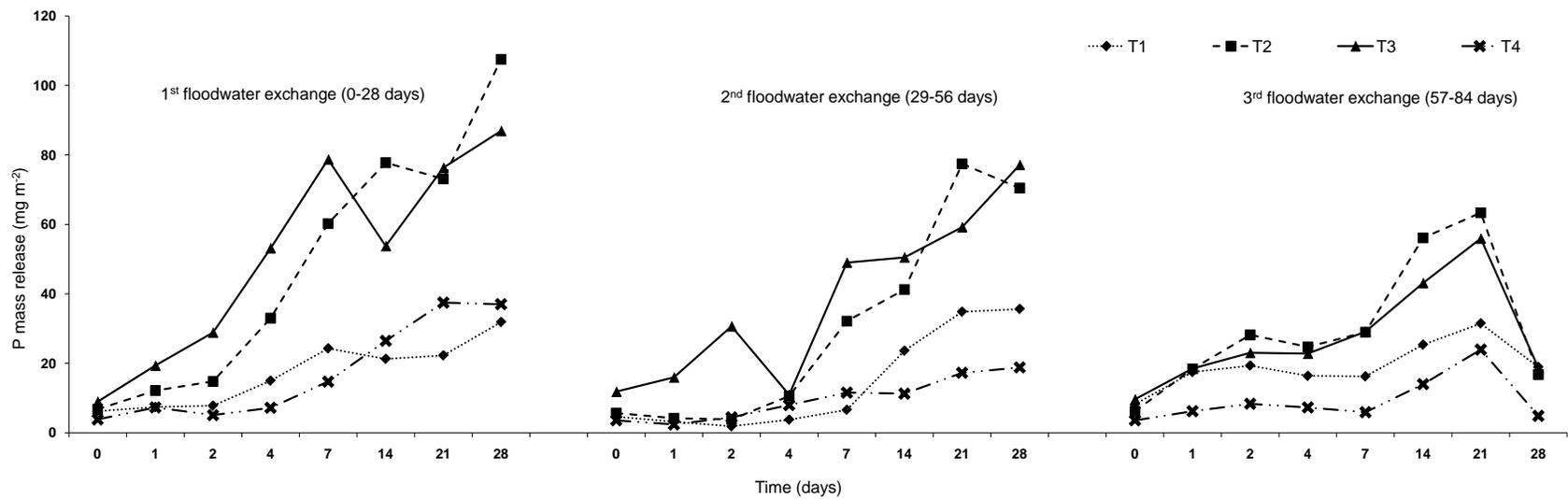


Figure 4-2. Phosphorus release from Miami canal sediments T1-T4 and exchange 1, 2 and 3.

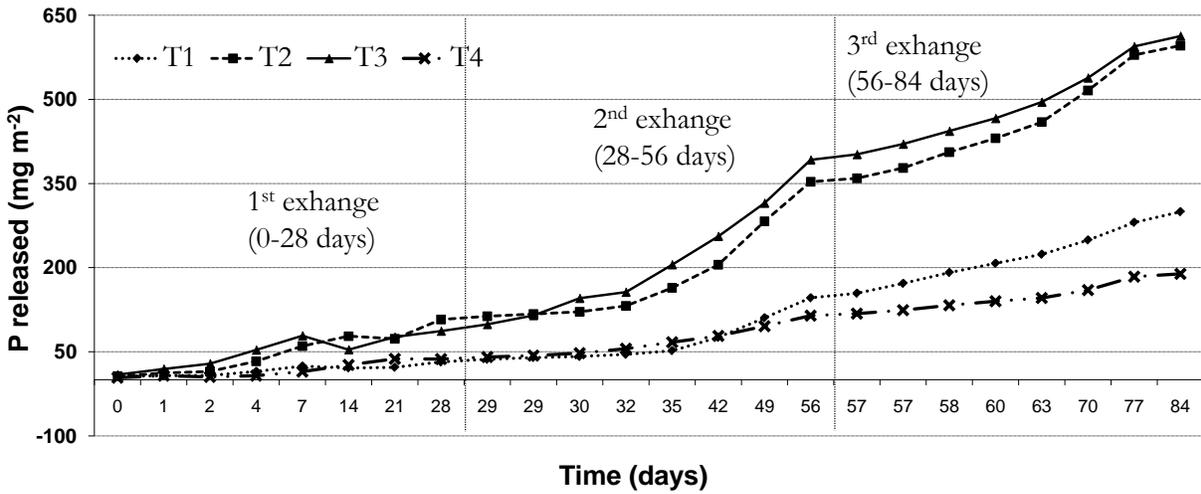


Figure 4-3. Total P released from Miami canal sediments over exchange 1, 2 and 3.

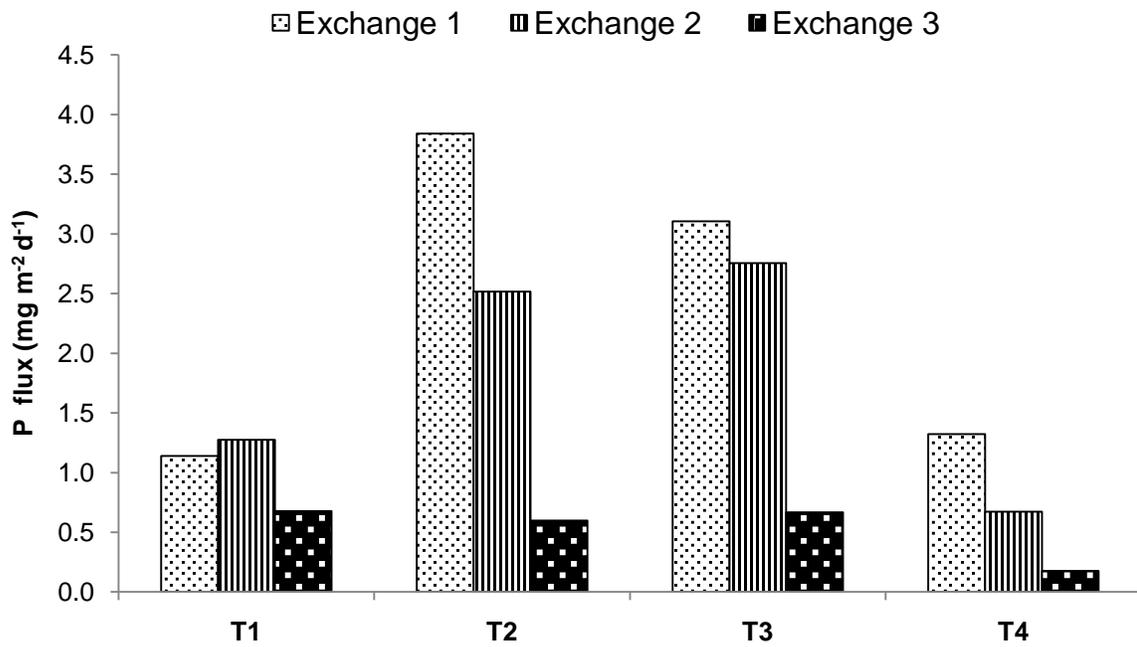


Figure 4-4. Phosphorus flux from Miami canal sediments T1-T4 and exchange 1, 2 and 3.

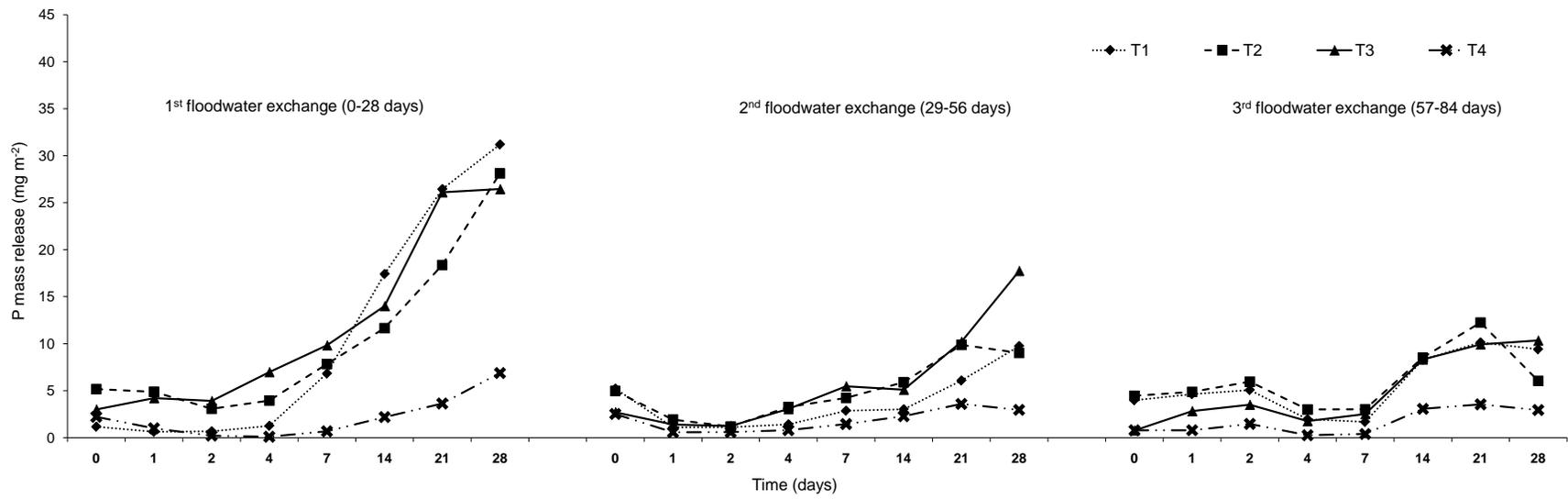


Figure 4-5. Phosphorus release from WPB canal sediments T1-T4 and exchange 1, 2 and 3.

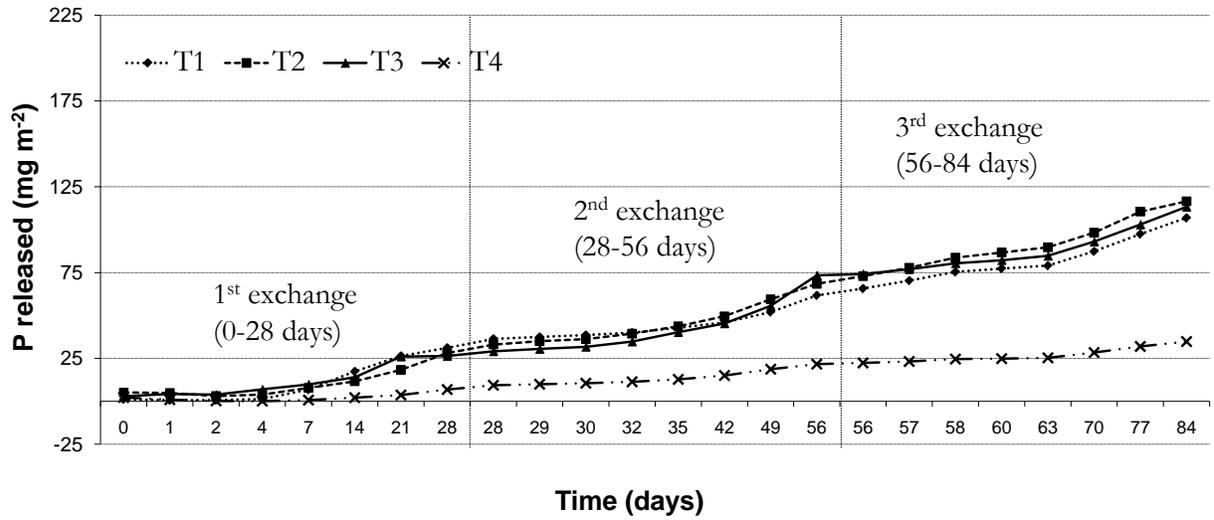


Figure 4-6. Total P released from WPB canal sediments over exchange 1, 2 and 3.

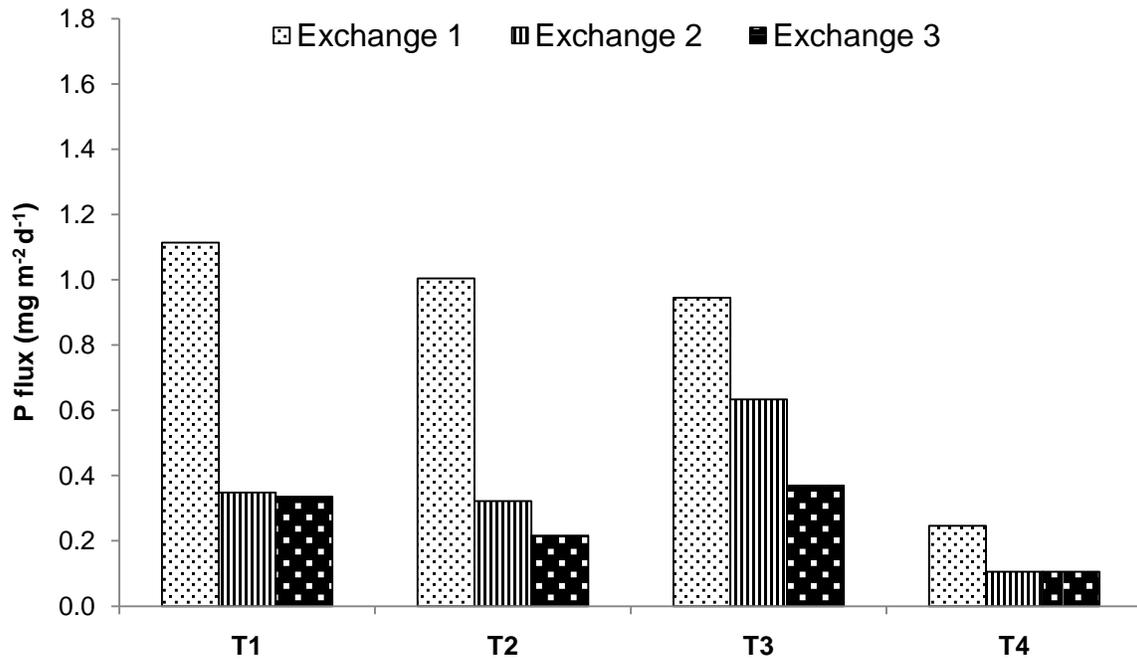


Figure 4-7. Phosphorus flux from WPB canal sediments T1-T4 and exchange 1, 2 and 3.

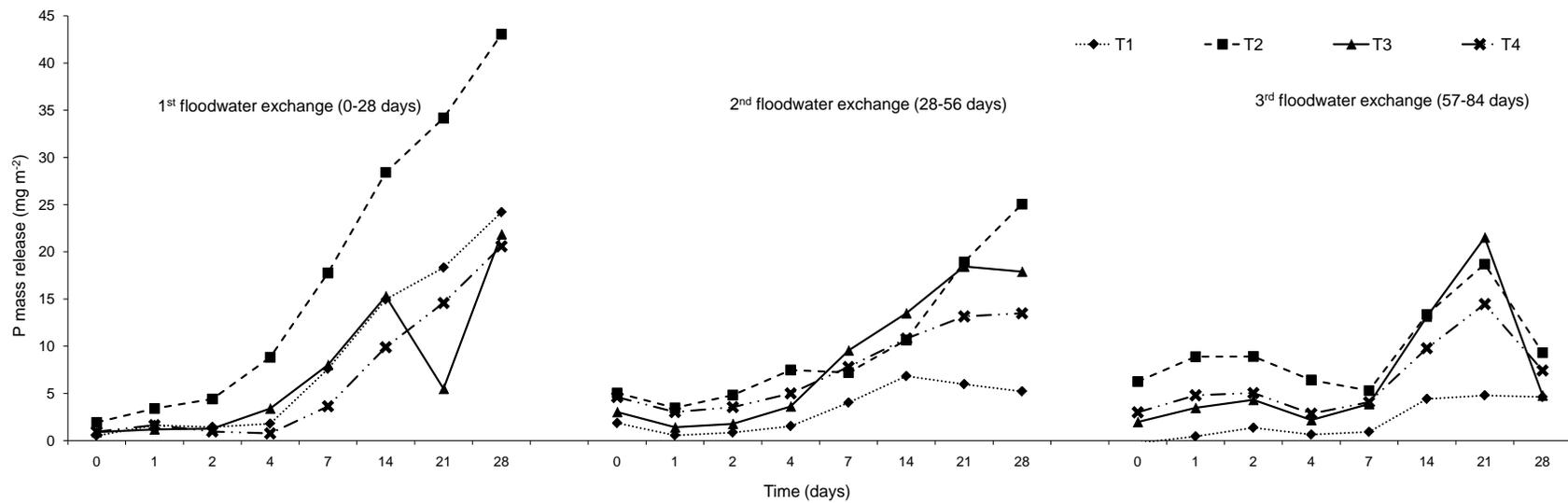


Figure 4-8. Phosphorus release from Ocean canal sediments T1-T4 and exchange 1, 2 and 3.

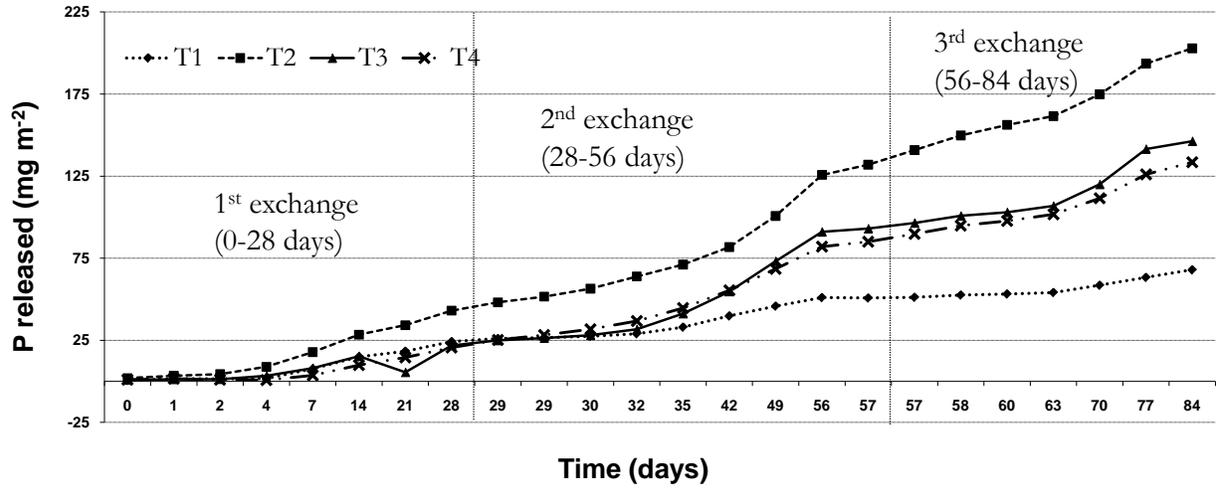


Figure 4-9. Total P released from Ocean canal sediments over exchange 1, 2 and 3.

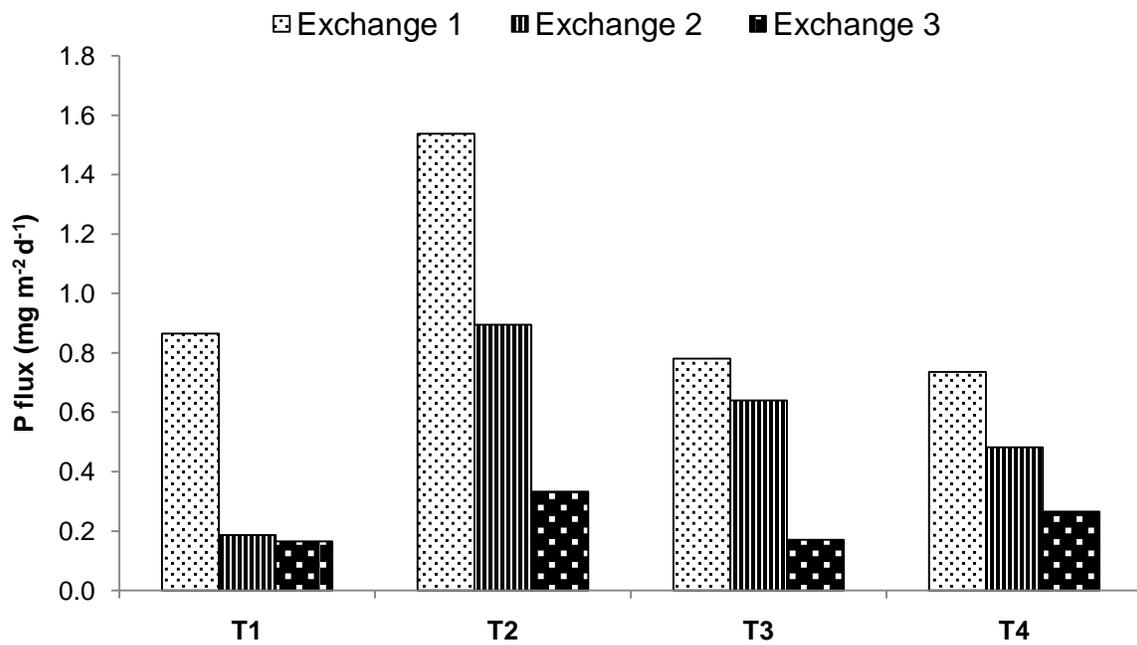


Figure 4-10. Phosphorus flux from Ocean canal sediments T1-T4 and exchange 1, 2 and 3.

Table 4-1. Ammonium oxalate extractable Fe, Al, and acetic acid extractable Ca, Mg from Miami, WPB and Ocean canal sediments.

Canal	Transect	Fe _{ox} mg kg ⁻¹	Al _{ox} mg kg ⁻¹	Ca mg kg ⁻¹	Mg mg kg ⁻¹
Miami	T1	677	195	26000	1280
	T2	661	170	17600	678
	T3	906	124	8240	615
	T4	606	123	24900	461
WPB	T1	62.6	230	1820	213
	T2	489	980	18500	754
	T3	971	122	7150	1240
	T4	846	123	6530	796
Ocean	T1	385	99.4	22000	644
	T2	169	59.9	31600	582
	T3	330	122	20800	685
	T4	248	59.3	32400	468

Table 4-2. Correlation of total P released from canal sediments over exchange 1, 2 and 3 with sediment physicochemical properties BD, %LOI, pH, Fe, Al, Ca and Mg.

	Fe	Al	Ca	Mg	BD	%LOI	pH
Total P released	0.64*	0.64*	0.42 ns	0.47 ns	-0.28 ns	0.29 ns	-0.30 ns

Table 4-3. Correlation of total P released from canal sediments over exchange 1, 2 and 3 with total P and sediment P fractions.

	Total P	KCl	NaOH Pi	NaOH Po	HCl	Res
Total P released	0.41**	0.33 ns	0.004 ns	0.25 ns	0.25 ns	0.04 ns

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

ns Not significant.

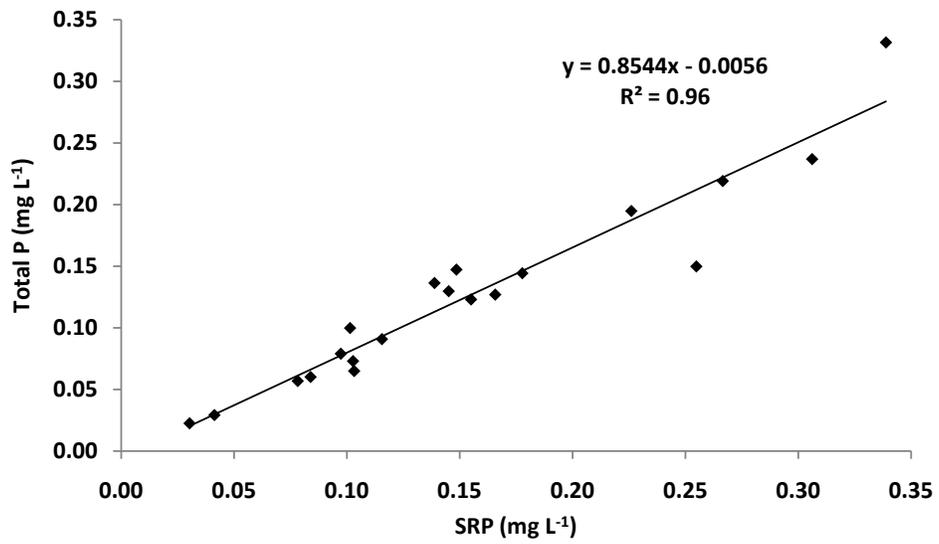


Figure 4-11. Correlation between water column total P and SRP from sediment incubation study.



Figure 4-12. Sediment surface layer of sediment core from Ocean canal.

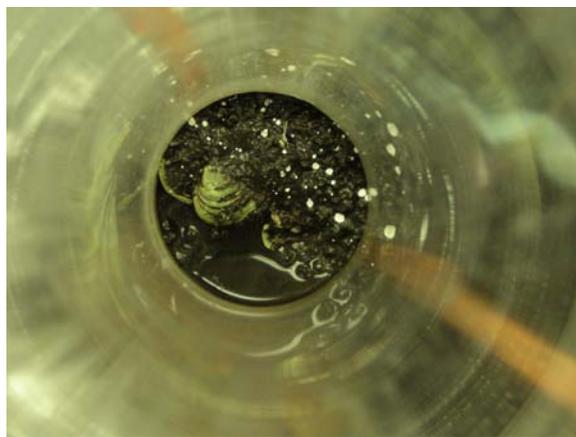


Figure 4-13. Sediment surface layer of sediment core from WPB canal.



Figure 4-14. Sediments from WPB canal.

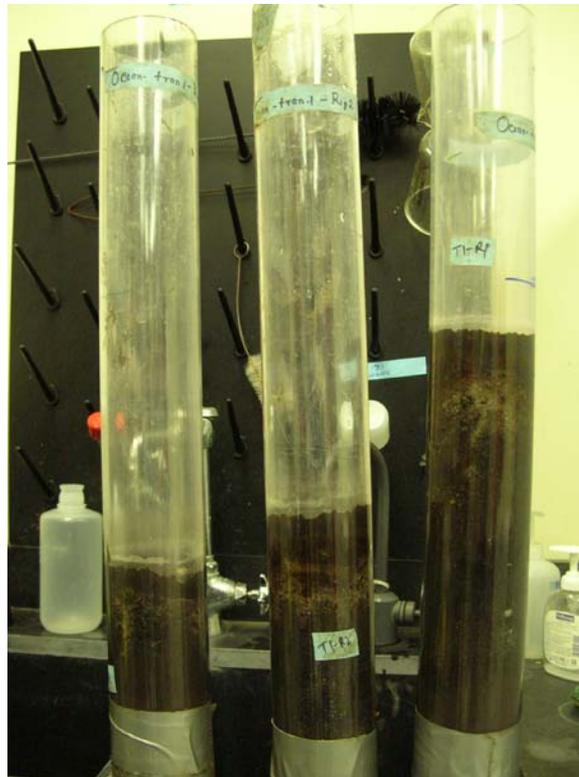


Figure 4-15. Sediment cores from WPB canal showing layers of CaCO_3 .

CHAPTER 5 DETERMINATION OF EQUILIBRIUM PHOSPHORUS CONCENTRATIONS OF EAA MAIN CANALS

5.1 Introduction

Phosphorus (P) is the limiting nutrient for algal growth in freshwater ecosystems and P loading from the Everglades Agricultural Area (EAA) is considered to be the major cause of eutrophication in the Everglades (Pant et al., 2002). Phosphorus is usually considered to be the limiting nutrient in freshwater ecosystems, including streams and lakes whereas N is considered the limiting nutrient in marine ecosystems primarily due to enhanced iron sequestration by sulfides. The EAA lies in South Florida between lake Okeechobee to the north and the Water Conservation Areas (WCAs) and the Everglades National Park (ENP) to the south. The EAA is drained by a network of canals consisting of farm canals and main canals. The farm canals are managed by EAA farm owners and are used to drain and irrigate the farms. The drainage from the farm canals are pumped into the main canals which are managed by the South Florida Water Management District (SFWMD). The entire water system is hydrologically connected thus P sourced from the lake and the EAA farms can end up in the P limited ecosystem of the Everglades through the EAA canals. The EAA canal sediments can act as a sink or alternatively due to years of agriculture and subsequent accumulation of P within the canal sediments, can act as a P source to the overlying water column. Thus these EAA canals can determine the water quality entering the P sensitive ecosystems of the south. Within EAA canals, sediment physicochemical and biological processes can play a central part in affecting resultant P concentration in canal water, and subsequent loads to downstream water bodies. The EAA canal sediments are composed of calcareous parent material as well as deposited particulate material from

EAA farms. Equilibrium phosphorus concentration (EPC) measurements of EAA canal sediments can be useful to identify the sediments as sinks or sources of P. The EPC is defined as the aqueous P concentration in the water column at which no net flux i.e. release or retention occurs from the sediments to the water column; and the P in solution is in equilibrium with P in the solid phase (Reddy et al., 1999). When soluble reactive P (SRP) in overlying water is greater than the EPC of the sediment, the sediment will remove SRP from the water column, and the opposite is true when $SRP < EPC$. (Reddy et al., 1995; Pant and Reddy, 2001).

5.1.1 Importance of EPC Values

Equilibrium phosphorus concentration values give an indication of the previous loading within the sediments and the direction of P flux from the sediments (Martin, 2004). Identifying the canal sediments as P sources/sinks can help in effective management of the EAA canals that can improve the existing Best Management Practices (BMPs) for individual canals. Optimizing the effectiveness of the BMPs with respect to the EPC of the canals may improve performance and management of Storm Treatment Areas (STAs) that are used to treat agricultural runoff from the EAA. Agricultural input into the canals can result in a subsequent increase in the EPC values of the sediments and hence can reflect P loading (Reddy et al., 1998). The EPC values determined by Richardson and Vaiyithianaythan (1995) in WCA-2A showed a linear increase of EPC values from un-enriched to enriched sites. They had also reported higher EPC values at the inflow structures. Graetz and Nair (1995) determined EPC values in the north of lake Okeechobee watershed from the high animal density areas soils. These active dairy soils had EPC values ranging from 5.3 to 10.6 mg L⁻¹ whereas the EPC values for the native soils around 1.3 mg L⁻¹. The EPC values in un-enriched

southern Everglades soil determined by Zhou and Li (2001) ranged from 0.002 to 0.010 mg L⁻¹.

Equilibrium phosphorus concentration values can be determined from adsorption isotherms (EPC₀) and incubation of intact sediment cores (EPC_w). The EPC₀ is calculated from batch adsorption experiments with varying P spike concentrations. The EPC_w is the floodwater P concentration in intact sediment columns when there is no net P release/retention from the sediments. Equilibrium Phosphorus Concentration values are a measure of the potential of P loading from soils/sediments to the water column.

5.1.2 Linear Adsorption Isotherms

Phosphorus sorption isotherms can be used to determine the sediment EPC₀ values from soils and sediments (Ruttenberg, 1992; Novak et al., 2004). The standard method for determining EPC₀ by adsorption isotherms involves treating soil or sediment with varying P concentrations in KCl solution that are shaken overnight, centrifuged, filtered and analyzed for SRP (Pant and Reddy, 2001; Novak et al., 2004). The exchangeable P signifies the labile P that can desorb if the sediment acts as a P source. The difference in amounts of P added and recovered in solution at each concentration after equilibration are considered as P adsorbed /released by soil or sediment (Reddy et al., 1999; Pant and Reddy, 2001).

While it is common practice to determine sediment EPC₀ by linear adsorption isotherms, the experimental conditions do not represent the system and the parameters calculated from these adsorption isotherms can vary depending on contact/shaking time and temperature (McGechan and Lewis, 2002). Laboratory batch incubation isotherms involve 24 h of shaking, but in reality phosphate sorption equilibrium can take weeks or years to come into effect (Hansen et al., 1999). During the adsorption isotherm

experiments each particle is in contact with the extracting solution whereas in canals the sediment surface is in contact with the water column. The Langmuir equation was used to determine different adsorption parameters. The Langmuir equation was originally derived for describing the adsorption of gases onto solids and is based on assumptions of (i) a constant adsorption energy on a homogenous surface; (ii) no interaction between adsorbed molecules and (iii) the maximum adsorption being equal to a monomolecular layer of the adsorbed molecules (Bohn et al., 1985). These assumptions rarely occur in nature. Due to the various criticisms and limitations of using the linear adsorption isotherm we also determined EPC by incubation of intact sediment cores.

5.1.3 Incubation of Intact Sediment Cores

Equilibrium phosphorus concentration (EPC_w) values can also be calculated through intact sediment column experiments where P release/retention in soil/sediment columns are monitored with varying floodwater P concentration (Reddy et al., 1996; Nyugen and Sukias, 2002). The EPC_w values are determined by plotting sediment P retained/released against the floodwater P concentration as the P concentration at which there is no P flux (Reddy et al., 1999). The exchange of sediment P to the water column can occur by i) sedimentation of inorganic and organic particulate P ii) uptake of SRP by primary producers and its subsequent settling iii) sorption of soluble inorganic and organic P onto particles that settle out onto the sediments or the sorption of soluble inorganic and organic particles onto sediments (Reddy et al., 1999). Phosphorus is released from the sediments when the porewater P concentration exceeds the water column P concentration (Moore et al., 1991). Phosphorus flux from sediment cores can be regulated by i) processes within the water column (mineralization, sorption by

particulate matter, uptake and release by primary producers, ii) processes within the sediment column (mineralization, sorption, precipitation, dissolution and redox fluctuation) and other factors like pH, temperature, organic matter content, and presence of metals (Holdren and Armstrong, 1980; Moore et al., 1991). The possibility of the occurrence of all these processes within the incubated sediment cores may make the incubation experiment a better representation of the natural system, thus could be an improved way to determine EPC from P flux measurements.

We hypothesize that the EPC values would vary according to the P release potential of the canal sediments and the adsorption isotherm and incubation of intact sediment cores would yield similar EPC values.

Our objectives were (i) to determine the EPC of three main drainage canals of EAA: Miami, West Palm Beach (WPB) and Ocean canal. (ii) to compare the EPC values measured by two methods: adsorption isotherms (EPC_0) and (EPC_w).

5.2 Materials and Methods

A batch incubation experiment as well as in intact sediment core incubation study was conducted using the sediments collected from Miami, West Palm Beach (WPB) and Ocean canal. Procedures for determining sediment physicochemical properties, P fractions and amorphous Fe, Al, Ca and Mg are documented in chapter 3 and chapter 4.

5.2.1 Study Site Description

Sediments were collected from Miami canal situated in western EAA, West Palm Beach canal (WPB) situated in eastern EAA and Ocean canal situated in southeast EAA. Agricultural drainage water in EAA is pumped out of the farms to the farm canals

and to the main canals which then flows downstream. The description of the study sites for Miami, WPB and Ocean canals are discussed in chapter 3.

5.2.2 Collection of Sediment Cores

Intact sediment cores were collected from four different transects (T1, T2, T3 and T4) from Miami, WPB and Ocean canals (Figure. 4-1). Three cores from each of the 4 transects and from each of the 3 main canals leading to a total of 3(cores) x 4(transects) x 3(canals) = 36 cores along with 2 blank cores (no sediment) were taken for the incubation experiment. Description of the sediment core collection procedure is provided chapter 4.

5.2.3 Phosphorus Adsorption Isotherm

About 3 g of field moist sediments were mixed with 30 ml of P containing 0, 50, 100, 150, 200, 250, 500, and 1000 $\mu\text{g L}^{-1}$ of KH_2PO_4 solution (Reddy et al, 1998; Pant and Reddy, 2001) with soil to solution ratio of 1:10. The KH_2PO_4 was made in 0.01M KCl medium as an ionic medium like KCl helps to reduce the pH dependant sorption (Giesler et al., 2005). To determine the potential maximum P sorption capacity of the canal sediments additional P isotherms of 5000, 15,000, 20,000 and 30,000 $\mu\text{g L}^{-1}$ were conducted, and the data combined with the initial results. Sediment samples were shaken for 24 h on an orbital shaker and immediately centrifuged at 4000 rpm for 15 min. The extracts were immediately filtered through 0.45 μm membrane HV filter paper (Reddy et al., 1998; Giesler et al., 2005). The filtrates were analyzed for soluble reactive P (SRP) by ascorbic acid method (Murphy and Riley, 1962) using Lachat Quickchem FIA 8000 series. Quality assurance/quality control was strictly followed with calibration,

standards, spikes, and blanks routinely included in the analysis. A check standard, duplicate and spike was included every after 10 samples.

Estimation of EPC₀ by adsorption isotherms. Linear adsorption isotherms were used to determine sediment EPC values (Pant et al., 2002) which is given by

$S = KC - S_0$. The EPC values were calculated from regression statistics as the intersecting point on the x axis between S (y axis) against C (x axis) i.e. the concentration (C) when $S = 0$ (Pant et al., 2002; Smith et al., 2005)

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

K = Phosphorus sorption coefficient

C = Solution P concentration following 24 h of shaking $\mu\text{g L}^{-1}$

S_0 = Quantity of P originally sorbed by sediments (is the intercept on the y axis).

Linear Langmuir isotherms were used to calculate P sorption maximum (S_{max}) and other bonding energy (k), which is given by $C/S = [1/(k * S_{\text{max}}) + C/S_{\text{max}}]$ (Reddy et al., 1998; Rhue and Harris, 1999; Pant and Reddy, 2001; Essington, 2004).

C = Solution P concentration measured after 24 h equilibration (mg L^{-1})

S = Amount of P sorbed in solid phase (mg L^{-1})

S_{max} = P sorption maximum (mg kg^{-1})

k = Sorption constant related to P bonding energy (L mg^{-1})

The linear Langmuir isotherm was constructed by plotting C/S vs S_{max} . The slope is equal to $1/S_{\text{max}}$ and the intercept is equal to $1/(k * S_{\text{max}})$. The sorption constant k, is equal to the reciprocal of equilibrium P concentration at one half saturation and is related to the bonding energy of the soil for phosphorus. An increase in the value of k indicates an increase in the bonding energy of the soil for P. (Olsen and Watanabe,

1957). The Langmuir equation adsorption parameter S_{\max} , gives us an estimate of sediment P storage capacity.

5.2.4 Sediment Core Incubation

Five different floodwater exchanges consisting of 7 days each were performed with P spikes of 0.007, 0.05, 0.13, 0.27 and 0.35 mg L⁻¹ respectively. Spike for the 1st exchange was collected from A.R.M. Loxahatchee wildlife refuge which was of the required concentration thus not needing to add any further P. Other spikes were prepared a day before the exchange by adding appropriate P standard solution (KH₂PO₄) to water collected from the refuge. The description of the of the incubation experiment, sampling and other details are provided in chapter 4.

Estimation of EPC_w from sediment incubation study. Sediment EPC_w values were determined by plotting P release as y axis against floodwater P spike concentration as x axis. Sediment P release was calculated as linear changes in P mass in the overlying water after correction for sampling volume divided by the internal area of the sediment cores (Malecki et al., 2004). Phosphorus flux was calculated as the product of volume of water column multiplied and P concentrations of the water column explained in chapter 4 (Steinman and Reddy, 2004). The EPC_w values were determined as the intersection of daily P flux (y axis) with water column P concentration (x axis) which was accomplished by equating the straight line equation to zero and solving the value of x, i.e. the P concentration (Reddy et al., 1999; Leeds, 2006).

5.3 Results and Discussion

5.3.1 Miami Canal

5.3.1.1 Batch adsorption isotherm

Sediment EPC values from batch adsorption isotherm studies were determined by plotting solution equilibrium P concentration on the x axis and P released/retained on the Y axis (Figure 5-1). Batch incubation studies of Miami canal yielded EPC₀ values of 0.03, 0.03, 0.06 and 0.05 mg L⁻¹ of T1-T4 respectively (Table 5-1). Similar EPC₀ values were found by Reddy et al., 2007 from lake Okeechobee sediments where at depths 0, 30, 45, and 55 cm the EPC₀ values were on the order of 0.03, 0.01, 0.02 and 0.04 mg P L⁻¹. Higher EPC₀ (0.38, 0.30, and 0.34 mg P L⁻¹) values were found on the wetland soils of Orange County Florida experimental wetland site by Gale et al. (1994). The S_{max} values of Miami canal T1 to T4 were 666.7, 714.3, 909.1 and 1111 mg kg⁻¹. Thus T3 and T4 sediments have higher adsorption capacity than T1 and T2 sediments. The intensity of adsorption (k) of Miami canal transects T1 to T4 were 250, 357.1, 178.6 and 178.6 L kg⁻¹.

5.3.1.2 Incubation of intact sediment cores

Phosphorus release from T1-T4 exchange 1 to 5 on Miami canal sediments (Figure 5-2) shows that the sediments released P during exchange 1 and 2 and retained P in exchange 4 and 5. Thus the EPC_w values of the sediments should be between spike P concentration of exchange 2 (0.05 mg L⁻¹) and exchange 4 (0.27 mg L⁻¹). Sediment EPC_w values were obtained by plotting P release with floodwater spike concentration (Figure 5-3) were 0.124, 0.159, 0.125 and 0.075 mg L⁻¹ from T1-T4 respectively (Table 5-2).

There are notable differences between the EPC values generated by the adsorption isotherm and the incubation study method. First, the EPC values from the incubation study were higher than that obtained from adsorption isotherm studies by almost an order of magnitude which indicates that P release in sediment cores is higher than that in adsorption isotherms. This could be because EPC values from batch adsorption isotherms are calculated in laboratory conditions where sediments are not influenced by canal conditions like the presence of plants and algae that can affect P release (Gale et al., 1994). Furthermore, overnight shaking ensures aerobic conditions in the tubes which can lead to lower P release and thus low EPC values. This is in contrast to incubation experiments where reducing conditions develop in sediments that can influence P release from reduction of iron (Fe III). Oxygenated water has a redox potential of around +500 mV which decreases rapidly with depth and at sediment depth of 1-cm the redox potential and oxygen concentration can be about 200 mV and 0.1 mg L⁻¹ (Bostrom et al., 1982). Pant and Reddy (2001) conducted studies on the sorption characteristics of the estuarine sediments of the Indian River Lagoon System under different redox conditions. Under anaerobic and aerobic conditions the mean EPC values of 0.75 mg L⁻¹ and 0.05 mg L⁻¹, which made them conclude that higher EPC in the anaerobic conditions was due to P release from amorphous and poorly crystalline forms of iron (Fe III).

The reducing conditions arising in subsurface sediment layers can cause P release in incubation experiments as well as in canals resulting in higher P release and consequently higher EPC values. Sediment columns in porewater diffusion can also play a significant role in P release from canal sediments. Though EPC values from

adsorption isotherms were lower than that obtained from intact sediment study, according to batch adsorption study T4 had the highest EPC value while according to incubation study method it was quite the opposite. Physicochemical properties of the canal sediments (Chapter 3, Table 3-1) indicate that T4 had highest total P but the P fractions showed that this huge amount of total P was mostly bound as HCl-P (Chapter 3, Figure 3-3). It is possible that overnight shaking exposed all soil sorption sites bringing into solution P from otherwise unavailable pools. In contrast, in incubation experiments P diffuses from sediments to the water column without any external aid.

5.3.1.3 Phosphorus release and EPC_w

The EPC_w values were significantly correlated with sediment P release (0.082***). Phosphorus released from Miami canal T1, T2 and T3 (78.6, 121, 105 mg m⁻²) were higher than T4 (31.8 mg m⁻²) (Figure 5-4). High P release values lead to high EPC_w values which can be a result of high P loading in these sediments. High P loading and the resultant high P release from the soils from a dairy operation farm in Okeechobee, Florida yielded an EPC_w of 1.3 mg L⁻¹ (Pant and Reddy, 2003). The P retained by Miami canal sediments were -112, -99.0, -164 and -104 mg m⁻² for T1, T2, T3 and T4 respectively.

5.4.1 WPB Canal

5.4.1.1 Batch adsorption isotherm

The EPC_0 values of WPB canal transects were 0.02, 0.04, 0.04 and 0.36 respectively (Figure 5-5 and Table 5-3). The EPC value of T4 was almost an order of magnitude greater than rest of the transects. The k values of WPB canal sediments were 555.6, 500, 277.8 and 15.4 L kg⁻¹ from T1-T4 respectively. The high EPC value at

T4 is reflected in the very low k value. West Palm Beach canal T3 had the least S_{\max} (769 mg kg⁻¹) and T1 had the highest S_{\max} value (1430 mg kg⁻¹).

5.4.1.2 Incubation of intact sediment cores

Phosphorus release from T1-T4 exchange 1 to 5 from WPB canal sediments (Figure 5-6) show that during exchange 1 all the transects are releasing P. During exchange 2, at P spike concentration of 0.05 mg L⁻¹, T1 and T4 began retaining P while T2 and T3 sediments were still releasing P. During exchange 3 at P spike concentration of 0.13 mg L⁻¹ T2 and T3 began retaining P while at exchange 4 and 5 all transects are retaining P.

Sediment EPC_w values were obtained by plotting P release with floodwater spike concentration as shown in Figure 5-7. The EPC_w values for WPB canal sediments from T1 to T4 were 0.021, 0.078, 0.094 and 0.052 mg L⁻¹ (Table 5-4). Among WPB canal transects, T1 had the least EPC value while T3 had the highest EPC value which reflects higher P release in T1 compared to T3 as indicated by the P release curves of WPB canal. The EPC_w values of WPB canal sediments were lower than that of Miami canal sediments at all transects except T4 of Miami canal. Miami canal T4 consisted of sediments with high bulk density, high pH and very low P organic matter, i.e. the sediments were mineral in nature which may have prevented P release leading to low EPC_w values.

As evidenced by the data there were some striking differences between EPC values determined by adsorption studies and incubation of intact cores. In contrast to Miami canal sediments, the EPC values determined by intact sediment cores from WPB canal were similar compared to that by adsorption isotherm.

5.4.1.3 Phosphorus release and EPC_w

The EPC_w values were found to be positively correlated with sediment P release values for all canals. Phosphorus released from WPB canal was lower than that of Miami canal sediments at all transects and the P release values for T1, T2 and T3 were 12.4, 16.1, 7.6, $mg\ m^{-2}$ (Figure 5-8). Transect 4 had the least P release ($2.7\ mg\ m^{-2}$) value among WPB transects. Phosphorus retained by WPB canal sediments were higher than the P release values at all transects and the values were -98.4, -42.8, -58.1 $mg\ m^{-2}$ and -107.4 $mg\ m^{-2}$ for T1, T2, T3 and T4 respectively. High P release values resulted in higher EPC_w values at T1, T2, T3 and least EPC_w value at T4. Low P release values from WPB canal sediments were also observed in the incubation experiment (Chapter 4, Figure 4-6). Though WPB canal had similar sediment physicochemical properties as Miami canal, the low P release was thought to be due to the distribution of the carbonate layer that were effectively retaining P released from the sediments.

5.5.1 Ocean Canal

5.5.1.1 Batch adsorption isotherm

Linear adsorption isotherm on Ocean canal sediments yielded EPC values of 0.07 $mg\ L^{-1}$ at T1 (Figure 5-9). The EPC values of T2 to T4 were 0.66, 0.11 and 0.09 $mg\ L^{-1}$ (Table 5-5). Transect 2 of Ocean canal had the highest EPC value within Ocean canal sediments as well as all the canals. The k values of transects T1, T3 and T4 were 37.5, 31.9 and 33.9 $L\ kg^{-1}$. The least k value was observed at transect T2 ($15.7\ L\ kg^{-1}$). The k values are an indicator of the bonding energy of the soil for P and an increase in k indicates an increase in bonding energy and vice versa (Olsen and Watanbe, 1957).

The low k value at T2 indicates very low bonding energy for P which may have facilitated P release from soils and resulted in high EPC_0 value.

5.5.1.2 Incubation of intact sediment cores

Phosphorus release from Ocean canal sediments show that during exchange 1 with P spike concentration of 0.007 mg L^{-1} all transects were releasing P (Figure 5-10). In exchange 2 with P spike concentration of 0.05 mg L^{-1} T2-T4 are releasing P while the P release curve for T1 intersects the horizontal axis which indicates its equilibrium concentration. During exchange 3 with P spike concentration 0.12 mg L^{-1} all transects were retaining P except T2 which briefly released P before finally starting to retain P. Thus the EPC_w for T2-T4 was expected to be between spike concentration of exchange 2 and exchange 3. At exchange 4 and 5 all the transects were retaining P.

The EPC_w values were determined by plotting P released/retained against the water column SRP concentration. Ocean canal T1 yielded EPC_w value of 0.05 mg L^{-1} (Figure 5-11). The EPC values of T2 to T4 were 0.127, 0.084 and 0.071 mg L^{-1} (Table 5-6).

There were differences between EPC values determined by adsorption study and incubation sediment cores. Similar to WPB canal P release in Ocean canal is very low thus EPC determined by both methods are similar except in T2. The high EPC_0 value in T2 was most probably due to P released due to shaking but was not subject to diffusive P release during incubation experiment.

5.5.1.3 Phosphorus release and EPC_w

Phosphorus released from Ocean canal T1, T2 T3 and T4 were 2.8, 44.9, 20.7, and 21.2 mg m^{-2} (Figure 5-12). Higher P release from Ocean canal T2 compared to the rest of the transects gave rise to high EPC_w values among the transects. Total P

retained by both Miami and WPB canal sediments were higher than total P released by the sediments. Total P retained by Miami canal sediments were -79.8, -41.8, -70.3 and -87.3 mg m⁻² for transects T1, T2, T3 and T4 respectively.

5.6.1 EPC₀, EPC_w, k, S_{max} and Sediment Properties

Metal oxides such as Fe, Al, Ca and Mg provide positively charged surfaces that can bind P and influence sediment EPC₀ and EPC_w. Sediment EPC₀ values were not significantly correlated with the metal concentrations but EPC_w values were significantly correlated with Al, Ca and Mg concentrations (Table 5-7) which indicates that P from these metals influence the EPC_w values in EAA canal sediments. Sediment k values were significantly correlated with the Fe, Al and Mg concentrations. Sediment EPC_w and EPC₀ values similar to sediment P release (Chapter 4, Table 4-1 and 4-2) were not correlated to sediment physicochemical properties including BD, %LOI and pH (Table 5-8) and different P fractions (Table 5-9).

5.4 Conclusions

Sediment P release potentials affect EPC values determined by adsorption isotherms and incubation experiments. The EPC values determined by incubation experiments have been found to be higher than those determined by adsorption isotherms that was due to the reducing conditions developed over the period of the experiment (a total of 35 days) that promote P release in sediment cores. Though the incubation experiments were conducted with a water column that was maintained in aerobic condition by bubbling water through it, according to Bostrom et al. (1982) oxygenated water has a redox potential of around +500 mV. But this redox potential decreases rapidly and at sediment depth of 1cm the redox potential and oxygen concentration can be about 200 mV and 0.1 mg L⁻¹ (Bostrom et al., 1982). Both

methods yield similar EPC values when P release from sediments are low, which is particularly true for calcareous sediments (Chapter 3) for Miami canal T4 and Ocean canal sediments. The high EPC_0 value at Ocean canal T2 was thought as a consequence of very low k or bonding energy value that aided P release. Similar EPC_w and EPC_0 values for WPB canal sediments were observed due to low EPC_w values. This decrease in EPC_w values for WPB canal that was thought to occur as a result of the distribution of calcium carbonate layers thereby preventing P release (Chapter 4) which could also be the reason of the high k values (from adsorption isotherm experiment) among all the canals. Similar to Ocean canal T2, EPC_0 value of WPB canal T4 was very high than the rest of the transects and could be due to the very low bonding energy of the P in the sediments promoting P release. Thus future research is needed for the analysis of EPC values of these canal sediments using in situ techniques.

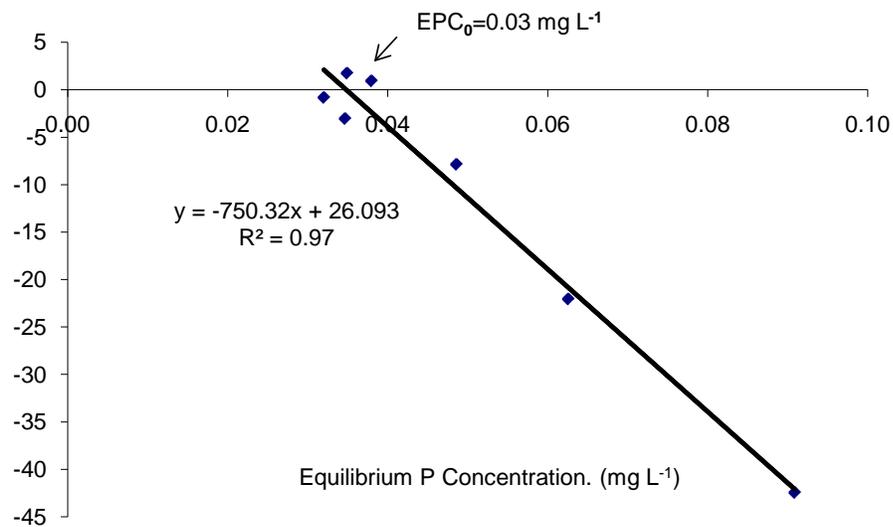


Figure 5-1. Determination of EPC_0 from linear adsorption isotherm for Miami canal, T1.

Table 5-1. Equilibrium Phosphorus Concentrations (EPC_0) from adsorption isotherms, maximum sorption capacity (S_{max}) and intensity of adsorption (k) for Miami canal T1, T2, T3 and T4 sediments.

Canal	Transect	EPC_0 ($mg L^{-1}$)	Equation	R^2 (%)	S_{max} ($mg kg^{-1}$)	Intensity of adsorption k ($L kg^{-1}$)
Miami	T1	0.03	$y = -750.32x + 26.093$	97	667	250
	T2	0.03	$y = -1004.9x + 28.222$	93	714	357
	T3	0.06	$y = -214.03x + 9.9754$	77	909	179
	T4	0.05	$y = -1605.9x + 82.112$	89	1110	179

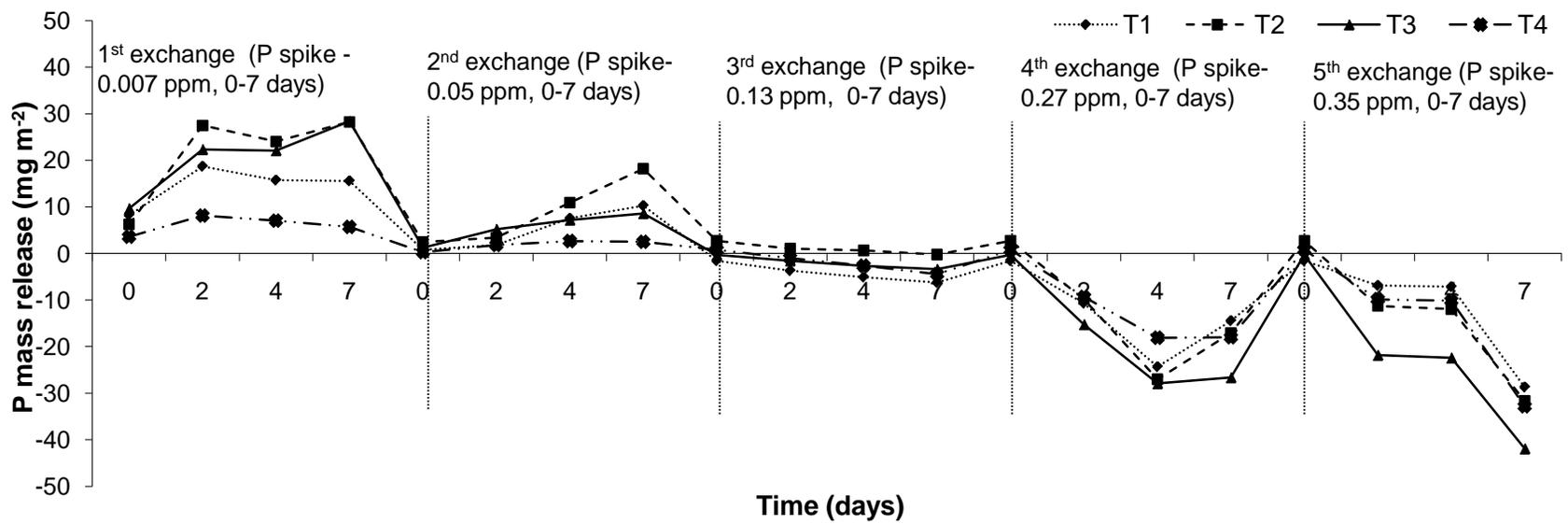


Figure 5-2. Cumulative P release from Miami canal T1-T4 sediments during exchanges 1-5.

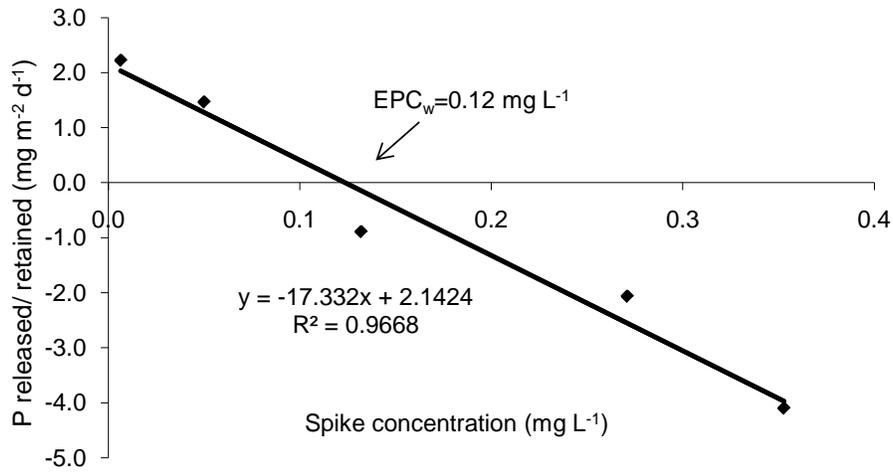


Figure 5-3. Determination of EPC_w of Miami canal T1 from sediment core incubation study.

Table 5-2. Equilibrium Phosphorus Concentrations (EPC_w) from sediment column incubation study for Miami canal T1, T2, T3 and T4 sediments.

Canal	Transect	EPC_w ($mg L^{-1}$)	Equation	R^2 (%)
Miami	T1	0.12	$y = -17.332x + 2.1424$	97
	T2	0.16	$y = -23.824x + 3.7976$	99
	T3	0.12	$y = -26.869x + 3.3678$	98
	T4	0.07	$y = -15.358x + 1.1516$	98

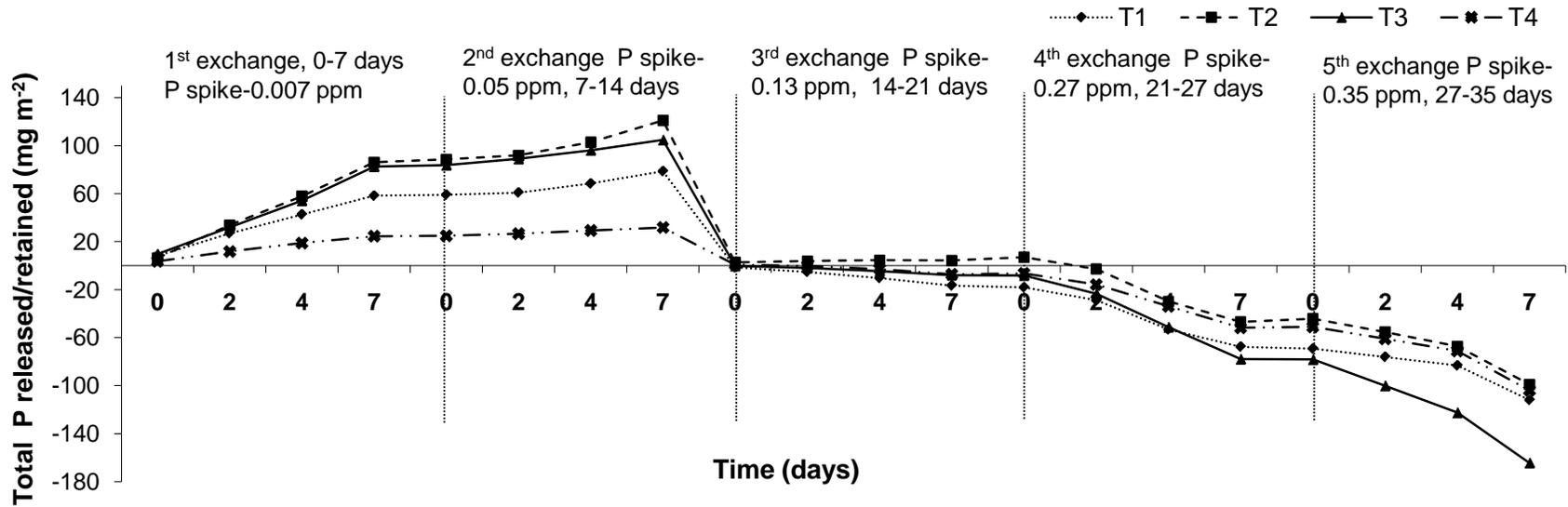


Figure 5-4. Total P released and retained from Miami canal T1-T4 sediments during exchanges 1-5.

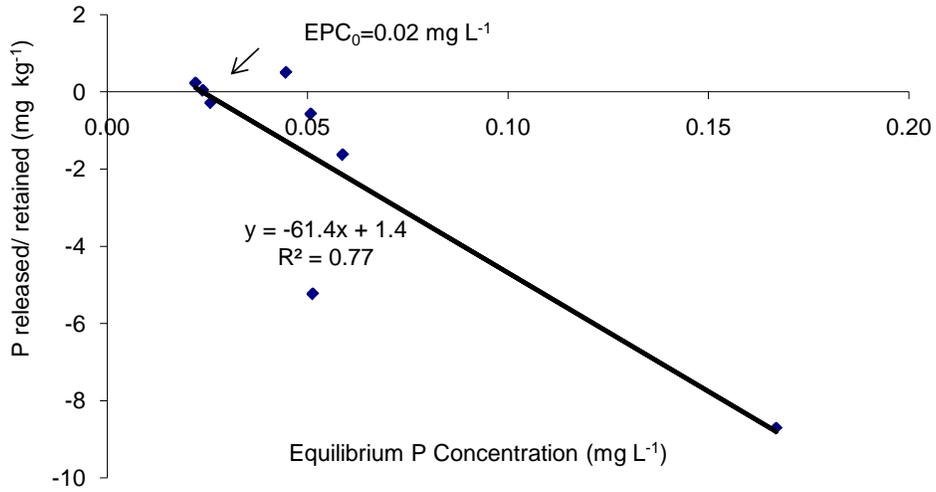


Figure 5-5. Determination of EPC_0 from linear adsorption isotherm for WPB canal T1.

Table 5-3. Equilibrium Phosphorus Concentrations (EPC_0) from adsorption isotherms, maximum sorption capacity (S_{max}) and intensity of adsorption (k) for WPB canal T1, T2, T3 and T4 sediments.

Canal	Transect	EPC_0 ($mg\ L^{-1}$)	Equation	R^2 (%)	S_{max} ($mg\ kg^{-1}$)	Intensity of adsorption k ($L\ kg^{-1}$)
WPB	T1	0.02	$y = -61.464x + 1.4581$	77	1430	556
	T2	0.04	$y = -1179.2x + 43.26$	90	1250	500
	T3	0.04	$y = -131.82x + 4.5003$	98	769	278
	T4	0.36	$y = -31.382x + 11.473$	85	1110	15.4

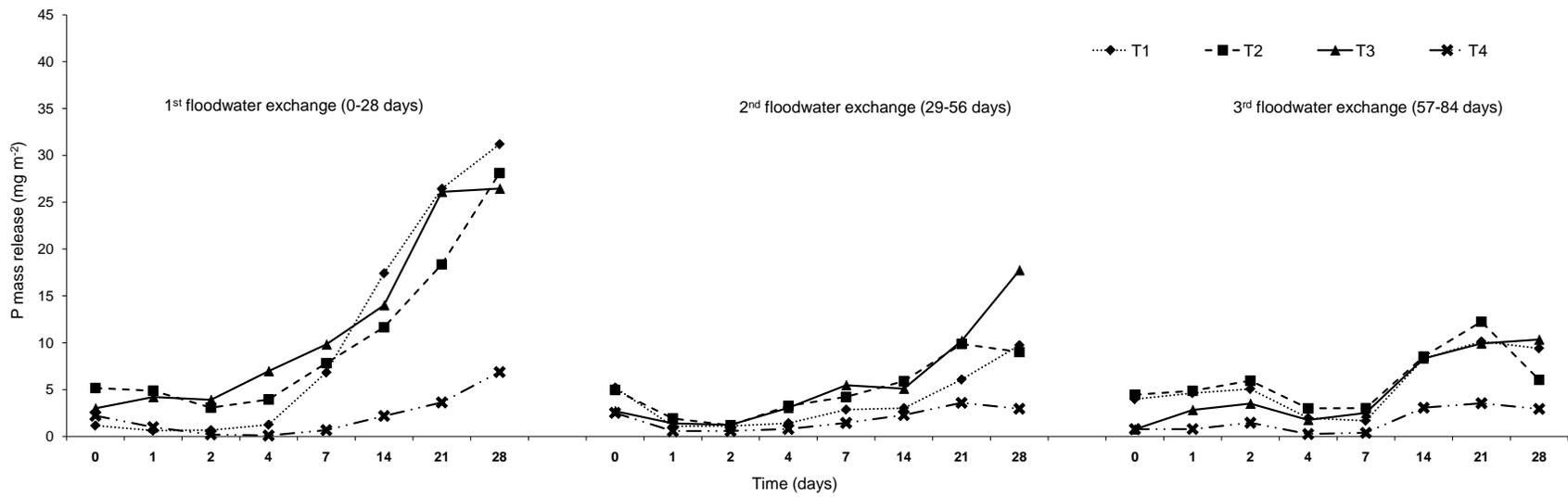


Figure 5-6. Cumulative P release from WPB canal T1-T4 sediments during exchanges 1-5.

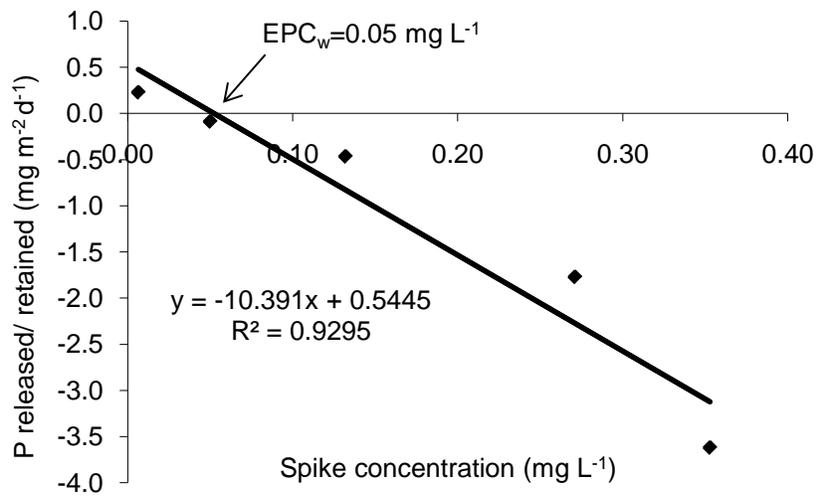


Figure 5-7. Determination of EPC_w for WPB canal T1 from sediment core incubation study.

Table 5-4. Equilibrium Phosphorus Concentrations (EPC_w) from sediment column incubation study for WPB canal T1, T2, T3 and T4 sediments.

Canal	Transect	EPC_w (mg L ⁻¹)	Equation	R^2 (%)
WPB canal	T1	0.05	$y = -10.391x + 0.5445$	93
	T2	0.09	$y = -9.2333x + 0.8656$	87
	T3	0.08	$y = -9.2317x + 0.7240$	89
	T4	0.02	$y = -10.617x + 0.2206$	95

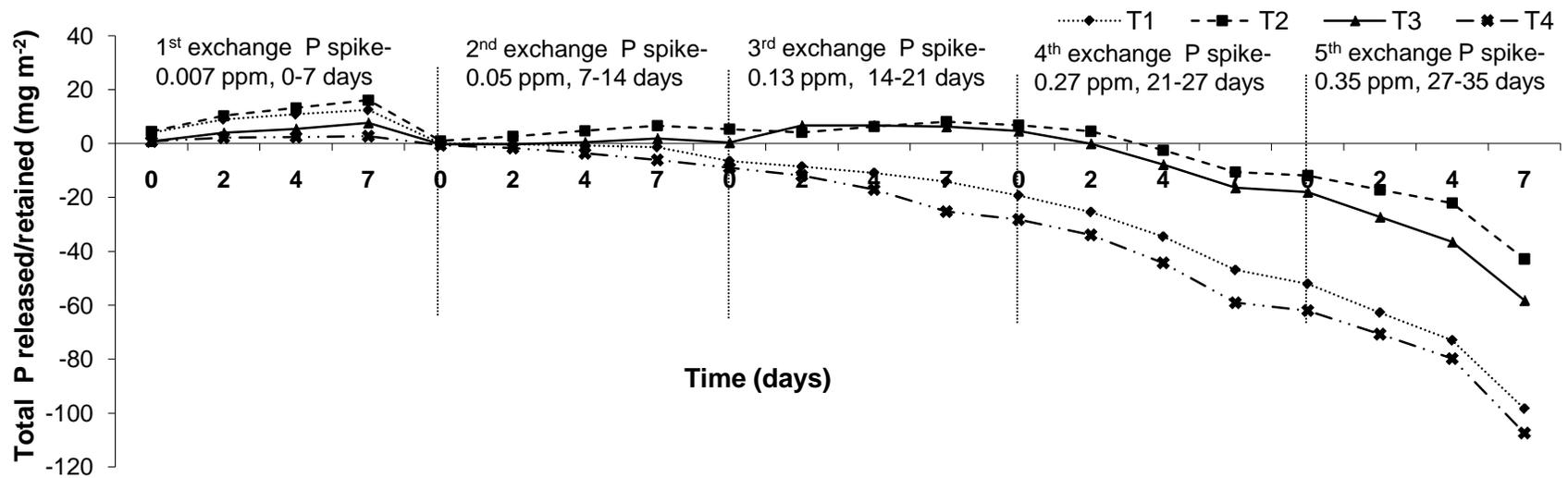


Figure 5-8. Total P released and retained from WPB canal T1-T4 sediments during exchanges 1-5.

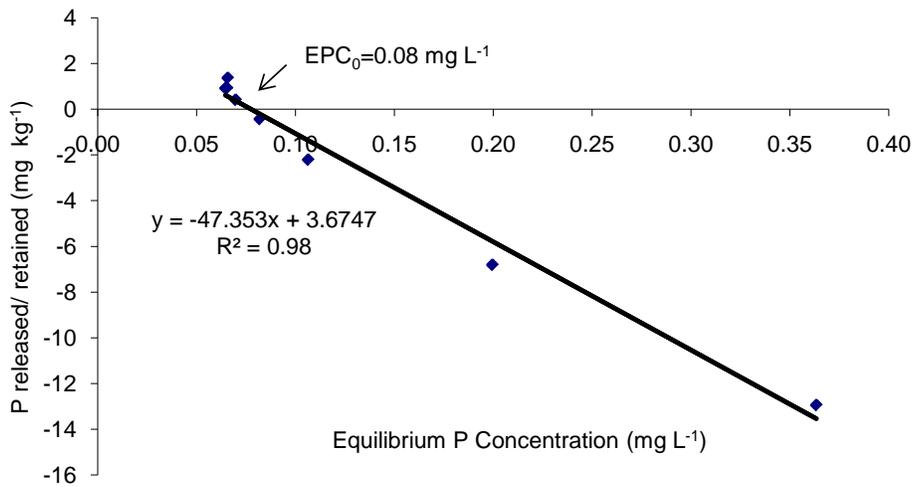


Figure 5-9. Determination of EPC_0 from linear adsorption isotherm for Ocean canal T1.

Table 5-5. Equilibrium Phosphorus Concentrations (EPC_0) from adsorption isotherms, maximum sorption capacity (S_{max}) and intensity of adsorption (k) for Ocean canal T1, T2, T3 and T4 sediments.

Canal	Transect	EPC_0 ($mg L^{-1}$)	Equation	R^2 (%)	S_{max} ($mg kg^{-1}$)	Intensity of adsorption k ($L kg^{-1}$)
Ocean	T1	0.08	$y = -47.353x + 3.6747$	98	189	37.5
	T2	0.66	$y = -30.328x + 19.985$	99	175	15.7
	T3	0.11	$y = -91.041x + 9.8118$	94	256	31.9
	T4	0.09	$y = -55.389x + 4.8051$	80	196	33.9

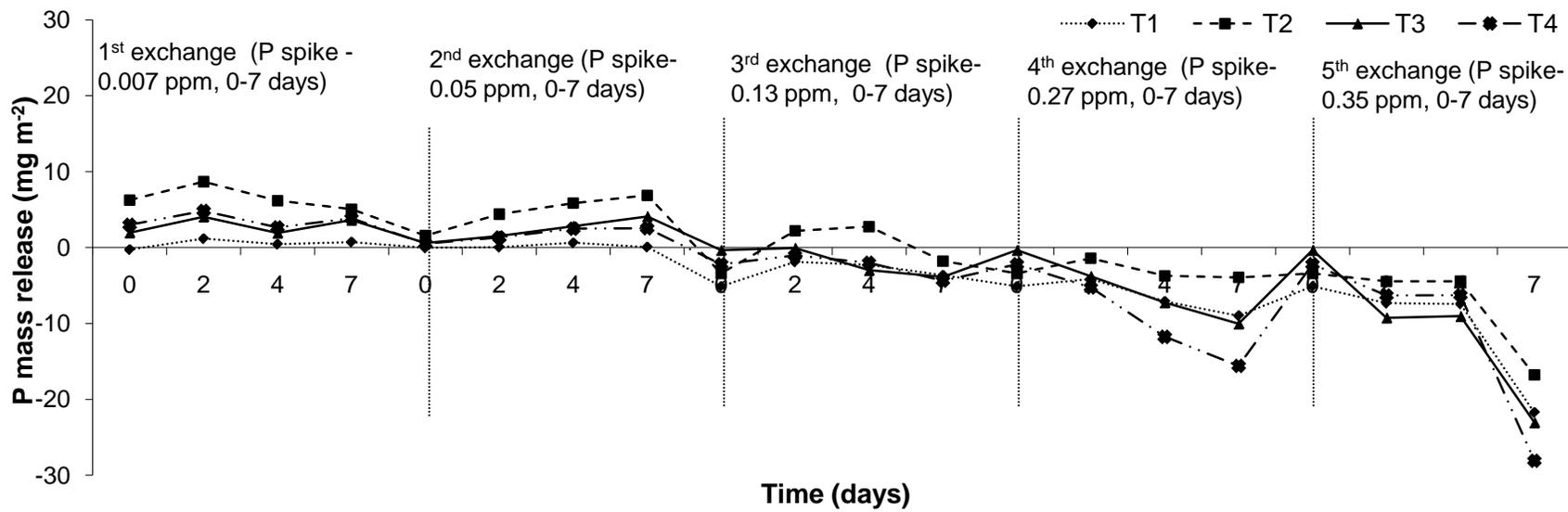


Figure 5-10. Cumulative P release from Ocean canal T1-T4 sediments during exchanges 1-5.

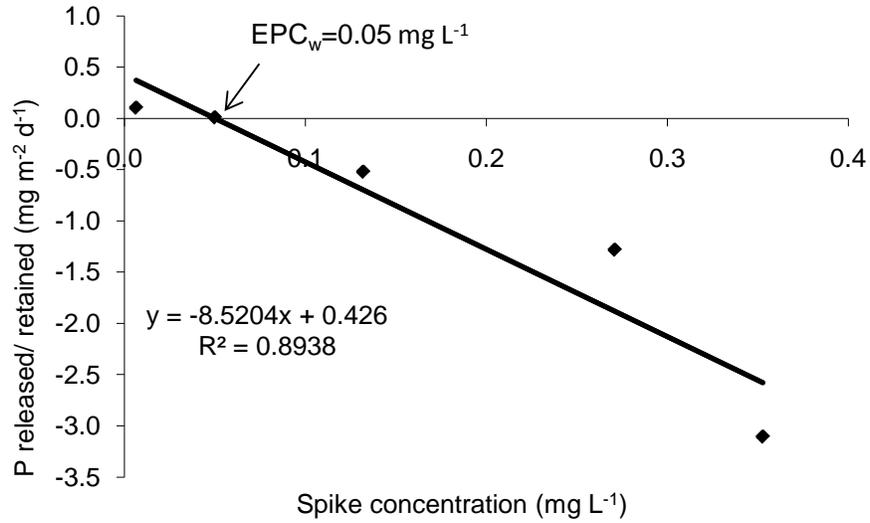


Figure 5-11. Determination of EPC_w for Ocean canal T1 from sediment core incubation study.

Table 5-6. Equilibrium Phosphorus Concentrations (EPC_w) from sediment column incubation study for Ocean canal T1, T2, T3 and T4 sediments.

Canal	Transect	EPC_w (mg L ⁻¹)	Equation	R^2 (%)
Ocean canal	T1	0.05	$y = -8.5204x + 0.426$	89
	T2	0.13	$y = -8.5251x + 1.0834$	87
	T3	0.08	$y = -10.615x + 0.8906$	94
	T4	0.07	$y = -12.955x + 0.9164$	97

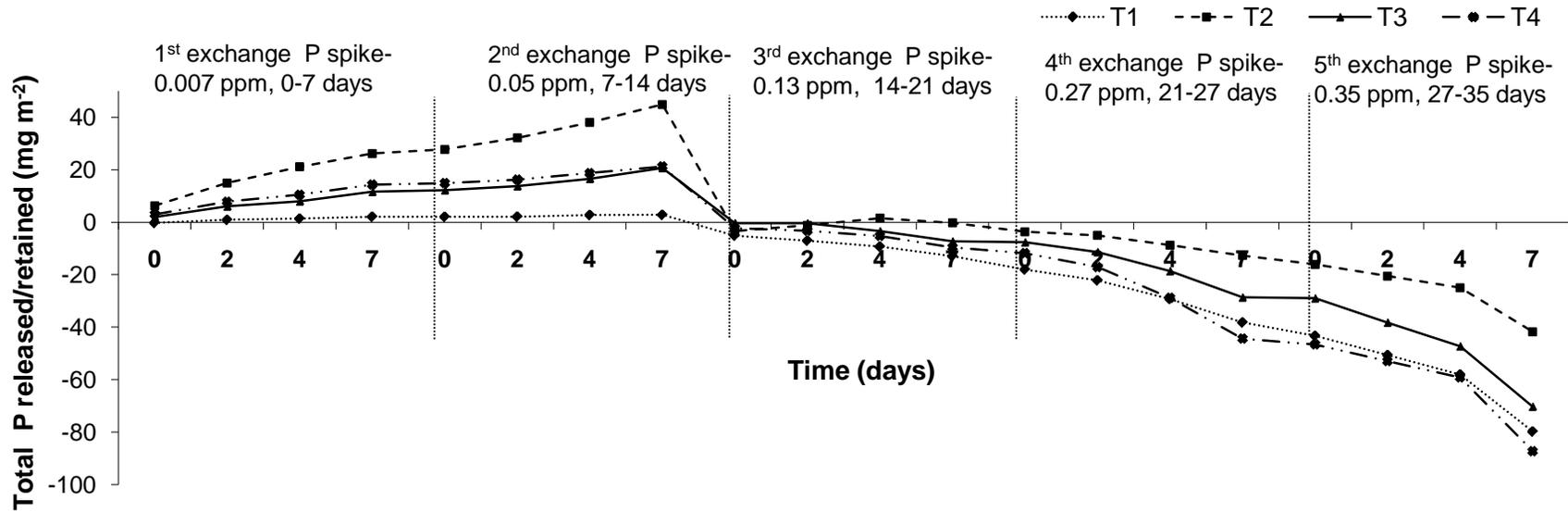


Figure 5-12. Total P released and retained from Ocean canal T1-T4 sediments during exchanges 1-5.

Table 5-7. Correlation between sediment metal (Fe, Al, Ca and Mg) and EPC₀, EPC_w, k and S_{max}.

	Fe mg kg ⁻¹	Al mg kg ⁻¹	Ca mg kg ⁻¹	Mg mg kg ⁻¹
EPC ₀ (mg L ⁻¹)	-0.04 ^{ns}	-0.04 ^{ns}	0.3 ^{ns}	0.09 ^{ns}
EPC _w (mg L ⁻¹)	0.56 ^{ns}	0.69 [*]	0.62 [*]	0.63 [*]
k (L kg ⁻¹)	0.88 ^{***}	0.73 [*]	0.06 ^{ns}	0.65 [*]
S _{max} (mg kg ⁻¹)	0.38 ^{ns}	0.16 ^{ns}	0.64 [*]	0.07 ^{ns}

Table 5-8. Correlation between sediment physicochemical properties with EPC₀ and EPC_w.

	BD	LOI	pH
EPC ₀	0.29 ^{ns}	-0.12 ^{ns}	0.57 ^{ns}
EPC _w	-0.27 ^{ns}	0.1 ^{ns}	-0.04 ^{ns}

Table 5-9. Correlation between sediment EPC₀ and EPC_w with sediment P fractions, total P and P released from intact sediment study.

	Labile P	NaOH Pi	NaOH Po	HCl P	Res P	Total P	P released
EPC ₀	0.23 ^{ns}	0.45 ^{ns}	0.50 ^{ns}	0.30 ^{ns}	0.34 ^{ns}	0.42 ^{ns}	
EPC _w	0.02 ^{ns}	0.07 ^{ns}	0.06 ^{ns}	0.02 ^{ns}	0.02 ^{ns}	0.04 ^{ns}	0.82 ^{***}

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

ns Not significant.

CHAPTER 6 SUMMARY AND CONCLUSIONS

The Everglades Agricultural Area (EAA) is located in South Florida between lake Okeechobee and the Everglades National Park. Nutrient enrichment from the EAA particularly phosphorus (P) is thought to be responsible for the ecosystem changes in the Everglades. Best Management Practices (BMP) in the EAA were implemented since 1995 to reduce the P loads. Despite the success of the BMPs, there are concerns about accumulated sediments in the canals of the EAA that can be a potential P source to the overlying water column affecting the water quality in downstream ecosystems. Investigation into the physicochemical properties of farm and main EAA canals, potential extent of P release, factors responsible for release from the sediments may further improve BMP performance and implementation. Farm canals receive drainage water directly from agricultural fields. Main canals receive irrigation from farm canals in addition to flow through water from lake Okeechobee.

6.1 Total Phosphorus Storage in Farm Canals

Our first objective was to investigate the physicochemical properties and P fractions in farm canals. Farm canals receive drainage water directly from farms, investigations into these sediment properties could reveal important information about P storage, and efficiency of the canal management practices in controlling P storage in these canals. Our investigations into sediment P storage in farm canal sediments revealed that sediment physicochemical properties and P storage were largely influenced by canal management practices. All farm canals are managed by farm owners to control dissolved and particulate P export but canal 06AB had management practices that include controlling floating aquatic vegetation and regular canal sediment

cleaning. We found 06AB sediments to have dominant mineral properties including higher bulk density, higher pH and lower organic matter than 09A and 00A canals, which reflects less contribution of floating aquatic vegetation into sediment accumulation. Everglades Agricultural Area canals were originally dug until the calcium carbonate bedrock and the sediments in the canal are the result of accumulation of particulates over time from the farms (Gleason and Spackman, 1974). A major portion of the sediments in EAA farm canals come from biological contribution i.e. floating aquatic vegetation (Stuck, 1996). Thus dominant mineral matter contribution indicates that canal 06AB has directed its management operations well, which has countered particulate accumulation. The lower accumulation of particulates in canal 06AB also resulted in lower total P content in sediments compared to 09A and 00A.

Estimation of 09A, 00A and 06AB canal area and volume were made by Google map, 2010 as described in Appendix D. Total P stored in these farm canals ranged from 0.2 to 0.4 metric tons (Table 6-1). Higher P storage in farm canals 09A and 00A than canal 06AB also indicate the effectiveness of the management practices in canal 06AB that resulted in lower P storage. Estimation of P storage in other farm canals could not be made as there are hundreds of farm canals spread across the EAA like web and quite difficult to get an estimation of the area covered by the farms using Google Earth.

6.2 Total Phosphorus Storage in Main Canals

Our next objective was to characterize the main canals that receive water from the farm canals and lake Okeechobee. Main canals are larger than farm canals in terms of length, width and depth. Main canals are managed by SFWMD and in contrast to farm canals no routine management practices are performed on the main canals except spraying chemicals to control floating aquatic vegetation. In comparison to the farm

canals, physicochemical properties of main canal reflected the geology of the area. Ocean canal sediments are mineral in nature with higher bulk density, higher pH, and lower total P content compared to Miami and WPB canal sediments (see chapter 3, Table 3-2 and Table 3-4). Both Miami and WPB canals were situated in lower geological terrains (Fort Thomson formation), whereas Ocean canal was situated in higher bedrock formations (Anastasia formation) (USGS, Figure 3.1). The areas of the main canals were calculated similar to farm canals and the volume of the sediments at depth 0-5 cm was calculated. Total P stored in Miami, WPB and Ocean canal sediments till depth 5 cm were 175, 25.4, and 7.11 MT respectively. The P storage values for the farm canals were an order of magnitude lower than main canals, which are due to smaller area and resultant lower volume of the farm canals. Phosphorus storage values indicated that large quantities of P are stored in EAA canals that could function as a P source to the system. Thus P fractionation was important to understand the reactivity and recalcitrance of the total P storage.

6.3 Phosphorus Fractions

The distribution of different P fractions in the farm and main canals were similar. The HCl extractable P was the dominant fraction with 59% to 70% of total P followed by residue-P fraction (17% to 34% of total P) (see chapter 2, Figure 2-2 and 3-3). This indicates that the majority of the inorganic P compounds in both these canals exist as bound to Ca and Mg which are generally considered as stable. Mineralogical analysis did not detect any P-containing minerals, which denotes one of two possibilities that either apatite-P is absent in canal sediments or apatite P concentration is below detectable limit. In both possibilities HCl-P can release P. Though the pH values in the main canal sediments are around 7, there can be diel fluctuations in pH resulting from

macrophyte and algae respiration causing enough acidity to hydrolyze HCl-P in sediment microzones (Carlton and Wetzel, 1987; Mortimer, 1941, 1942).

Organic P in both farm and main canals constituted about 13 and 6%, respectively of total P that is in contrast to high organic P content in the STAs, the WCAs and the ENP (Qualls and Richardson, 1995; Reddy et al., 1998). This is believed to be due to the unique hydrology in the downstream ecosystem that facilitates accumulation of organic particulates, which has lower mineralization rates due to wetland conditions (Qualls and Richardson, 1995; Reddy et al., 1998). The residue-P was the second highest P fraction in both farm and main canals that is generally thought to represent recalcitrant organic P. Thus the contribution of different P fractions towards P release is subject to further analysis, which was our next experiment.

6.4 Phosphorus Release from EAA Main Canals

Our third experiment was to determine the P release characteristics of sediments from three main canals of EAA: Miami Canal, West Palm Beach Canal (WPB) and Ocean Canal. Only main canal sediments were chosen for the experiment as farm canals ultimately drain into the main canals, which transport water to the downstream ecosystems. It was hypothesized due to years of P loading, these canals can now act as a P source through internal loading. Best management practices in EAA reduce dissolved and particulate P from the farms, but there are no management practices for the main canals. The knowledge of main canal P release potential could be helpful in setting management policies for these sediments.

All canals released P through a period of 84 days when sediments were incubated with low P concentration water that represents the downstream Everglades P concentrations but the magnitude of P released varied between canals (see chapter 4,

Figure 4-2, Figure 4-5 and Figure 4-8). Under field conditions with continuous addition of P, release of P can continue for a long time until further addition has been stopped and all the P sources are exhausted (Larsen et al., 1979; Ryding, 1981). Phosphorus release from Miami canal was higher than both WPB and Ocean canal sediments though the sediment total P values were similar in Miami and WPB canals. Using P release data, total internal P loading from the entire canal was estimated by multiplying release values by canal area (Table 6-2, Table 6-3 and Table 6-4). Though P release from Miami canal was higher than both WPB and Ocean canal, the estimated total P released from the entire surface area of WPB canal had higher values at T1, T2, T3 notably due to greater canal area than Miami canal.

Phosphorus release from the EAA main canals were significantly correlated with total P concentrations, which explains the low P release from Ocean canal sediments that had the lower total P concentrations (Table 4-3) than Miami and WPB canal. The different P fractions were not significantly correlated with P release. But the fact that P release was significantly correlated with total P led us to the conclusion that all P fractions may be contributing to P release and a complex combination of various factors were in effect in the canals. Similar correlation of P release with total P from sediments have been observed in eutrophic lake Alserio, (Italy), hypereutrophic lake Arungen (Norway), mesotrophic lake Balaton (Hungary), and oligotrophic lake Crystal (Minnesota) (Premazi and Provini, 1985; Graneli, 1979; Bostrom and Petterson, 1982; Messer et al., 1983). From the studies researchers concluded that in addition to reactive P, P fractions that were previously considered as non releasable or refractory, were also contributing to P fluxes from sediments.

Miami, WPB and Ocean canals were different between each other in terms of not only physicochemical properties but also canal depth and spatial distribution of carbonate layers (Figure 6-1, 6-2 and 6-3). Miami canal is situated in a low geological terrain, had higher total P concentration (1430 mg kg^{-1}) and total P storage (175 kg) in the top 0-5 cm layer than WPB and Ocean canal sediments. West Palm Beach canal contained interspersed carbonate layers that was most probably responsible for lower total P storage (25.4 kg) than Miami canal. In addition, the carbonate layers in WPB canal were thought to inhibit P release from sediments. Ocean canal sediments had dominant mineral properties with lower total P values among the three canals and also lower P release. Depth measurements conducted during sampling indicated that Ocean canal was a shallow canal with a layer of coarse shell and limestone rock fragments on sediment surface. Thus not only the chemical composition of sediment P but also the spatial distribution of sediment may control P release in EAA canals.

6.5 Internal P loading from EAA Main Canal Sediments

Estimates of annual internal P loads from EAA main canal sediments (Table 6-2; Table 6-3; Table 6-4) were made using cumulative P release data (Chapter 4). The annual P internal load estimates were made by multiplying the P release values by the canal areas for exchanges 1, 2 and 3 respectively. The detailed calculation of the internal P load derivation is provided in Appendix G. The average annual internal P load over exchanges 1, 2 and 3 for Miami, WPB and Ocean canal are provided in Table 6-5. Our estimation show that annual internal P load from Miami canal can vary from 0.2 to 0.8 MT, while WPB canal internal P loads can vary from 0.1 to 0.4 MT and Ocean canal internal P loads can vary from 0.1 to 0.2 MT. Comparison of EAA canal internal P load to the P load from the EAA of 129 MT in water year 2009 (SFER, 2010a) shows that the

internal P load is a very small portion of the entire P load from EAA. But it has to be recalled that the internal P load calculated here takes into account diffusive P flux only. In reality P flux from EAA canals can be much higher than the calculated value due to sediment transport and resuspension. Water flow in EAA canals are controlled by pumps and undergo rapid fluctuations from stagnant conditions to very high velocity that can cause resuspension and sediment transport. Sediment resuspension has been reported to cause about 20 to 30 times greater P release than undisturbed sediments (Sondergaard et al., 1992). Particularly it was observed that bioturbation and resuspension caused higher P flux in calcareous lake sediments compared to non-calcareous lake sediments (Graneli, 1979).

6.6 Equilibrium Phosphorus Concentrations

Following the determination that the main canal sediments potentially can function as P sources, our fourth experiment aimed to determine the limit of P concentrations that determines the function of the sediment as P source or sink i.e. the equilibrium P concentration or EPC_w values of the canal sediments. The mean EPC_w values for Miami canal sediments determined by intact sediment columns were $0.12 \pm 0.03 \text{ mg L}^{-1}$, for West Palm Beach canal $0.06 \pm 0.03 \text{ mg L}^{-1}$ and Ocean canal $0.08 \pm 0.03 \text{ mg L}^{-1}$. The EPC_w values reflected the P release patterns of the canals observed from canal sediments in our third experiment. Canals with higher P release values had higher EPC_w values than canals with lower P releases. Thus higher P releases in Miami canal sediments resulted in higher EPC_w values than WPB and Ocean canals. Comparison of the EPC_w values with water column SRP concentrations (Table 6-6) of the canals indicated that Miami canal T1, T2, T3 and Ocean canal T2 were acting as P sources to the water column.

6.7 Conclusions

Everglades Agricultural Area canal sediments are an important part of the entire Everglades system but there was not enough information on this part of the ecosystem compared to the STAs, WCAs and the ENP. Physicochemical properties indicated that organic matter content varied from 20-70% and the sediments had very low bulk density due to which, they are susceptible to transport to the P limited ecosystems in the south. Though sediment samples contained considerable organic matter, organic P fraction accounted just about 6-13% of total P. This is in contrast to the wetland sediments of the STAs, WCAs and the ENP where sediment hydrology promotes P sequestration and consequently has higher organic P content. Dissolved organic P content in the Everglades (Qualls and Richardson, 2003) is a point of concern but our studies showed that inorganic P comprised majority (96%) of the P released. Though the individual P fractions varied between canals, the percent distribution of the different fractions were similar with HCl-P and Residue-P being the largest P fractions comprising almost 80-90% of total P. Phosphorus release from EAA canal sediments was not correlated with different P fractions but was significantly correlated with total P. Thus we speculate that all P fractions were contributing to P release and a complex interaction of various factors was in effect in the canals. However, P internal P load estimates from the canals were a very small portion compared to total EAA P load. This internal P load from the canals was an estimate of the diffusive P flux only as this research did not consider sediment transport and resuspension impacts on P release. Sediment EPC_W values suggested portions of the canals were functioning as a P source to the water column. Further studies are necessary to estimate internal P loading from the canal sediments with water velocity, sediment transport and resuspension as some of the factors.

The EAA main canals are the interface between the nutrient enriched EAA and the STA filter marshes (Figure 6-4). The STAs filter the inflow water through P uptake and sedimentation. Inflow water concentrations to the STAs in water year 2009 (SFER, 2010a) were recorded as 182, 246, 122, 96, 254 and 264 $\mu\text{g L}^{-1}$ for STA 1E, 1W, 2, 3/4, 5 and 6 respectively. The outflow concentrations were recorded as 21, 26, 18, 13, 56 and 93 $\mu\text{g L}^{-1}$ for STA 1E, 1W, 2, 3/4, 5 and 6 respectively. The STAs require regular maintenances and periodic rehabilitation of the marshes. Management practices within the main canals can result in reduced inflow concentrations and P load to the STAs that can boost STA performance and increase its longevity. This could lead to a reduction in cost of STA rehabilitation and most importantly can get closer to the target P concentrations of 10 ppb in the Everglades. Management practices in the canals can include periodic dredging the stretch of canals particularly at portions of Miami canal and Ocean canal. In addition to dredging, berming the canal banks can prevent the accumulation of particulate P into the canals. Thus management of P concentrations in the outflow from the EAA main canals can be a key component in maintaining oligotrophic nutrient status in the Everglades.

Table 6-1. Estimation of total P storage in EAA main (Miami, WPB, Ocean) and farm (09A, 00A, 06AB) canal sediments.

Canal	Total P mg kg ⁻¹	BD g cm ⁻³	Total P mg cm ⁻³	Area m ²	Sediment volume till 5 cm depth cm ³	Total P stored (total P x volume) mg	Total P stored MT
09A	794	0.19	0.15	5.56x10 ⁴	2.78x10 ⁹	4.20x10 ⁸	0.4
00A	1520	0.12	0.18	3.67x10 ⁴	1.83x10 ⁹	3.35x10 ⁸	0.3
06AB	576	0.37	0.21	2.10x10 ⁴	1.05x10 ⁹	2.24x10 ⁸	0.2
Miami	1430	0.26	0.37	9.45x10 ⁵	4.72x10 ¹⁰	1.75x10 ¹¹	175
WPB	1130	0.22	0.25	2.03x10 ⁶	1.02x10 ¹¹	2.54x10 ¹⁰	25.4
Ocean	590	0.35	0.21	6.89x10 ⁵	3.44x10 ¹⁰	7.11x10 ⁹	7.11

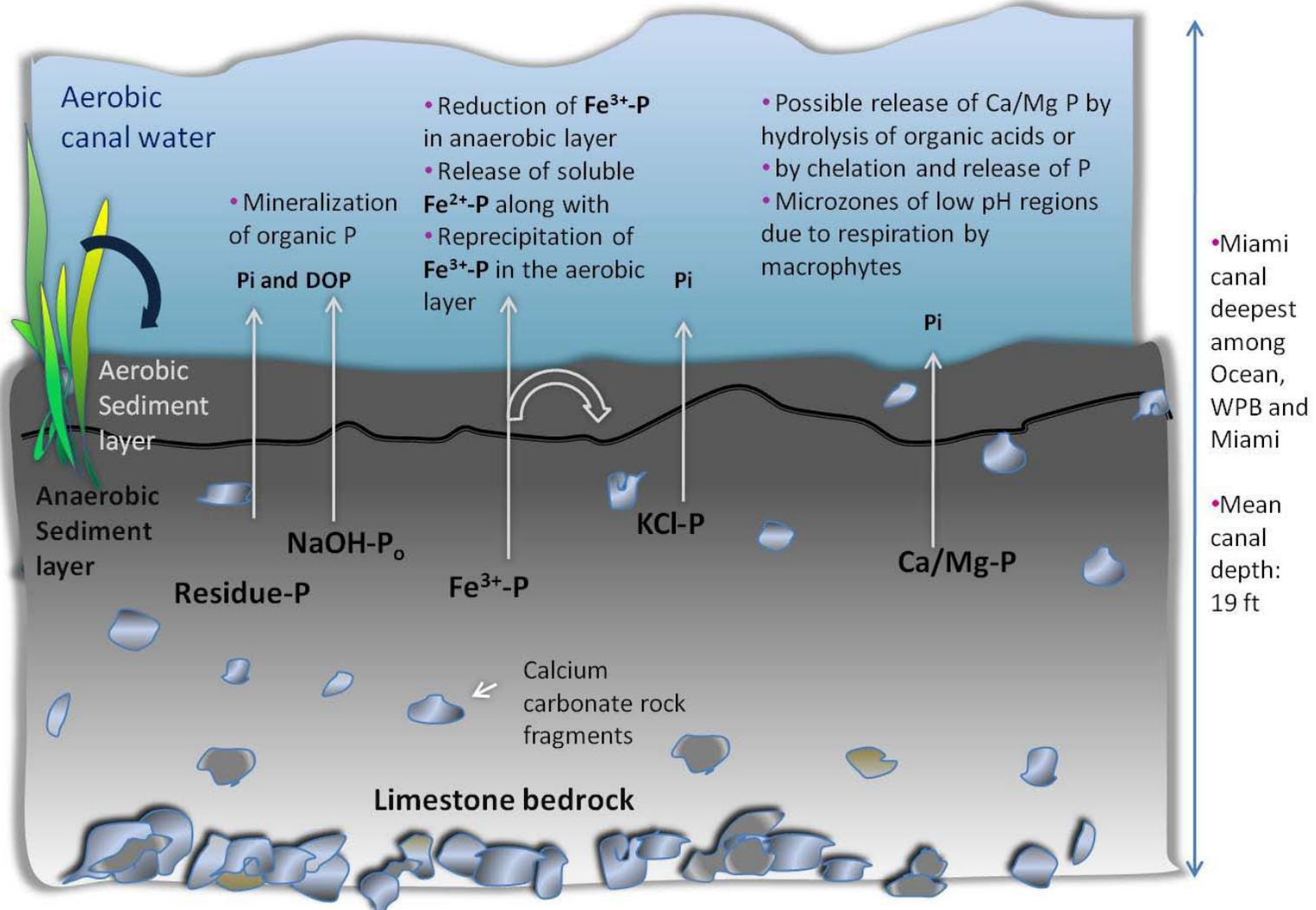


Figure 6-1. Schematic representation of P release from a section of Miami canal sediments

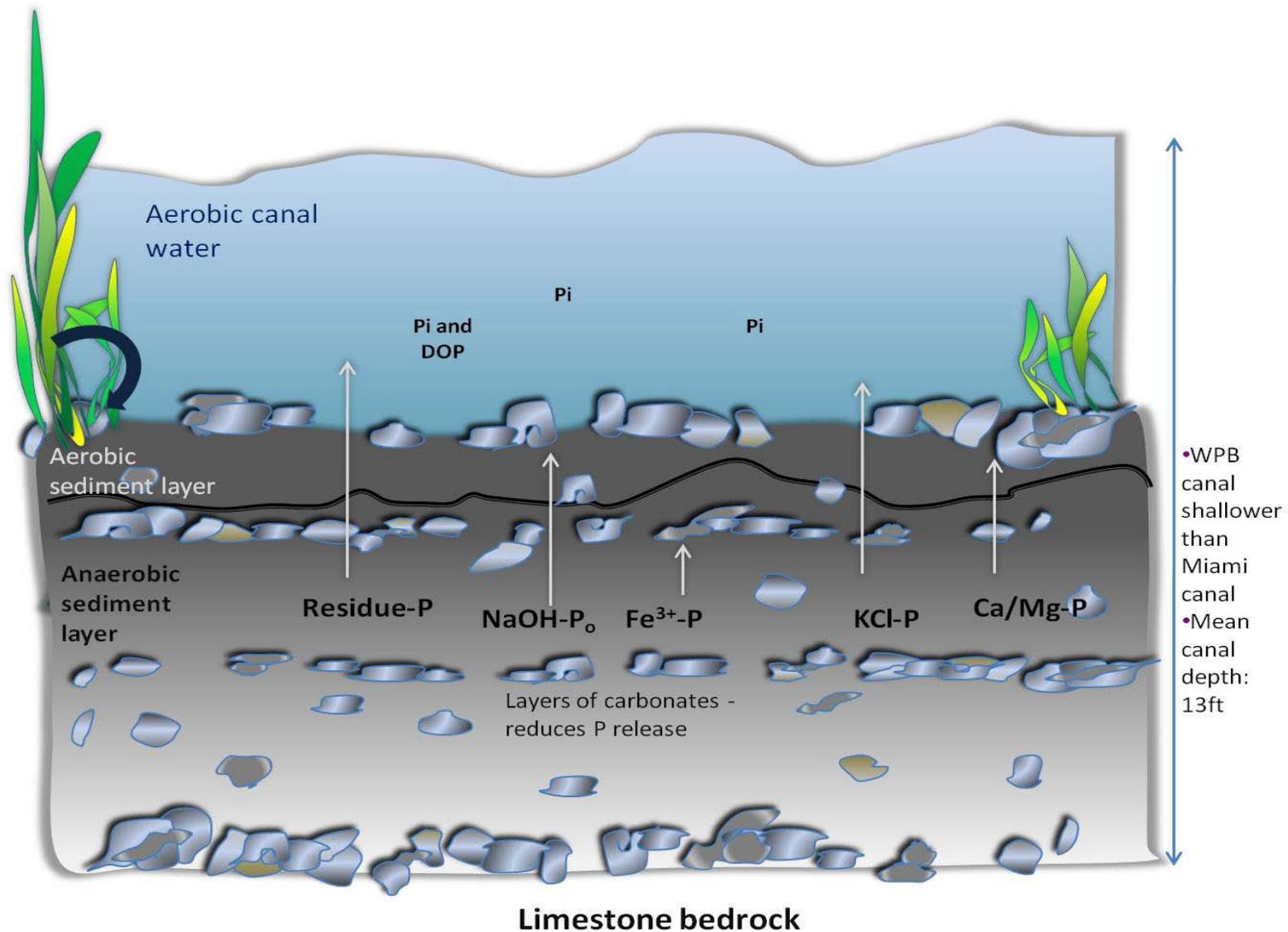


Figure 6-2. Schematic representation of P release from a section of WPB canal sediments

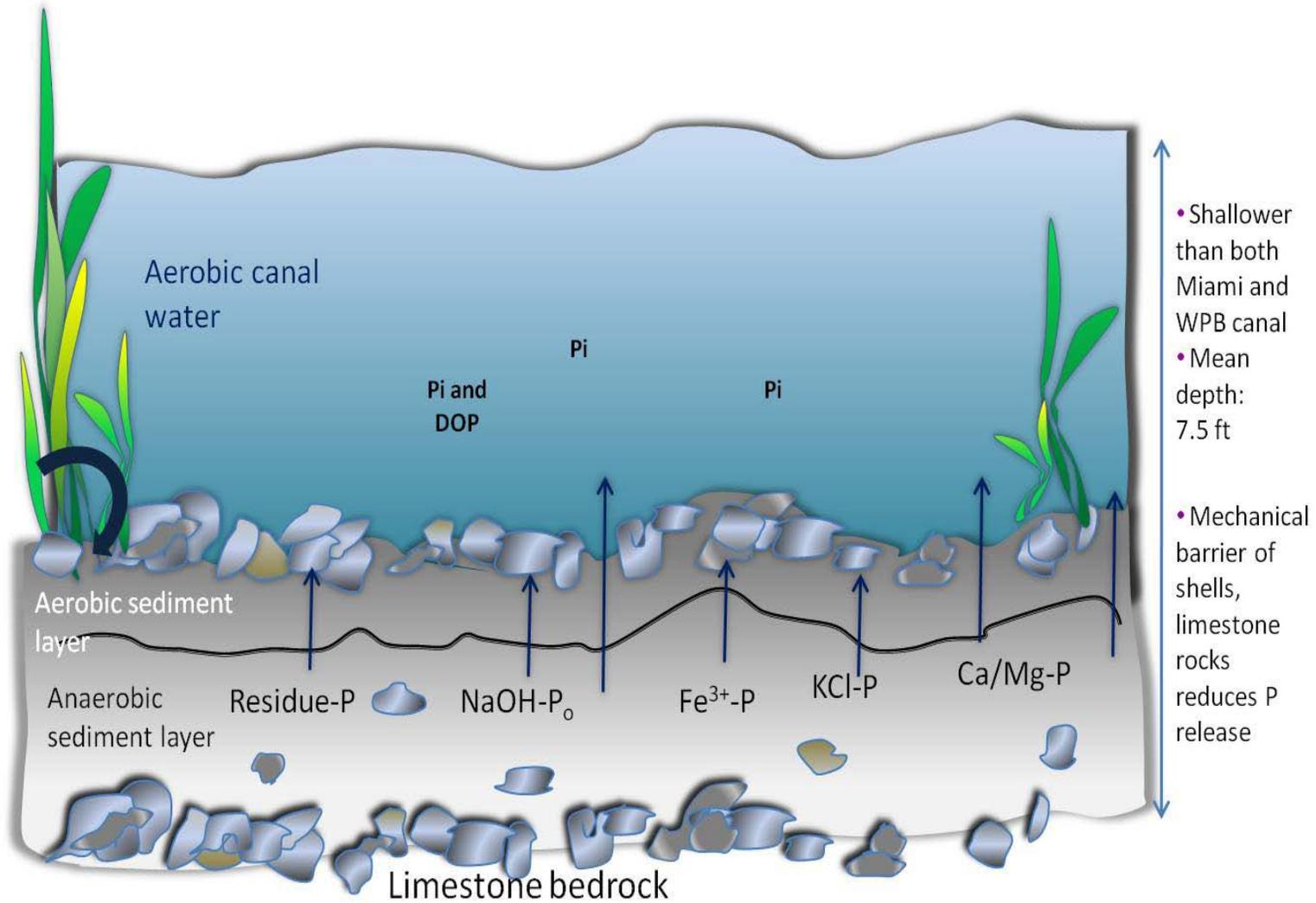


Figure 6-3. Schematic representation of P release from a section of Ocean canal sediments

Table 6-2. Estimation of annual internal P loading from Miami canal exchanges 1, 2 and 3.

Miami canal	Exchange 1		Exchange 2		Exchange 3	
	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT
T1	31.9	0.4	35.6	0.4	18.9	0.2
T2	108	1.3	70.5	0.9	16.7	0.2
T3	86.9	1.1	77.1	0.9	18.7	0.2
T4	37.0	0.5	18.8	0.2	4.89	0.1

Table 6-3. Estimation of annual internal P loading from WPB canal exchanges 1, 2 and 3.

WPB canal	Exchange 1		Exchange 2		Exchange 3	
	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT
T1	31.2	0.8	9.74	0.3	9.40	0.2
T2	28.1	0.7	9.01	0.2	6.04	0.2
T3	26.5	0.7	17.7	0.5	10.34	0.3
T4	6.90	0.2	3.00	0.1	2.94	0.1

Table 6-4. Estimation of annual internal P loading from Ocean canal sediments during exchanges 1, 2 and 3.

Ocean canal	Exchange 1		Exchange 2		Exchange 3	
	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT	Cumulative P release in 28 days mg m ⁻²	Cumulative P released from canal /year MT
T1	24.2	0.8	5.21	0.3	4.62	0.2
T2	43.1	0.7	18.9	0.2	9.31	0.2
T3	21.9	0.7	18.8	0.5	4.78	0.3
T4	20.6	0.2	13.2	0.1	7.42	0.1

Table 6-5. Estimation of annual internal P loading from Miami, WPB and Ocean canal sediments over exchange 1, 2 and 3.

Miami canal	Mean cumulative P released from canal /year over exchanges 1, 2 and 3 MT	WPB canal	Mean cumulative P released from canal /year over exchanges 1, 2 and 3 MT	Ocean canal	Mean cumulative P released from canal /year over exchanges 1, 2 and 3 MT
T1	0.4	T1	0.4	T1	0.1
T2	0.8	T2	0.4	T2	0.2
T3	0.8	T3	0.5	T3	0.1
T4	0.2	T4	0.1	T4	0.1

Table 6-6. Comparison of EPC_w and SRP concentrations of Miami, WPB and Ocean canal sediments.

Transect	Miami canal		WPB canal		Ocean canal	
	EPC_w (mg L ⁻¹)	Water column SRP (mg L ⁻¹)	EPC_w (mg L ⁻¹)	Water column SRP (mg L ⁻¹)	EPC_w (mg L ⁻¹)	Water column SRP (mg L ⁻¹)
T1	0.12	0.03	0.05	0.06	0.05	0.06
T2	0.16	0.03	0.09	0.06	0.13	0.07
T3	0.12	0.03	0.08	0.05	0.08	0.07
T4	0.07	0.05	0.02	0.06	0.07	0.06

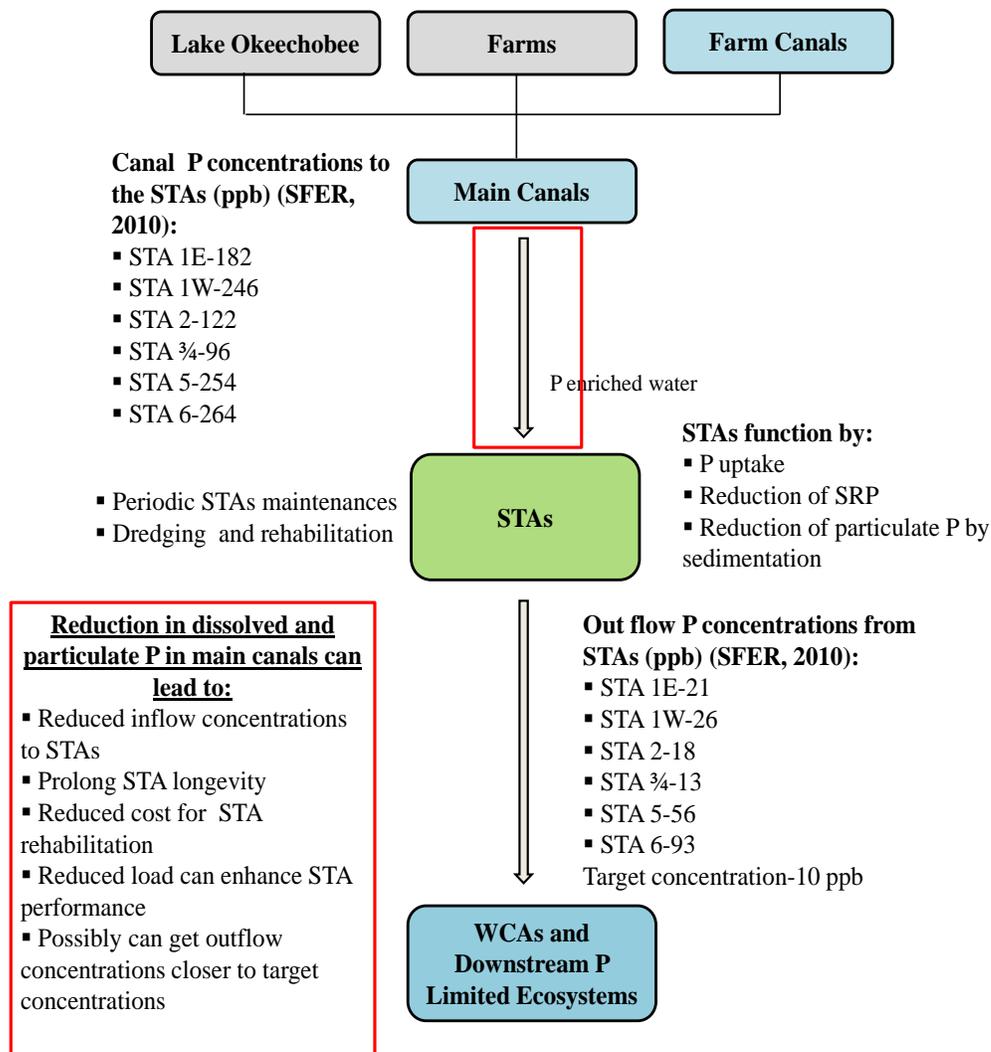


Figure 6-4. Water and nutrient flow through the Everglades system.

APPENDIX A INORGANIC P FRACTIONATION

An inorganic fractionation scheme was used to determine the main P fractions in the sediments of main district canals and typical farm canals in the EAA. Inorganic P fractionation was determined by sequential extraction (Hieltjes and Lijklema, 1980, Reddy et al., 1998). The sediment was prepared by weighing the wet weight equivalent of 0.3 g of dry sediment into previously weighed 50 ml polypropylene centrifuge tubes. The KCl-Pi content of the sediment was determined by adding 30 mL of 1.0 M KCl and agitating on a mechanical shaker for 2 h. The suspensions were then centrifuged at 8000 rpm for 10 minutes and filtered (0.45 μ m) using a vacuum pump. The filtrates from each tube were collected in labeled 50 mL scintillation vials. The weight of the centrifuge tube, sample and KCl residue was again recorded after filtration. The filtrates were stored at 4°C and analyzed for SRP using a Spectrophotometer within 30 days after collection (EPA Method 365.1, 1993). The NaOH-Pi and the NaOH-P contents of the sediment were determined by extraction with 30 mL of 0.1 M NaOH on a mechanical shaker for 17 h, centrifugation at 8000 rpm for 15 minutes, and vacuum filtration (0.45 μ m) into pre-labeled 50 mL scintillation vials.

The filtrates were stored at 4°C and analyzed for extractable Pi and digested for total P. To analyze for NaOH-Pi, 7 mL of each filtrate was pipetted into labeled centrifuge tubes and acidified with 7 drops of concentrated sulfuric acid (36 N). The acidified filtrates were centrifuged at 6000 rpm for 5 minutes. The supernatants were decanted and analyzed for SRP.

To analyze for NaOH-P, 5 mL of each filtrate was pipetted into a labeled 250 mL conical flask and treated with 1 mL of 11 N sulfuric acid and 0.4 g of potassium

persulfate. The samples were digested at 125°C for 3 hours and at 380°C for 4 hours. After cooling to approximately 100°C, 10 mL of distilled water was added to each flask and shaken. The digests samples were analyzed for total P. The Humic and Fulvic acid Po content of the sediment was calculated by subtracting the NaOH-Pi (Fe/Al bound Pi) from the NaOH-P values.

The HCl-Pi (Ca bound P) content of the sediment was determined by adding 30 mL of 0.5 M HCl to each sample. The samples were then placed on a mechanical shaker for 24 h. After 24 hours the samples were centrifuged at 8000 rpm for 15 minutes. The contents were then filtered by suction (0.45 µm) into pre-labeled 50 mL scintillation vials. The weight of the centrifuge tube with HCl residue was recorded after filtration. The filtrates were stored at 4°C and analyzed for SRP.

The residue P content of the soil was determined utilizing the ignition method (Andersen, 1974). Samples were transferred from the centrifuge tube into a weighed and pre-labeled 50 mL beakers using double distilled water. The samples were dried in an oven at 70°C until constant weight and the dry weights recorded. The beakers were then placed in a muffle furnace at $500 \pm 50^\circ\text{C}$ for 4 hours then allowed to cool overnight. After cooling in the muffle furnace, the beakers were further cooled to room temperature and then weighed to determine loss on ignition. The ash was then moistened with double distilled water and 20 mL of 6 N HCl was added. The samples were then placed on a hot plate at 100-120°C until dry, and then the temperature was set at high (260-280°C) for 30 minutes. The samples were then removed from the hot plate and allowed to cool to room temperature followed by the addition of 2.25 mL 6 N HCl to each beaker. The samples were again put on the hot plate and just brought to a boil which occurs

within a couple of minutes and removed. The filtrate from the ashed samples were transferred to 50 mL volumetric flasks after filtration and analyzed for total P.

APPENDIX B EXTRACTABLE Fe AND Al

The sediments were pretreated for CaCO_3 by placing 0.5 g of sediment in a 50 mL polypropylene centrifuge tube to which was added 30 mL of 1.0 M ammonium acetate solution. The solution was allowed to react for 1 h with intermittent stirring. The pH was measured and adjusted to 5.5 by drop-wise addition of acetic acid. This was repeated hourly until the pH stays approximately constant. The resultant solution was centrifuged, decanted, and washed with deionized water to remove the dissolved Ca and acetate, and left to air dry.

About 0.5 g of sediment was weighed out and to it was added 20 mL of ammonium oxalate solution (pH 3.0) in a centrifuge tube. The centrifuge tubes were shaken in a reciprocating shaker for 4 h. We simulated dark conditions in the laboratory by wrapping the centrifuge tubes with Al foil and turning the lights off. Following shaking the tubes were centrifuged at 6000 rpm for 10 minutes. The supernatant was filtered with a 0.45 μm filter paper. The concentrations of Fe and Al in the extracts were determined using Inductively Coupled Plasma spectroscopy (ICP) (Spectro Analytical CIROS CCD).

APPENDIX C EXTRACTABLE Ca AND Mg

To 10 mL of sediment 25 mL of 0.5 N Acetic acid was added and left to react overnight (approximately 20 h). The samples were then shaken for 50 minutes on an end-to-end shaker. The samples were filtered using Whatman no. 5 filter paper and the filtrates collected.

APPENDIX D ESTIMATION OF AREA AND VOLUME OF EAA CANALS

Estimation of EAA farm and main canal length as well as width were done using Google maps, 2010. Width of the canal against a given unique latitude and longitude value, was calculated by the 'add path' function and choosing 'meters' as the unit of choice. The areas of canals were obtained by multiplying the calculated canal length by canal breadth. Canal volume till 0-5 cm depth was calculated by multiplying canal area by required depth (5 cm). The total P storage at 0-5 cm depth was determined by multiplying total P content (mg kg^{-1}) of the canals by sediment bulk density (g cm^{-3}) and canal volume. Suitable unit conversions were performed on the calculations.

APPENDIX E
FIGURES

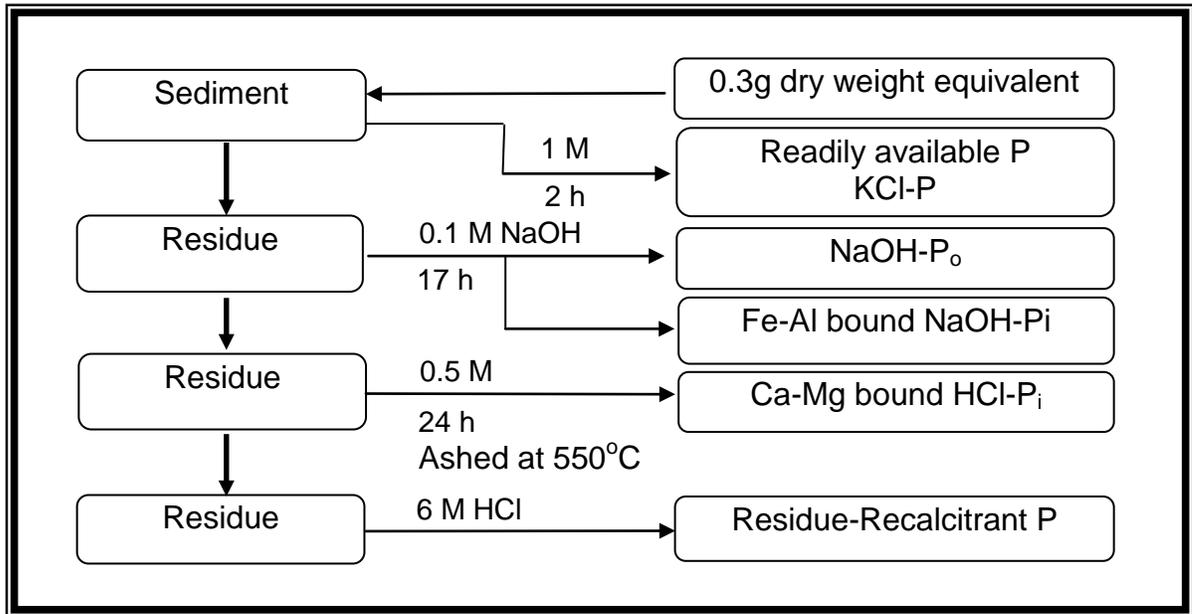


Figure E-1. Inorganic P fractionation scheme.

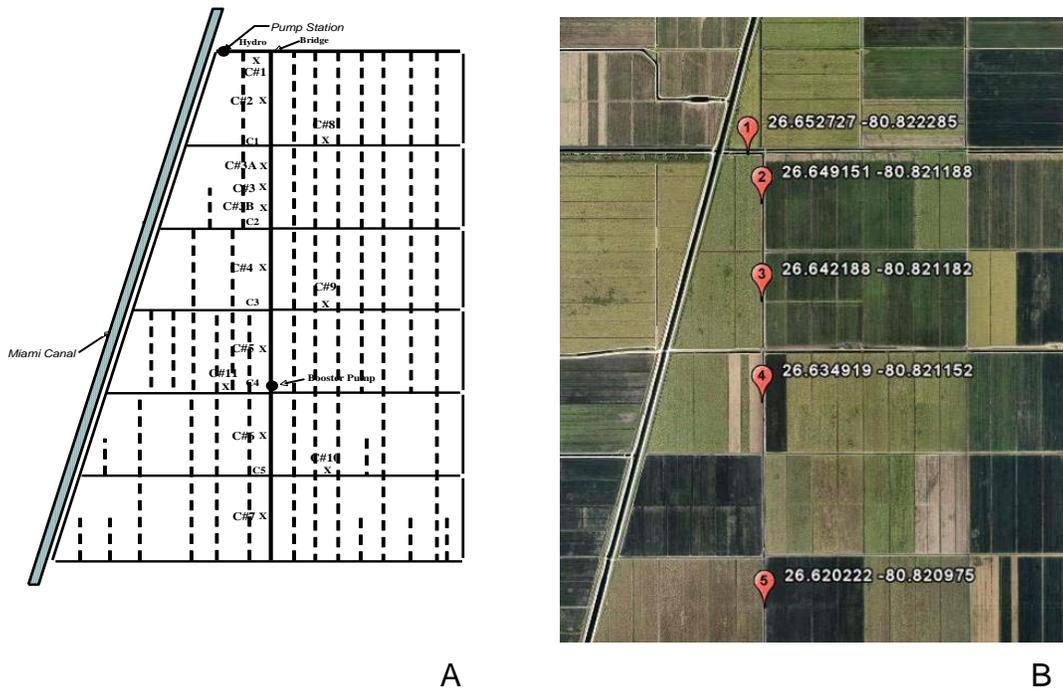
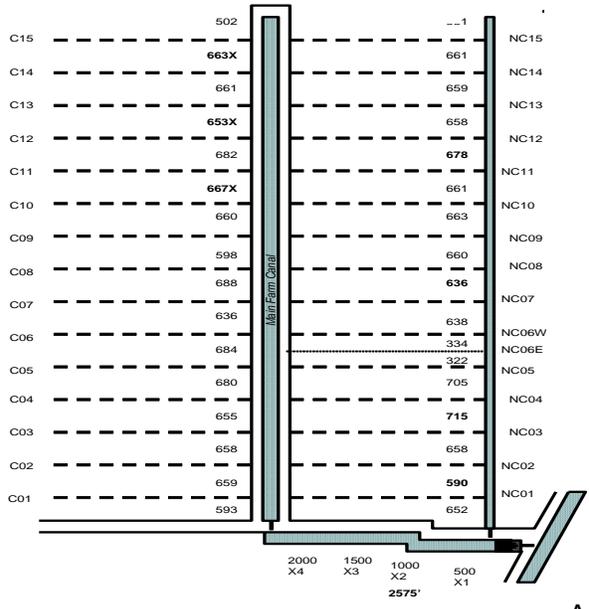


Figure E-2. Map of farm canal 09A. B. Sampling transects (T1-T5) in farm canal 09A (Google Maps 2010).

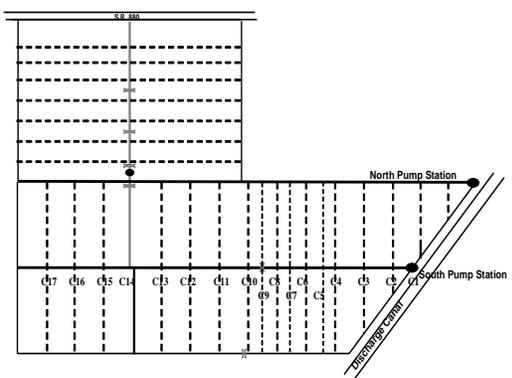


A

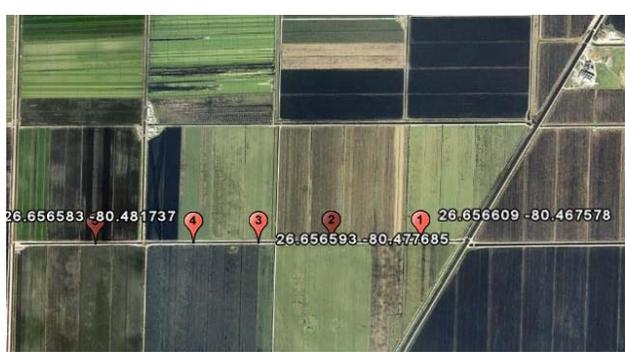


B

Figure E-3. Map of farm canal 00A. B. Sampling transects (T1-T5) in farm canal 09A (Google Maps 2010).



A



B

Figure E-4. Map of farm canal 06AB. B. Sampling transects (T1-T5) in farm canal 09A (Google Maps 2010).

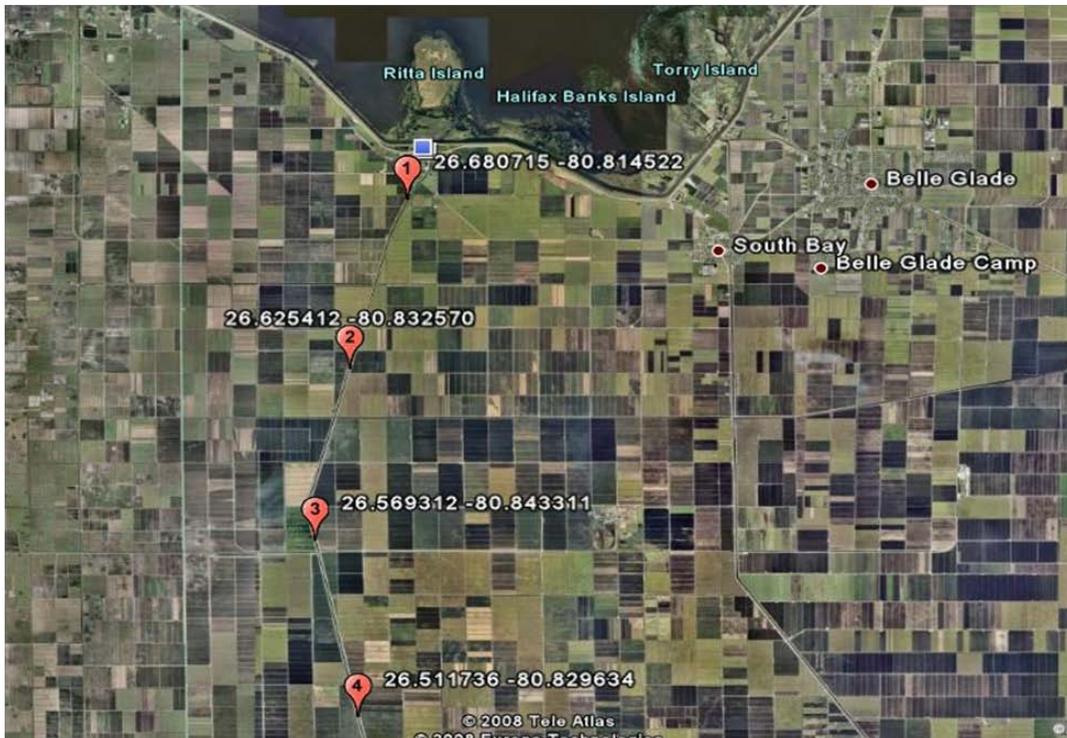


Figure E-5. Sampling transects (T1-T4) in Miami canal (Google Maps 2010).

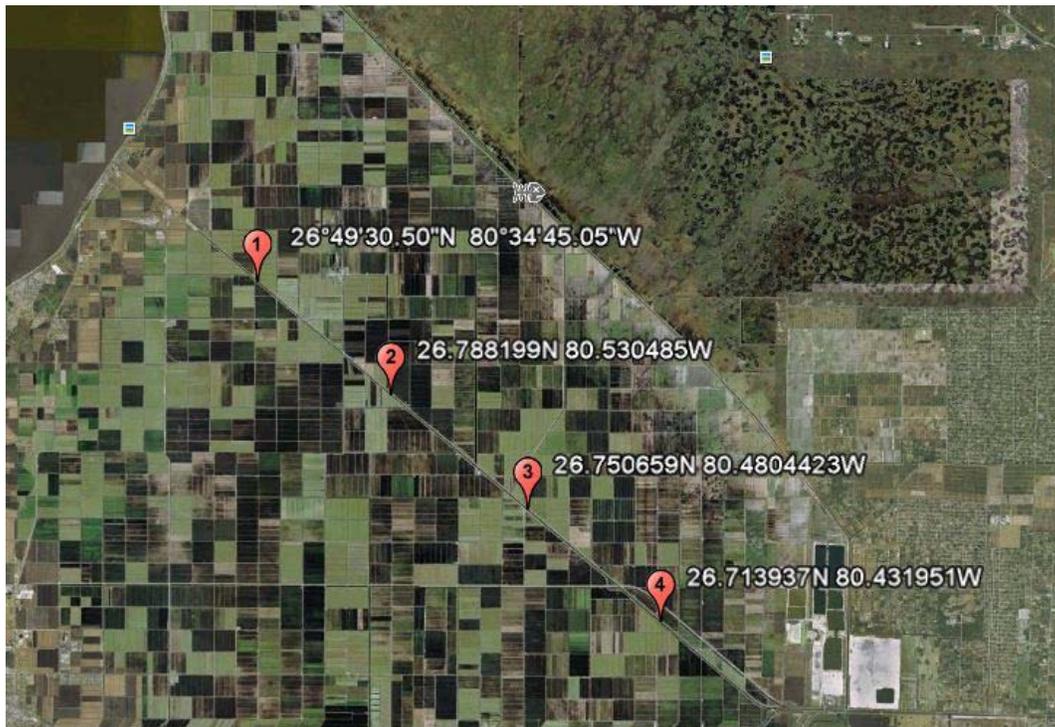


Figure E-6. Sampling transects (T1-T4) in WPB canal (Google Maps 2010).

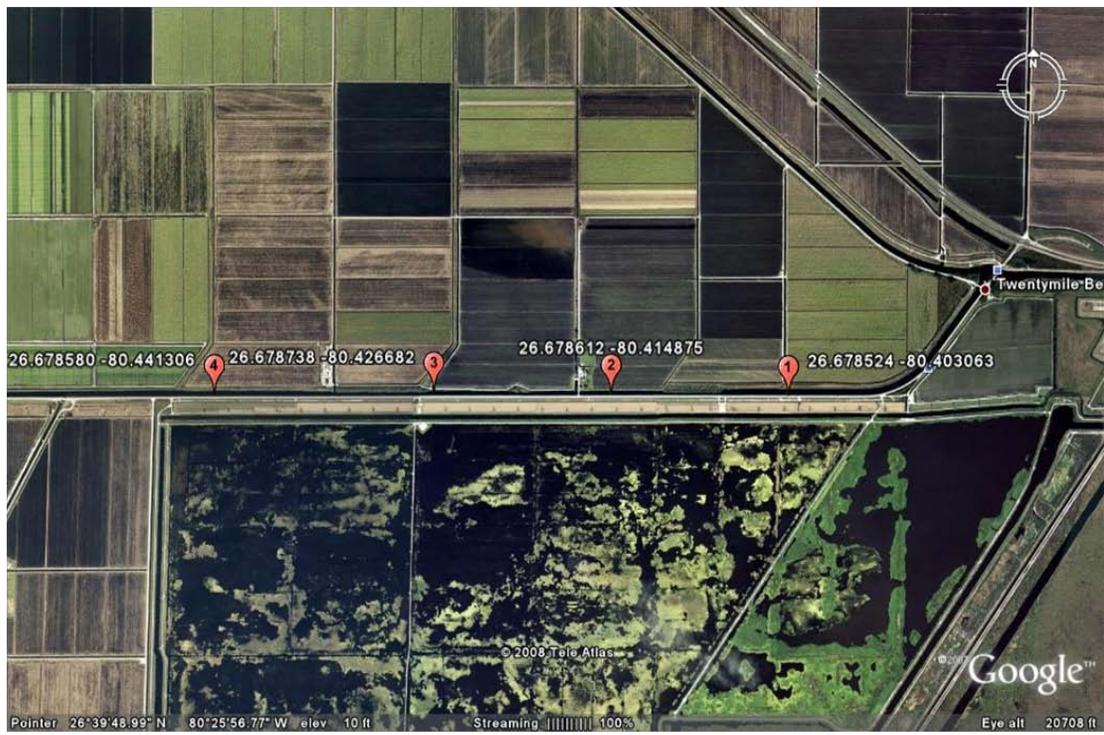


Figure E-7. Sampling transects (T1-T4) in Ocean canal (Google Maps-2010).

APPENDIX F
LATITUDE AND LONGITUDE OF EAA FARM AND MAIN CANALS

Table F-1. Latitude and longitude values of farm canal 09A transects.

Farm canal 09A	No of reps taken	Distance between transects (m)	Breadth (m)	Latitude	Longitude
T1	3		15.5	26.652727	-80.822285
T2	3	209.3	12.1	26.649151	-80.821188
T3	3	393.1	10.3	26.642188	-80.821182
T4	3	410.3	7.7	26.634919	-80.821152
T5	3	829.7	8.4	26.620222	-80.820975

Length of farm canal 09A calculated: 5153 m.

Table F-2. Latitude and longitude of farm canal 00A transects

Farm canal 00A	No of reps taken	Distance between transects (m)	Breadth (m)	Latitude	Longitude
T1	3		5.5	26.764664	-80.506107
T2	3	292.2	6.0	26.761760	-80.510928
T3	3	308.7	4.9	26.761770	-80.517081
T4	3	302.7	8.0	26.761811	-80.523113
T5	3	302.5	8.1	26.761823	-80.529141

Length of farm canal 00A calculated: 5642 m.

Table F-3. Latitude and longitude of farm canal 06AB transects

Farm canal 06AB	No of reps taken	Distance between transects (m)	Breadth (m)	Latitude	Longitude
T1	3		7.12	26.656609	-80.467578
T2	3	279.7	6.8	26.656612	-80.473144
T3	3	228.2	8.5	26.656593	-80.477685
T4	3	203.6	8.4	26.656583	-80.481737
T5	3	306.1	6.8	26.656578	-80.487829

Length of farm canal 06AB calculated: 2786 m.

Table F-4. Latitude and longitude values of Miami canal transects.

Miami canal	No of replicates	Distance between transects (km)	Breadth (m)	Latitude	Longitude
T1	3		33.3	26.680715	-80.814522
T2	3	11.0	26.8	26.625412	-80.832570
T3	3	10.5	33.4	26.569312	-80.843311
T4	3	10.9	32.6	26.511736	-80.829634

Length of Miami canal calculated: 29900 m.

Table F-5. Latitude and longitude of WPB canal transects.

WPB canal	No of replicates	Distance between transects (km)	Breadth (m)	Latitude	Longitude
T1	3		26.7	26.713937	-80.431951
T2	3	10.5	23.8	26.750659	-80.480423
T3	3	10.8	33.4	26.788199	-80.530485
T4	3	10.5	36.5	26.825139	-80.579180

Length of WPB canal calculated: 67600 m.

Table F-6. Latitude and longitude of Ocean canal transects.

Ocean canal	No of replicates	Distance between transects (km)	Breadth (m)	Latitude	Longitude
T1	3		33.8	26.678580	-80.441306
T2	3	2.4	28.3	26.678738	-80.426682
T3	3	1.9	29.3	26.678612	-80.414875
T4	3	1.9	39.7	26.678524	-80.403063

Length of Ocean canal calculated: 21000 m.

APPENDIX G
ESTIMATION OF ANNUAL INTERNAL P LOADING FROM EAA MAIN CANALS

Table G-1. Estimation annual internal P loading from Miami canal exchange 1.

Miami canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	31.9	3.01x10 ⁷ †	3.93x10 ⁸	0.4
T2	108	1.01x10 ⁸	1.32x10 ⁹	1.3
T3	86.9	8.21x10 ⁷	1.07x10 ⁹	1.1
T4	37.0	3.49x10 ⁷	4.56x10 ⁸	0.5

† Estimated area of Miami canal 9.45x10⁵ m².

Table G-2. Estimation annual internal P loading from Miami canal exchange 2.

Miami canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	35.6	3.36x10 ⁷	4.39x10 ⁸	0.4
T2	70.5	6.66x10 ⁷	8.68x10 ⁸	0.9
T3	77.1	7.29x10 ⁷	9.50x10 ⁸	0.9
T4	18.8	1.78x10 ⁷	2.32x10 ⁸	0.2

† Estimated area of Miami canal 9.45x10⁵ m².

Table G-3. Estimation annual internal P loading from Miami canal exchange 3.

Miami canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	18.9	1.79x10 ⁷	2.33x10 ⁸	0.2
T2	16.7	1.58x10 ⁷	2.06x10 ⁸	0.2
T3	18.7	1.77x10 ⁷	2.30x10 ⁸	0.2
T4	4.89	4.62x10 ⁶	6.02x10 ⁷	0.1

† Estimated area of Miami canal 9.45x10⁵ m².

Table G-4. Estimation annual internal P loading from WPB canal exchange 1.

WPB canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	31.2	6.33x10 ⁷	8.26x10 ⁸	0.8
T2	28.1	5.70x10 ⁷	7.44x10 ⁸	0.7
T3	26.5	5.38x10 ⁷	7.01x10 ⁸	0.7
T4	6.90	1.40x10 ⁷	1.83x10 ⁸	0.2

† Estimated area of WPB canal 2.03x10⁶ m².

Table G-5. Estimation annual internal P loading from WPB canal exchange 2.

WPB canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	9.74	1.98x10 ⁷	2.58x10 ⁸	0.3
T2	9.01	1.83x10 ⁷	2.38x10 ⁸	0.2
T3	17.7	3.59x10 ⁷	4.68x10 ⁸	0.5
T4	3.00	6.09x10 ⁶	7.94x10 ⁷	0.1

† Estimated area of WPB canal 2.03x10⁶ m².

Table G-6. Estimation annual internal P loading from WPB canal exchange 3.

WPB canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	9.40	1.91x10 ⁷	2.49x10 ⁸	0.2
T2	6.04	1.23x10 ⁷	1.60x10 ⁸	0.2
T3	10.34	2.10x10 ⁷	2.74x10 ⁸	0.3
T4	2.94	5.97x10 ⁶	7.78x10 ⁷	0.1

† Estimated area of WPB canal 2.03x10⁶ m².

Table G-7. Estimation annual internal P loading from Ocean canal exchange 1.

Ocean canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	24.2	1.67x10 ⁷	2.17x10 ⁸	0.8
T2	43.1	2.97x10 ⁷	3.87x10 ⁸	0.7
T3	21.9	1.51x10 ⁷	1.97x10 ⁸	0.7
T4	20.6	1.42x10 ⁷	1.85x10 ⁸	0.2

† Estimated area of Ocean canal 6.89x10⁵ m².

Table G-8. Estimation annual internal P loading from Ocean canal exchange 2.

Ocean canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	5.21	3.59x10 ⁶	4.68x10 ⁷	0.3
T2	18.9	1.30x10 ⁷	1.70x10 ⁸	0.2
T3	18.8	1.30x10 ⁷	1.69x10 ⁸	0.5
T4	13.2	9.09x10 ⁶	1.19x10 ⁸	0.1

† Estimated area of Ocean canal 6.89x10⁵ m².

Table G-9. Estimation annual internal P loading from Ocean canal exchange 3.

Ocean canal	Cumulative P release in 28 days mg m ⁻²	Cumulative P released in 28 days from entire canal mg	Cumulative P released from canal /year mg	Cumulative P released from canal /year MT
T1	4.62	3.18x10 ⁶	4.15x10 ⁷	0.2
T2	9.31	6.41x10 ⁶	8.36x10 ⁷	0.2
T3	4.78	3.29x10 ⁶	4.29x10 ⁷	0.3
T4	7.42	5.11x10 ⁶	6.66x10 ⁷	0.1

† Estimated area of Ocean canal 6.89x10⁵ m².

LIST OF REFERENCES

- Abtew, W., and N. Khanal. 1994. Water budget analysis for the Everglades Agricultural Area Drainage Basin. *Water Resources Bulletin*. 30:429-439.
- Abtew, W., and J. Obeysekera. 1996. Drainage generation and water use in the Everglades Agricultural Area basin. *Journal of American Water Research Association*. 32:1147-1158.
- Ahlgren, I. 1980. A dilution model applied to a system of shallow eutrophic lakes after diversion of sewage effluents. *Archiv fuer Hydrobiologie*. 89:17-32.
- Ahlgren, J., K. Reitzel, L. Tranvik, A. Gogoll, and E. Rydin. 2006. Degradation of organic phosphorus compounds in anoxic Baltic Sea sediments: a ³¹P nuclear magnetic resonance study. *Limnology and Oceanography*. 51:2341-2348.
- Andersen, J.M. 1982. Effect of nitrate concentration in lake water on phosphate release from the sediment. *Water Research*. 16:119-126.
- Andersen, J.M. 1975. Influence of pH on release of phosphorus from lake sediments. *Archiv fuer Hydrobiologie*. 76:411-419.
- Andersen, J.M. 1974. An ignition method for determination of phosphorus in lake sediments. *Water Research*. 10:329-331.
- Andersen, J.M. 1974. Nitrogen and phosphorus budgets and the role of sediments in six shallow Danish lakes. *Archiv fuer Hydrobiologie*. 74:528-550.
- Anderson, D.L., and Hutcheon Engineers. 1992. Reduction of phosphorus concentration in agricultural drainage of the EAA by precipitation, coagulation, and sedimentation. Update Report to the Florida Sugarcane League. Clewiston, Florida.
- Andreis, H.J. 1993. Best management practices for on-farm phosphorus reductions through sediment control. Presentation to the South Florida Water Management District. West Palm Beach, Florida.
- Beck, M.A., and P.A. Sanchez. 1996. Soil phosphorus movement and budget after 13 years of fertilized cultivation in the Amazon basin. *Plant Soil*. 184:23-31.
- Blomqvist, S., A. Gunnars, and R. Elmgren. 2004. Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: A matter of salt. *Limnology Oceanography*. 49:2236-2241.
- Boers, P., and F. de Bles. 1991. Ion concentration of interstitial water as indicators for phosphorus release processes and reactions. *Water Research*. 25:591-598.

- Boers, P.C.M., and O. Van Hese. 1988. Phosphorus release from the peaty sediments of the Loosdrecht lakes (The Netherlands). *Water Research*. 22:355-363.
- Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1985. *Soil Chemistry*. John Wiley and Sons, New York.
- Bostrom, B., M. Jansson, and C. Fersberg. 1982. Phosphorus release from lake sediments. *Archiv für Hydrobiologie-Beiheft Ergebnisse der Limnologie*. 18:5-59.
- Bostrom, B., and K. Pettersson. 1982. Different patterns of phosphorus release from lake sediments in laboratory experiments. *Hydrobiologia*. 92:415-429.
- Bottcher, A.B., and F.T. Izuno. 1994. *Everglades Agricultural Area (EAA) - water, soil crop, and environmental management*. University Press of Florida, Gainesville, Florida.
- Bottcher, A.B., F.T. Izuno, and E.A. Hanlon. 1995. Procedural guide for the development of farm-level best management practice plans for phosphorus control in the Everglades Agricultural Area. University of Florida, Cooperative Extension Service, Institute of Food and Agricultural Sciences, Circular 1177. Available at:
http://www.sfwmd.gov/portal/page/portal/xrepository/sfwmd_repository_pdf/wq14100.pdf. (verified on 20th May 2010).
- Bowman, R.A., and C.V. Cole. 1978. An exploratory method for fractionation of organic phosphorus from grassland. *Soil Science*. 125:95-101.
- Brady, N.C., and R.R. Weil. 2002. *The Nature and Properties of Soils*. Prentice Hall, Upper Saddle River, New Jersey.
- Buffle, J., R.R. deVitre, D. Perret, and G.G. Leppard. 1989. Physico-chemical characteristics of a colloidal iron phosphate species formed at the oxic-anoxic interface of a eutrophic lake. *Geochimica et Cosmochimica Acta*. 53:399-408.
- Cade-Menun, B.J., and C.M. Preston. 1996. A comparison of soil extraction procedures for ³¹P NMR spectroscopy. *Soil Science*. 161:770-785.
- Carlton, R.G., and R.G. Wetzel. 1985. A box corer for studying metabolism of epipellic microorganisms in sediment under in situ conditions. *Limnology and Oceanography*. 30:422-426.
- Carpenter, S.R. 1983. Submersed macrophyte community structure and internal loading: relationship to lake ecosystem productivity and succession. p 105-111. *In* J. Taggart (ed.). *lake restoration, protection and management*. United States Environmental Protection Agency. Washington, D.C.
- CH2M-Hill, 1978. *Water quality studies in the Everglades Agriculture Area of Florida*. Report Submitted to the Florida Sugarcane League. Clewiston, Florida.

- Chang, S.C., and Jackson, M.L. 1957. Fractionation of soil phosphorous. *Soil Science*. 84:133-144.
- Cheesman, A.W., P.W. Inglett, B.L. Turner, and K.R. Reddy. 2010. Phosphorus transformations during decomposition of wetland macrophytes. *Environmental Science and Technology*. Available at <http://pubs.acs.org/doi/abs/10.1021/es102460h> (verified on 30th November 2010).
- Chimney, M.J., and G. Goforth. 2001. Environmental impacts to the Everglades ecosystem: a historical perspective and restoration strategies. *Water Science and Technology*. 44:93-100.
- Clark, M.W., and K.R. Reddy. 2002. Contribution of internal phosphorus loads in South Florida water conservation area canal sediments. Wetland Biogeochemistry Laboratory, Soil and Water Science Department, University of Florida, Gainesville, Final Report (Personal communication).
- Clymo, R.S., J.R. Kramer, and D. Hammerton. 1984. Sphagnum dominated peat bog: a naturally acid ecosystem. *Philosophical Transactions of the Royal Society of London*. 305:487-499.
- Collins, S.D. 2005. Utilizing in-situ benthic mesocosms to quantify phosphorus and nitrogen fluxes in South Florida agricultural canals. Ph.D. dissertation, University of Florida, Gainesville, Florida.
- Craft, C.B., and C.J. Richardson. 1993. Peat accretion and N, P, and organic C accumulation in nutrient-enriched and unenriched Everglades peatlands. *Ecological Applications*. 3:446-458.
- D'Angelo, E.M., and K.R. Reddy. 1994. Diagenesis of organic matter in a wetland receiving hypereutrophic lake water I: distribution of dissolved nutrients in the soil and water column. *Journal of Environmental Quality*. 23:925-936.
- Daroub, S.H., T.A. Lang, O.A. Diaz, and S. Grunwald. 2009. Long-term water quality trends after implementing best management practices in South Florida. *Journal of Environmental Quality*. 38:1683-1693.
- Daroub, S.H., J.D. Stuck, T.A. Lang, and O.A. Diaz. 2002a. Particulate phosphorus in the Everglades Agricultural Area: I-Introduction and Sources UF/IFAS Extension Publication (EDIS): SL197.
- Daroub, S.H., J.D. Stuck, T.A. Lang, and O.A. Diaz. 2002b. Particulate phosphorus transport in the Everglades Agricultural Area: II-Transport Mechanisms. UF/IFAS Extension Publication (EDIS): SL198.
- Davis, S.M. and J.C. Ogden. 1994. *Everglades-the ecosystem and its restoration*. St. Lucie Press, Delray Beach, Florida.

- Davison, W., and C. Woof. 1984. A study of the cycling of manganese and other elements in a seasonally anoxic lake, Rostherne Mere, UK. *Water Research*. 18:727-734.
- DeBusk, W.F., and K.R. Reddy. 1998. Turnover of detrital organic carbon in a nutrient-impacted Everglades marsh. *Soil Science Society of America Journal*. 62:1460-1468.
- 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 of America Journal*. 58:543-552.
- De Groot, C.J., and H.L. Golterman. 1993. On the presence of organic phosphate in some Camargue sediments: evidence for the importance of phytate. *Hydrobiologia*. 252:117-126.
- Diaz, O.A., K.R. Reddy, and P.A. Moore. 1994. Solubility of inorganic P in stream water as influenced by pH and Ca concentration. *Water Research*. 28:1755-1763.
- Diaz, O.A., S.H. Daroub, J.D. Stuck, M.W. Clark, T.A. Lang, and K.R. Reddy. 2006. Sediment inventory and phosphorus fractions for Water Conservation Area canals in the Everglades. *Soil Science Society of America Journal*. 70:863-871.
- Diaz, O.A., T.A. Lang, S.H. Daroub, and M. Chen. 2005. Best management practices in the everglades agricultural area: controlling particulate phosphorus and canal sediments. UF/IFAS Extension Publication (EDIS): SL228.
- Dierberg, F.E., and T.A. DeBusk. 2008. Particulate phosphorus transformations in South Florida stormwater treatment areas used for Everglades protection. *Ecological Engineering*. 34:100-115.
- Doren, R.F., T.V. Armentano, L.D. Whiteaker, and R.D. Jones. 1997. Marsh vegetation patterns and soil phosphorus gradients in the Everglades ecosystem. *Aquatic Botany*. 56:145-163.
- Dunne, E.J., N. Culleton, G. O'Donovan, R. Harrington, and K. Daly. 2005. Phosphorus retention and sorption by constructed wetland soils in the Southeast of Ireland. *Water Research*. 39:4355-4362.
- Dunne, E.J., K.R. Reddy, and M.W. Clark. 2006. Phosphorus release and retention by soils of natural wetlands. *International Journal of Environmental Pollution*. 28:496-516.
- Earnest, C.M. 1988. Compositional analysis by Thermogravimetry. American Society for Testing Materials, Philadelphia.

- Engle, D.L., and J.M. Melack. 1990. Floating meadow epiphyton: biological and chemical features of epiphytic material in an Amazon floodplain lake. *Freshwater Biology*. 23:479-494.
- Essington, M.E. 2004. *Soil and water chemistry: an integrative approach*. CRC Press, Boca Raton, Florida.
- Fan, C.X., L. Zhang, and W.C. Qu. 2001. Lake sediment resuspension and caused phosphate release-a simulation study. *Journal of Environmental Science*. 13:406-410.
- Filippelli, G.M., and M.L. Delaney. 1992. Similar phosphorus fluxes in ancient phosphorite deposits and a modern phosphogenic environment. *Geology*. 20:709-712.
- Filippelli, G.M., and M.L. Delaney. 1994. The oceanic phosphorus cycle and continental weathering during the Neogene. *Paleoceanography*. 9:643-652.
- 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.
- Froelich, P.N., M.A. Arthur, W.C. Burnett, M. Deakin, V. Hensley, R. Jahnke, L. Kaul, K. H. Kim, K. Roe, A. Soutar, and C. Vathakanon. 1988. Early diagenesis of organic matter in Peru continental margin sediments: Phosphorite precipitation. *Marine Geology*. 80:309-343.
- Froelich, P.N., G.P. Klinkhammer, M.L. Bender, N.A. Luedtke, G.R. Heath, D. Cullen, B. Hartman, and V. Maynard. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochimica et Cosmochimica Acta*. 43:1075-1090.
- 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.
- Giesler, R., T. Andersson, L. Lovgren, and P. Persson. 2005. Phosphate sorption in aluminum and iron rich humus soils. *Soil Science Society of America Journal*. 69:77-86.
- Ginsburg, R.N. 1956. Environmental relationships of grain size and constituent particles in soils South Florida carbonate sediments. *Bulletin of the American Association of Petroleum Geologists*. 40:2384-2427.
- Gleason, P.J., A.D. Cohen, W.G. Smith, H.K. Brooks, P.A. Stone, R.L. Goodrich, and W. Spackman. 1974. The environmental significance of Holocene sediments from the Everglades and saline tidal plain. p. 287-341. *In* P.J. Gleason (ed) *Environments of South Florida: present and past*. Miami Geological Society, Miami, Florida.

- Gleason, P.J., and W. Spackman Jr. 1974. Calcareous periphyton and water chemistry in the Everglades. p. 146-181. *In* P.J. Gleason (ed.) *Environments of South Florida: present and past*. Miami Geological Society, Miami, Florida.
- Gleason, P.J., and P. Stone. 1994. Age, origin, and landscape evolution of the Everglades peatland. P. 149-197. *In* S.M. Davis, S.M., and J.C. Ogden (eds.) *Everglades the ecosystem and its restoration*. St. Lucie Press, Delray Beach, Florida.
- Golterman, H.L. 2001. Phosphate release from anoxic sediments or 'What did Mortimer really write?' *Hydrobiologia*. 450:99-106.
- Golterman, H.L. 1998. The distribution of phosphate over ironbound and calcium-bound phosphate in stratified sediments. *Hydrobiologia*. 364:75-81.
- Golterman, H.L. 1975. *Physiological Limnology - An Approach to the Physiology of lake Ecosystems*. p. 489. *In* V.T. Chow (ed.) *Developments in water science 2*, Elsevier Science Publications. Amsterdam.
- Gosselink, J.G., R. Hatton, and C.S. Hopkinson. 1984. Relationship of organic carbon and mineral content to bulk density in Louisiana marsh soils. *Soil Science*. 137:177-180.
- Graetz, D.A., and V.D. Nair. 1995. Fate of phosphorus in Florida Spodosols contaminated with cattle manure. *Ecological Engineering*. 5:183-207.
- Graneli, W. 1979. The influence of *Chironomus plumosus* larvae on the exchange of dissolved substances between sediment and water. *Hydrobiologia*. 66:149-159.
- Griffin, R.A., and J.J. Jurinak. 1973. The Interaction of phosphate with calcite. *Soil Science Society of America Proceedings*. 37:847-850.
- Haggard, B.E., P.A. Moore, Jr., and P.B. DeLaune. 2005. Phosphorus flux from bottom sediments in lake Eucha, Oklahoma. *Journal of Environmental Quality*. 34:724-728.
- Hakanson, L., and M. Jansson. 1983. *Principles of lake sedimentology*. Springer-Verlag, New York.
- Hallaa, M.Y., H. Hartikainen, P. Ekholm, E. Turtolac, M. Puustinen, and K. Kallio. 1995. Assessment of soluble phosphorus load in surface runoff by soil analyses. *Agriculture, Ecosystems and Environment*. 56:53-62.
- Hansen, H.C.B., P.E. Hansen, and J. Magid. 1999. Empirical modelling of the kinetics of phosphate sorption to macropore materials in aggregated subsoils. *European Journal of Soil Science*. 50:317-327.

- Harris, W.G., M.M. Fisher, X. Cao, T. Osborne, and L. Ellis. 2007. Magnesium-rich minerals in sediment and suspended particulates of South Florida water bodies: implications for turbidity. *Journal of Environmental Quality*. 36:1670-1677.
- Harris, W.G., H.D. Wang, and K.R. Reddy. 1994. Dairy manure influence on soil and sediment composition: implications for phosphorus retention. *Journal of Environmental Quality*. 23:1071-1081.
- Hayes, F.R. 1964. The mud water interface. *Oceanography Marine Biology I-Annual Review*. 2:121-145.
- Herbert, T.D., and J.L. Sarmiento. 1991. Ocean nutrient distribution and oxygenation: limits on the formation of warm saline bottom water in the oceans over the past 90 my. *Geology*. 19:702-705.
- Hieltjes, A.H.M., and L. Lijklema. 1980. Fractionation of inorganic phosphates in calcareous sediments. *Journal of Environmental Quality*. 9:405-407.
- Holden, G.C., and D.E. Armstrong. 1980. Factors affecting phosphorus release from intact lake sediment cores. *Environmental Science and Technology*. 14:79-87.
- House, W.A., and F.H. Denison. 2002. Total phosphorus content of river sediments in relation to calcium, iron and organic matter concentrations. *Science of the Total Environment*. 341-352.
- Hupfer, M., and J. Lewandowski. 2005. Retention and early diagenetic transformation of phosphorus in lake Arendsee (Germany): consequences for management strategies. *Archiv fuer Hydrobiologie*. 164:143-167.
- Hupfer, M., B. Rube, and P. Schmieder. 2004. Origin and diagenesis of polyphosphate in lake sediments: A ^{31}P NMR study. *Limnology and Oceanography*. 49:1-10.
- Hutcheon Engineers. 1995. Sediment control demonstration project summary report. Report submitted to the Everglades Agricultural Area Environmental Protection District. West Palm Beach, Florida.
- Ingall, E.D., and R.A. Jahnke. 1994. Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters. *Geochimica et Cosmochimica Acta*. 58:2571-2575.
- Ingall, E.D., and R.A. Jahnke. 1997. Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis. *Marine Geology*. 139:219-229.
- Inskeep, W.P., and J.C. Silvertooth. 1988. Inhibition of apatite precipitation in the presence of fulvic, humic and tannic acids. *Soil Science Society of America Journal*. 52:941-946.

- Islam, A., and B. Ahmed. 1973. Distribution of inositol phosphates, phospholipids, and nucleic acids and mineralization of inositol phosphates in some Bangladesh soils. *European Journal of Soil Science*. 24:193-198.
- Ivanoff, D.B., K.R. Reddy, and J.S. Robinson. 1998. Chemical fractionation of organic phosphorus in selected Histosols. *Soil Science*. 163:36-45.
- Izuno, F.T., and R.W. Rice. 1999. Implementation and verification of BMPs for reducing P loading in the EAA. Final Project Report submitted to the Florida Department of Environmental Protection and the Everglades Agricultural Area Environmental Protection District. Tallahassee, Florida.
- Jackson, M.L. 1975. Soil chemical analysis-advanced course. Published by the author, Madison, Wisconsin.
- Jacobsen, O.S. 1978. Sorption, adsorption and chemisorption of phosphate by Danish lake sediments. *Vatten*. 4:230-243.
- James, W.F., J.W. Barko, and H.L. Eakin. 1995. Internal phosphorus loading in lake Pepin, Upper Mississippi River. *Journal of Freshwater Ecology*. 10:269-276.
- James, W.F., J.W. Barko, H.L. Eakin, and D.R. Helsel. 2000. Distribution of sediment phosphorus pools and fluxes in relation to alum treatment. *Journal of American Water Resource Association*. 36:647-656.
- Janardhanan, L. 2007. Phosphorus sorption by soils of the Everglades Agricultural Area. Ph.D. dissertation, University of Florida, Gainesville, Florida.
- Janardhanan, L., and S.H. Daroub. 2010. Phosphorus sorption in organic soils in South Florida. *Soil Science Society of America Journal*. 74:1597-1606.
- Jensen, H.S., and B. Thamdrup. 1993. Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia*. 253:47-59.
- Jepsen, R., J. Roberts, and W. Lick. 1997. Effects of bulk density on sediment erosion rates. *Water Air Soil Pollution*. 99:21-31.
- Jones, L.A. 1948. Soils, geology and water control in the Everglades region. *Agricultural Experiment Station Bulletin No. 442*. University of Florida. Gainesville, Florida.
- Kadlec, R.H., and R.L. Knight. 1996. *Treatment Wetlands*. Lewis Publishers, Boca Raton, Florida.
- Kamp-Nielsen, L. 1974. Mud-water exchange of phosphate and other ions in undisturbed sediment cores and the factors affecting the exchange rates. *Archiv fuer Hydrobiologie*. 73:218-237.

- Karathanasis, A.D., and B.F. Hajek. 1982. Quantitative evaluation of water adsorption on soil clays. *Soil Science Society of America Journal*. 46:1321-1325.
- Kasozi, N.K. 2007. Characterization of sorption and degradation of pesticides in carbonatic and associated soils from south Florida and Puerto Rico, and Oxisols from Uganda. Ph.D. dissertation, University of Florida, Gainesville, Florida.
- Kasselouri, V., G. Dimopoulos, and G. Parissakis. 1995. Effect of acetic and tartaric acid upon the thermal decomposition of CaCO_3 . *Cement and Concrete Research*. 25:477-484.
- Kelderman, P. 1984. Sediment-water exchange in lake Greveilingen under different environmental conditions. *Netherlands Journal of Sea Research*. 18:286-311.
- Khalid, R.A., W.H. Patrick Jr., and R.D. DeLaune. 1977. Phosphorus sorption characteristics of flooded soils. *Soil Science Society of America Journal*. 41:305-310.
- Khalid, R.A., W.H. Patrick, Jr. and R.P. Gambrell. 1978. Effect of dissolved oxygen on chemical transformations of heavy metals, phosphorus and nitrogen in an estuarine sediment. *Estuarine and Coastal Marine Science*. 6:21-35.
- Kitano, Y., M. Okumura, and M. Idogaki. 1978. Uptake of phosphate ions by calcium carbonate. *Geochemical Journal*. 12:29-37.
- Koch, M.S., R.E. Benz, and D.T. Rudnick. 2001. Solid-phase phosphorus pools in highly organic carbonate sediments of Northeastern Florida Bay. *Estuarine, Coastal and Shelf Science*. 52:279-291.
- Koch, M.S., and K.R Reddy. 1992. Distribution of soil and plant nutrients along a trophic gradient in the Florida Everglades. *Soil Science Society of America Journal*. 56:1492-1499.
- Laenen, A, and A.P. LeTourneau. 1996. Upper Klamath Basin nutrient-loading study- Estimates of wind-induced resuspension of bed sediment during periods of low lake elevation. *United States Geological Survey Open File Report*. 11:95-414.
- Larsen, P., D.W. Schultsa, and K.W. Maluegi. 1981. Summer internal phosphorus supplies in Shagawa lake, Minnesota. *Limnology and Oceanography*. 26:740-753.
- Lee, G.F., W.C. Sonzogni, and R.D. Spear. 1977. Significance of oxic versus anoxic conditions for lake Mendota sediment phosphorus release. p. 294-306. *In*: H.L. Golterman, (ed.) *Interactions between sediments and fresh water*. The Hague.
- Leeds, J.A. 2006. Phosphorus sorption and flux in northern everglades soil under drained and flooded conditions. Ph.D. dissertation, University of Florida, Gainesville, Florida.

- Lick, W., and J. McNeil. 2001. Effects of sediment bulk properties on erosion rates. *Science of the Total Environment*. 266:41-48.
- Lide, D.R. 2005. *Handbook of Chemistry and Physics*. CRC press, Boca Raton, Florida.
- Light, S.S., and W.J. Dineen. 1994. Water control in the Everglades: a historical perspective. p 47-84. *In* S. M. Davis and J. C. Ogden (eds.) *Everglades: the ecosystem and its restoration*. St. Lucie Press, Delray Beach, Florida.
- Lijklema, L. 1977. The role of iron in the exchange of phosphate between water and sediments. p. 313-317. *In* H. L. Golterman (ed.) *Interactions between sediments and fresh water*. The Hague.
- Lijklema, L. 1985. Internal loading, mechanisms and assessment of magnitude, *Proceedings of the International Congress on Lakes Pollution and Recovery*. Rome.1:194-198.
- Lijklema, L. 1980. Eutrophication: the role of sediments. *Hydrobiology Bulletin*. 14:98-105.
- Lijklema, L. 1980. Interaction of orthophosphate with iron (III) and aluminum hydroxides. *Environmental Science and Technology*. 14:537-541.
- Likens, G.E., F.H. Bormann, and N.M. Johnson. 1981. Interaction between major biogeochemical cycles in terrestrial ecosystems. p. 93-112. *In*: G.E. Likens, (ed.) *Some perspectives of the major biogeochemical cycles*. Wiley, New York.
- Lillebo, A.I., J.M. Neto, M.R. Flindt, J.C. Marques, and M.A. Pardal. 2004. Phosphorous dynamics in a temperate intertidal estuary. *Estuarine Coastal and Shelf Science*. 61:101-109.
- Loeppert, R.H., and W.P. Inskeep. 1996. Iron. p. 639-664. *In* D.L. Sparks (ed.) *Methods of soil analysis*. Part 3. SSSA Book Ser. no. 5. Madison, Wisconsin.
- LOTAC. 1990. *Lake Okeechobee Technical Advisory Council Final Report*. Tallahassee, Florida., Florida Department of Environmental Protection.
- Lucotte, M., and D. Anglejan. 1988. Processes controlling phosphate adsorption by iron hydroxides in estuaries. *Chemical Geology*. 67:75-83.
- Malecki, L.M., J.R. White, and K.R. Reddy. 2004. Nitrogen and phosphorus Flux Rates from Sediment in the Lower St. Johns River Estuary. *Journal of Environmental Quality*. 33:1545-1555.
- Maltby, E, and P.J. Dugan. 1994. Wetland ecosystem protection, management and restoration: An international perspective .p. 29-46. *In*: S.M. Davis and J.C. Ogden (eds.) *Everglades-the ecosystem and its restoration*. St. Lucie Press, Delray Beach, Florida.

- Marsden, M.W. 1989. Lake restoration by reducing external phosphorus loading: the influence of sediment phosphorus release. *Freshwater Biology*. 21:139-162.
- Martin, C.S. 2004. Phosphorus flux from the sediments in the Kissimmee chain of lakes. Ph.D. dissertation, University of Florida, Gainesville, Florida.
- McCormick, P.V., P.S. Rawlik, K. Lurding, E.P. Smith, and F.H. Sklar. 1996. Periphyton-water quality relationships along a nutrient gradient in the northern Florida Everglades. *Journal of the North American Benthological Society*. 15:433-449.
- McDowell, R.W., and A.N. Sharpley. 2001. Approximating phosphorus release from soils to surface runoff and subsurface drainage. *Journal of Environmental Quality*. 30:508-520.
- McGechan, M.B., and D.R. Lewis. 2002. Sorption of phosphorus by soil, part 1: principles, equations and models. *Biosystems Engineering*. 82:1-24.
- McKeague, J.A., and J.H. Day. 1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science*. 46:13-22.
- McKelvie, I.D. 2005. Separation, preconcentration and speciation of organic phosphorus in environmental samples. p. 1-20. In B.L. Turner, E. Frossard, and D.S. Baldwin (eds.) *Organic phosphorus in the environment*. CABI Publishing, Wallingford, UK.
- Messer, J.J., J.M. Ihnat, B. Mok, and D. Wegner. 1983. Reconnaissance of sediment phosphorus relationships in Upper Flaming Gorge reservoir. *Water Quality Series Utah Water Research Laboratory*. Q-83/02:84
- 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.
- Millero, F.J., F. Huang, X. Zhu, X. Liu, and J.Z. Zhang. 2001. Adsorption and desorption of phosphate on the calcite and aragonite in seawater. *Aquatic Geochemistry*. 7:33-56.
- Moller-Andersen, J. 1974. Nitrogen and phosphorus budget and the role of sediments in six shallow Danish lakes. *Archives fuer Hydrobiologie*. 74:528-550.
- Monk, C.D. 1968. Successional and environmental relationships of the forest vegetation of North Central Florida. *American Midland Naturalist*. 79:441-457.
- Moore, P.A., and K.R. Reddy. 1994. Role of eh and pH on phosphorus geochemistry in sediments of lake Okeechobee, Florida. *Journal of Environmental Quality*. 23:955-964.

- Moore, P.A., K.R. Reddy, and M.D. Fisher. 1998. Phosphorus flux between sediment and overlying water in lake Okeechobee, Florida: Spatial and temporal variations. *Journal of Environmental Quality*. 27:1428-1439.
- Moore, P.A. Jr., K.R. Reddy, and D.A. Graetz. 1991. Phosphorus geochemistry in the sediment–water column of a hypereutrophic lake. *Journal of Environmental Quality*. 20:869-875.
- Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology*. 29:280-329.
- Mortimer, C.H. 1942. The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology*. 30:147-201.
- Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta*. 27:31-36.
- Newman, S., K.R. Reddy, W.F. DeBusk, Y. Wang, M.M. Fisher, and G. Shih. 1997. Spatial distribution of soil nutrients in a northern Everglades marsh: water conservation area 1. *Soil Science Society of America Journal*. 61:1275-1283.
- Nielsen., K.L. 1974. Mud-water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting the exchange rates. *Archiv fuer Hydrobiologie*. 73:218-237.
- Noe, G.B., D.L. Childers, and R.D. Jones. 2001. Phosphorus biogeochemistry and the impact of phosphorus enrichment: why is the Everglades so unique? *Ecosystems*. 4:603-624.
- 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.
- Nriagu, J.O., and C.I. Dell. 1974. Diagenetic formation of iron phosphates in recent lake sediments. *American Mineralogist*. 59:934-946.
- Nguyen, L., and J. Sukias. 2002. Phosphorus fractions and retention in ditch sediments receiving surface runoff and subsurface drainage from agricultural catchments in the North Island, New Zealand. *Agriculture Ecosystems and Environment*. 92:49-69.
- Obeysekera, J., J. Browder, L. Hornung, and M.A. Harwell. 1999. The natural South Florida system I: Climate, geology, and hydrology. *Urban Ecosystems*. 3:223-244.
- Olila, O.G., and K.R. Reddy. 1993. Phosphorus sorption characteristics of sediments in shallow eutrophic lakes of Florida. *Archiv Fuer Hydrobiologie*. 129:45-65.

- Olila, O.G., K.R. Reddy, and W.G. Harris. 1995. Forms and distribution of inorganic phosphorus in sediments of two shallow eutrophic lakes in Florida. *Hydrobiologia*. 302:147-161.
- Olila, O.G., K.R. Reddy, and W.G. Harris. 1994. Forms and distribution of inorganic P in sediments of two shallow eutrophic lakes in Florida. *Hydrobiologia*. 302:147-161.
- Olsen, S.R., and F.S. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the langmuir isotherm. *Soil Science Society of America Proceedings*. 21:144-149.
- 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.
- Pant, H.K., and K.R. Reddy. 2001. Hydrologic influence on stability of organic phosphorus in wetland detritus. *Journal of Environmental Quality*. 30:668-674.
- Pant, H.K., K.R. Reddy, and F.E. Dierberg. 2002. Bioavailability of organic phosphorus in a submerged aquatic vegetation-dominated treatment wetland. *Journal of Environmental Quality*. 31:1748-1756.
- Pant, H.K., K.R. Reddy, and R.M. Spechler. 2002. Phosphorus retention in soils from a prospective constructed wetland site. *Soil Science*. 167:607-615.
- Patrick, W.H. jr., S. Gotoh, and B.G. Williams. 1973. Strengite dissolution in flooded soils and sediments. *Science*. 179:564-565.
- Petterson, K., and B. Boström. 1985. Phosphorus exchange between sediment and water in lake Balaton. p 427-435. *In* P. G. Sly (ed.) *Sediments and water interactions*. Springer, New York.
- Petuch, E.J., and C.E. Roberts. 2007. *The geology of the everglades and adjacent areas*. CRC Press, Boca Raton, Florida.
- Pizarro, J., N. Belzile, M. Filella, G.G. Leppard, J.C. Negre, D. Perret, and J. Buffle. 1995. Coagulation/sedimentation of submicron particles in a eutrophic lake. *Water Research*. 29:617-632.
- Poon, C.P.C. 1977. Nutrient exchange kinetics in water-sediment interface. *Programs in Water Technology*. 9:881-895.
- Porter, J.W., and K.G. Porter. 2002. *The everglades Florida bay and coral reefs of the Florida keys: an ecosystem sourcebook*. CRC press, Boca Raton, Florida.
- Premazzi, G., and A. Provini. 1985. Internal phosphorus loading in lakes: a different approach to its evaluation. *Hydrobiologia*. 120:574-580.

- Qualls, R.G., and C.J. Richardson. 2008. Decomposition of litter and peat in the Everglades: the Influence of phosphorus concentrations. p. 441-459. *In* M.M. Caldwell, G. Heldmaier, R.B. Jackson, O.L. Lange, H.A. Mooney, E.D. Schulze, U. Sommer (eds.) *The Everglades experiments: lessons for ecosystem restoration*. Springer, New York.
- Qualls, R.G., and C.J. Richardson. 2003. Factors controlling concentration, export, and decomposition of dissolved organic nutrients in the Everglades of Florida. *Biogeochemistry*. 62:197-229.
- Quall, R.G., and C.J. Richardson. 1995. Forms of soil phosphorus along a nutrient enrichment gradient in the northern Everglades. *Soil Science*. 160:183-198.
- Rader, R.B., and C.J. Richardson. 1994. Response of macroinvertebrates and small fish to nutrient enrichment in the northern Everglades. *Wetlands* 14:134-146.
- Reddy, K.R., G.A.O' Connor, and P.M. Gale. 1998. Phosphorus sorption capacities of wetland soils and stream sediments impacted by dairy effluent. *Journal of Environmental Quality*. 27:438-447.
- Reddy, K.R., and R.D. Delaune. 2008. *Biogeochemistry of wetlands: science and applications*. CRC Press, Boca Raton, Florida.
- Reddy, K.R., R.D. DeLaune, W.F. DeBusk, and M.S. Koch. 1993. Long-term nutrient accumulation rates in the Everglades. *Soil Science Society of America Journal*. 57:1147-1155.
- Reddy, K.R., O.A. Diaz, L.J. Scinto, and M. Agami. 1995. Phosphorus dynamics in selected wetlands and streams of the lake Okeechobee basin. *Ecological Engineering*. 5:183-207.
- 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., M.M. Fisher, Y. Wang, J.R. White, and R.T. James. 2007. Potential effects of sediment dredging on internal phosphorus loading in a shallow, subtropical lake. *Lake and Reservoir Management*. 23:27-38.
- Reddy, K.R., R.H. Kadlec, E. Flaig, and P.M. Gale. 1999. Phosphorus retention in streams and wetlands: a review. *Critical Reviews in Environmental Science and Technology*. 29:83-146.
- Reddy, K.R., Y. Wang, W.F. DeBusk, M.M. Fisher, and S. Newman. 1998. Forms of soil phosphorus in selected hydrologic units of Florida Everglades. *Soil Science Society of America Journal*. 62:1134-1147.

- Reynoldson, B., and H. Hamilton. 1982. Spatial heterogeneity in whole lake sediments towards a loading estimate. *Hydrobiologia*. 91:235-240.
- Rhue, R.D., and W.G. Harris. 1999. Phosphorus sorption/desorption reactions in soils and sediments. p.187-206. In: K.R. Reddy, G.A. O' Connor and C.L. Schelske (eds.) *Phosphorus biogeochemistry in subtropical ecosystems*. Lewis Publishers, Boca Raton, Florida.
- Rice, R.W., F.T. Izuno, and R.M. Garcia. 2002. Phosphorus load reductions under best management practices for sugarcane cropping systems in the Everglades Agricultural Area. *Agricultural Water Management*. 56:17-39.
- Richardson, C.J. 1999. The role of wetlands in storage, release, and cycling of phosphorus on the landscape: a 25-year retrospective. p. 47-68. *In* K.R. Reddy (ed.) *Phosphorus biogeochemistry in subtropical ecosystems*. Lewis Publishers, New York.
- Richardson, C.J., and P. Vaithyanathan. 1995. Phosphorus sorption characteristics of the Everglades soils along an eutrophication gradient. *Soil Science Society of America Journal*. 59:1782-1788.
- Riley, E.T., and E.E. Prepas. 1984. Role of internal phosphorus loading in two shallow, productive lakes in Alberta, Canada. *Canadian Journal of Fish and Aquatic Sciences*. 41:845-855.
- Robinson, J.S., C.T. Johnston, and K.R. Reddy. 1998. Combined chemical and ³¹P NMR spectroscopic analysis of phosphorus in wetland organic soils. *Soil Science*. 163:705-713.
- Ruttenberg, K.C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography*. 37:1460-1482.
- Ruttenberg, K.C., and R.A. Bemer. 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochimica et Cosmochimica Acta*. 57:991-1007.
- Ryding, S.O. 1981. Reversibility of man-induced eutrophication: experiences of a lake recovery study in Sweden. *International Review of Hydrobiology*. 66:449-503.
- Ryding, S.O., and C. Forsberg. 1977. Sediments as a nutrient source in shallow polluted lakes. p. 227-234. *In*: H.L. Golterman, (ed.) *Interactions between sediments and fresh water*. The Hague.
- Sanchez, C.A. 1990. Soil-testing and fertilization recommendations for crop production on organic soils in Florida. University of Florida, Agricultural Experiment Station Bulletin. No. 876. University of Florida. Gainesville, Florida.

- Sanchez, C.A., and P.S. Porter. Phosphorus in the organic soils of EAA. p. 62-80. *In* A.B. Bottcher and F.T. Izuno (eds) Everglades Agricultural Area (EAA):Water, Soil, Crop and Environmental Management, University Press of Florida, Gainesville, Florida.
- SAS Institute. 2003. SAS Version 9.2. SAS Inst., Cary, NC.
- Scholl, D.W. 1966. Florida Bay: a modern site of limestone formation. p. 212-227. *In* R.W. Fairbridge (ed.) Encyclopedia of Oceanography. Chapman-Reinhold, New York.
- Scott, T.M. 1997. Miocene to Holocene history of Florida. p. 21-25. *In* A.F. Randazzo, and D.S. Jones (eds.) The Geology of Florida, University Press of Florida, Gainesville, Florida.
- Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong, and R.F. Harris. 1971. Sorption of inorganic phosphate in lake sediments. Soil Science Society of America Proceedings. 35:244-249.
- Singh, N.B., and N.P. Singh. 2007. Formation of CaO from thermal decomposition of calcium carbonate in the presence of carboxylic acids. Journal of Thermal Analysis and Calorimetry. 89:159-162.
- Sinke, A. J., C.A.A. Cornelese, P. Keizer, O.F.R. van Tongeren, and T.E. Cappenberg. 1990. Mineralization, pore water chemistry and phosphorus release from peaty sediments in the eutrophic Loosdrecht lakes, The Netherlands. Freshwater Biology. 23:587-599.
- Smith, D.R., B.E. Haggard, E.A. Warnemuende, and C. Huang. 2005. Sediment phosphorus dynamics for three tile fed drainage ditches in Northeast Indiana. Agricultural Water Management. 71:19-32.
- Smith, S.V. 1984. Phosphorus versus nitrogen limitation in the marine environment. Limnology and Oceanography. 29:1149-1160.
- Snyder, G.H., and J.M. Davidson. 1994. Everglades agriculture: past, present, and future. p. 85-115. *In* S. M. Davis and J. C. Ogden (eds.) Everglades: the ecosystem and its restoration. St.Lucie Press, Delray Beach, Florida.
- Søndergaard, M. 1989. Phosphorus release from a hypertrophic lake sediment: experiments with intact sediment cores in a continuous flow system. Archiv für Hydrobiologie. 116:45-59.
- Southeast District Assessment and Monitoring Program. 2001. Ecosummary South Florida Water Management District Miami Canal (C-6). Available at http://www.dep.state.fl.us/southeast/ecosum/ecosums/C-6_Canal.pdf. (verified on 20th May 2010).

- Southeast District Assessment and Monitoring Program. 1999. Ecosummary West Palm Beach Canal. Available at <http://www.dep.state.fl.us/southeast/ecosum/ecosums/wpbcanal.pdf>. (verified on 20th May 2010).
- South Florida Environmental Report. 2010a. Hydrology of the South Florida Environment. South Florida Water Management District. Available at https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_sfer/tab2236037/2010%20report/v1/vol1_table_of_contents.html. (verified 5th May 2010).
- South Florida Environmental Report. 2010b. Introduction to the 2010 South Florida Environmental Report-Volume I. South Florida Water Management District. Available at https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_sfer/tab2236037/2010%20report/v1/vol1_table_of_contents.html. (verified 5th May 2010).
- South Florida Environmental Report. 2009. Phosphorus Source Controls for the South Florida Environment. South Florida Water Management District. Available at https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_sfer/tab2236041/2009report/report/v1/vol1_table_of_contents.html. (verified 5th May 2010).
- South Florida Environmental Report. 2006. Implementation and verification of BMPs for reducing P loading in the Everglades Agricultural Area. Available at http://www.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/2006_sfer/volume1/vol1_table_of_contents.html (verified 5th May 2010).
- South Florida Environmental Report. 2004a. Implementation and verification of BMPs for reducing P loading in the EAA and Everglades Agricultural Area BMPs for reducing particulate phosphorus transport. Available at http://www.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/final/index.html (verified 5th May 2010).
- South Florida Environmental Report. 2004b. On farm particulate phosphorus Measurement and Control. South Florida Water Management District. Available at https://my.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/final/index.html (verified 5th May 2010).
- South Florida Environmental Report. 2003. Implementation and verification of BMPs for reducing P loading in the EAA. Available at http://www.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/ecr2003/index.html (verified 5th May 2010).
- South Florida Environmental Report. 2002. Performance and optimization of agricultural best management practices. Available at http://www.sfwmd.gov/portal/page/portal/pg_grp_sfwmd_sfer/portlet_prevreport/2002_ecr/contents.html (verified 5th May 2010).

- Sondergaard, M., P. Kristensen, and E. Jeppesen. 1992. Phosphorus release from resuspended sediment in the shallow and wind-exposed lake Arreso, Denmark. *Hydrobiologia*. 228:91-99.
- Sonzogni, W.C., S.C. Chapra, D.E. Armstrong, and T.J. Logan. 1982. Bioavailability of phosphorus inputs to lakes. *Journal of Environmental Quality*. 11:555-563.
- Stauffer, R.E., and D.E. Armstrong. 1986. Cycling of iron, manganese, silica, phosphorus, calcium and potassium in two stratified basins of Shagawa lake, Minnesota. *Geochimica et Cosmochimica Acta*. 50:215-229.
- Steinman, R., and K.R. Reddy. 2004. The reduction of internal phosphorus loading using alum in Spring lake, Michigan. *Journal of Environmental Quality*. 33:2040-2048.
- Stevens, R.J., and C.E. Gibson. 1977. Sediment release of phosphorus in Lough Neagh, Northern Ireland. p. 343-347. *In*: H.L. Golterman, (ed.) *Interactions between sediment and freshwaters*. Junk-Pudoc Publications, The Hague, Wageningen.
- Stockman, K.W., R.N. Ginsburg, and E.A. Shinn. 1967. The production of lime mud by algae. *South Florida Journal of Sedimentary Research*. 37:633-648.
- Stuck, J.D. 1996. Particulate phosphorus transport in the water conveyance systems of the Everglades Agricultural Area (EAA). Ph.D. dissertation, University of Florida, Gainesville, Florida.
- Stuck, J.D., F.T. Izuno, K.L. Campbell, and A.B. Bottcher. 2001. Farm level studies of particulate phosphorus transport in the Everglades Agricultural Area. *Transactions of the American Society of Agricultural Engineers*. 44:1105-1116.
- Stuck, J.D., T.A. Lang, O.A. Diaz, S.A. Daroub, and T. Aziz. 2002. Studies of particulate phosphorus sources and potential management practices for control in the Everglades Agricultural Area. *Seventh Biennial Stormwater Research and Watershed Management Conference*.
- Stumm, W., and J.O. Leckie. 1970. Phosphate exchange with sediments; its role in the productivity of fresh waters. *Advances in Water Pollution Research*. 2:1-6.
- Stumm, W., and J.J. Morgan. 1970. *Aquatic Chemistry*. Wiley Intersciences, New York.
- Sundareshwar, P.V., J.T. Morris, P.J. Pellechia, H.J. Cohen, D.E. Porter, and B.C. Jones. 2001. Occurrence and ecological significance of pyrophosphate in estuaries. *Limnology and Oceanography*. 46:1570-1577.
- Suzumura, M., and A. Kamatani. 1995. Origin and distribution of inositol hexaphosphate in estuarine and coastal sediments. *Limnology and Oceanography*. 40:1254-1261.

- Svendsen, L.M., Kronvang, B, Kristensen, and P. Graesbol. 1995. Dynamics of Phosphorus compounds in a lowland river system. *Hydrological Processes*. 9:119-142.
- Swift, D.R., and R.B. Nicholas. 1987. Periphyton and water quality relationships in the Everglades Water Conservation Areas. Technical Publications. 87-2. South Florida Water Management District, West Palm Beach, Florida.
- Thiede, J., and T.H. van Andel. 1977. The paleoenvironment of anaerobic sediments in the late Mesozoic South Atlantic Ocean. *Earth and Planetary Science Letters*. 33:301-309.
- Thomas, G.W. 1996. Soil pH and soil acidity. p. 475-490. *In* D.L. Sparks (ed.) *Methods of soil analysis Part 3: Chemical methods* 3rd ed. SSSA and ASA, Book Ser 5. SSSA, Madison, Wisconsin.
- Tiessen, H., J.W.B. Stewart, and J.O. Moir. 1983. Changes in organic and inorganic phosphorus composition of two grassland soils and their particle size fractions during 60-90 years of cultivation. *European Journal of Soil Science*. 34:815-823.
- Tiren, T., and K. Pettersson. 1985. The influence of nitrate on the phosphorus flux to and from oxygen depleted lake sediments. *Hydrobiologia* 120:207-223.
- Turner, B.L., N. Mahieu, and L.M. Condrón. 2003. Phosphorus-31 nuclear magnetic resonance spectral assignments of phosphorus compounds in soil NaOH-EDTA extracts. *Soil Science Society of America Journal*. 67:497-510.
- Turner, B.L., and S. Newman. 2005. Phosphorus cycling in wetlands: The importance of phosphate diesters. *Journal of Environmental Quality*. 34:1921-1929.
- Turner, B.L., S. Newman, A.W. Cheesman, and K.R. Reddy. 2007. Sample pretreatment and phosphorus speciation in wetland soils. *Soil Science Society of America Journal*. 71:1538-1546.
- Turner, B.L., and S. Newman. 2005. Phosphorus cycling in wetland soils: the importance of phosphate diesters. *Journal of Environmental Quality*. 34:1921-1929.
- Turner, B.L., S. Newman, and J. Newman. 2006. Organic phosphorus sequestration in subtropical treatment wetlands. *Environmental Science and Technology*. 40:727-733.
- Turner, B.L., D.T. Westermann, D.L. Bjorneberg, and J.A. Aase. 2002. Phosphorus release kinetics as affected by aqueous solutions. *Research and Extension Regional Water Quality Conference*. Available at: http://www.swwrc.wsu.edu/conference/Papers/DT_Westermann.pdf. (verified on 30th November 2010).

- Tracey, P.T. 2006. Implementation of the long-term plan for achieving water quality goals in the Everglades Protection Area. South Florida Water Management District, West Palm Beach, Florida.
- United States Environmental Protection Agency. 1983. Methods for chemical analysis of water and wastes. Environmental Monitoring and Support Laboratory. Cincinnati, Ohio.
- United States Environmental Protection Agency. 1989. Statistical analysis of groundwater monitoring data at Resource Conservation and Recovery Act (RCRA) facilities interim final guidance; EPA/530-SW-89-026; U.S. EPA; Office of solid waste management; Washington, D.C.
- Van Veen, H.W., T. Abee, G.J.J. Kortstee, W.N. Konings, and A.J.B. Zehnder. 1993. Characterization of two phosphate transport systems in *Acinetobacter johnsonii* 210A. *Journal of Bacteriology*. 175:200-206.
- Walker, W.W. Jr. 2001. Development of a phosphorus TMDL for Upper Klamath lake, Oregon: Concord, Massachusetts, submitted to Oregon Department of Environmental Quality, Bend, Oregon, 78 p. [http://www.deq.state.or.us/wq/TMDLs/UprKlamath/Walker_Report.pdf verified on 1st October 2003.
- Welch, E.B., and G.D. Cooke. 1995. Internal phosphorus loading in shallow lakes: importance and control. *Lake Reservoir Management*. 11:273-281.
- Whalen, P.J., J. VanArman, J. Milliken, D. Swift, S. Bellmund, D. Worth, T.D. Fontaine, L. Golick, and S. Formati. 1992. Surface water improvement and management plan for the Everglades. South Florida Water Management District, West Palm Beach, Florida.
- White, I., M.D. Melville, B.P. Wilson, and J. Sammut. 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management*. 5:55-72.
- White, J.R., and K.R. Reddy. 2003. Nitrification and denitrification rates of everglades wetland soils along a phosphorus-impacted gradient. *Journal of Environmental Quality*. 32:2436-2443.
- White, J.R., and K.R. Reddy. 2001. Influence of selected inorganic electron acceptors on organic nitrogen mineralization in Everglades soils. *Soil Science Society of America Journal*. 65:941-948.
- White, J.R., and K.R. Reddy. 2000. Influence of phosphorus loading on organic nitrogen mineralization rates in Everglades soils. *Soil Science Society of America Journal*. 64:1525-1534.

- White, J.R., K.R. Reddy, and J. Majer-Newman. 2006. Hydrologic and vegetation effects on water column phosphorus in wetland mesocosms. *Soil Science Society of America Journal*. 70:1242-1251.
- White, J.R., K.R. Reddy, and M.Z. Moustafa. 2004. Influence of hydrologic regime and vegetation on phosphorus retention in Everglades Stormwater Treatment Area wetlands. *Hydrological Processes*. 18:343-355.
- Whittig, L.D., and W.C. Allardice. 1986. X-ray diffraction techniques. p. 331-362. *In* A. Klute (ed.) *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*, Soil SSSA, Madison, Wisconsin.
- Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1970. Adsorption and desorption of inorganic phosphorus by lake sediments. *Environmental Science Technology*. 4:517-519.
- Zhou, A.M., H.X. Tang, and D.S. Wang. 2005. Phosphorus adsorption on natural sediments: Modeling and effects of pH and sediment composition. *Water Research*. 39:1245-1254.
- Zhou, M., and L. Yuncong. 2001. Phosphorus-sorption characteristics of calcareous soils and limestone from the Southern Everglades and adjacent farmlands. *Soil Science Society of America Journal*. 65:1404-1412.

BIOGRAPHICAL SKETCH

Jaya Das was born in the city of Calcutta, India. She went to school at Bata Girls' High School until 1996. Thereafter, she was admitted to the prestigious University of Calcutta where she received her Bachelor in Science (B.Sc.) in chemistry in 2000. She completed a Post Graduate Diploma in Computer Applications from the University of Kalyani in 2001. Thereafter, she returned to University of Calcutta to complete her Master of Science (M.Sc) in agricultural chemistry and soil science in 2003. She decided to pursue higher studies and joined the Ph.D. program in the Soil and Water Science Department at University of Florida in fall of 2005 with Dr. Samira Daroub and Dr. George O'Connor as her advisors. Since then she has been engaged in research about nutrient dynamics, transport and their consequences in wetland ecosystems.