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Physicochemical assessment and phosphorus storage of canal sediments within the Everglades Agricultural Area, Florida

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Abstract

Purpose Excess nutrients such as phosphorus (P) transported from the Everglades Agricultural Area (EAA) in South Florida, USA, to downstream water bodies have been identified as contributing to trophic imbalances within the Florida Everglades. Decades of farming drainage from the EAA has led to accumulation of sediments in regional canals which may be transported to downstream ecosystems and act as potential internal source of P.

Materials and methods Intact sediment cores were collected from three main conveyance and three farm canals within the EAA. Physicochemical assessment, mineralogy, P speciation, and storage were determined for surface and subsurface layers.

Results and discussion The main conveyance canal sediments had higher total P (TP) concentrations $(1,280\pm 360 \text{ mg kg}^{-1})$ than the farm canals $(960\pm 540 \text{ mg kg}^{-1})$, while farm canal sediments showed higher organic matter content (28–53 %) compared to the main canal (24–27 %) sediments. The minerals found in main conveyance canal sediments were similar to those found in Lake Okeechobee. The

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O. Diaz South Florida Water Management District, West Palm Beach, FL, USA labile KCl–P fraction comprised <2 % of TP from all canal sediments, while NaOH-Pi (i=inorganic) fraction consisted of 1-14 % of TP. The majority of P in the canal sediments was contained in the HCl-P fraction (Ca-P and Mg-P), comprising >50 % of TP in the main and farm canal sediments. An estimated 73 metric tons (mt) of P was stored in the 0-10-cm layer of the three main conveyance canals within the EAA boundary of which 57-mt P is reactive and potentially available for release at different time scales. Conclusions The EAA canal sediments are highly organic with low bulk density and susceptible of being transported to downstream ecosystems. Many factors can impact the potential release of the reactive stored P, including redox potential of sediments as well as the overlying water column P concentration. Further investigation of potential P release from these sediments is warranted.

Keywords Best management practice · Canals · Everglades Agricultural Area · Phosphorus · Sediments

1 Introduction

The Everglades Agricultural Area (EAA) in South Florida, USA, presently covers an area of 2,872 km² (SFER 2011) of the Florida Everglades consisting primarily of rich organic soils. The EAA has been actively drained by ditches and canals to sustain a \$2 billion annual agriculture industry. Agricultural drainage water is pumped from the EAA farm canals into main conveyance canals (West Palm Beach (WPB), Hillsboro, North New River, and Miami), through stormwater treatment areas (STAs) to the Water Conservation Areas (WCAs), before finally being discharged into the Everglades National Park (ENP). The farm canals are used to irrigate and drain the farms. The main conveyance canals originate from Lake Okeechobee and ultimately drain into the Atlantic Ocean (Light and Dineen 1994). In addition to the four main conveyance canals, three connecting canals (Bolles, Cross, and Ocean) connect to the other main canals to help regulate stage and flow (SFER 2009).

Phosphorus (P) from EAA agricultural drainage is thought to be one of the main causes of eutrophication and ecosystem imbalances within the WCAs and the ENP (Whalen et al. 1992). In response, restoration efforts have focused on reducing P loading from EAA and reestablishment of a more natural hydroperiod to sensitive wetland areas within the WCAs and ENP (Light and Dineen 1994). Current remediation plans require EAA farmers to implement Best Management Practices (BMPs), for example, modification of pumping practices, protection of canal banks with vegetation, minimization of fertilizer application, use of cover crops, and retention of on-farm drainage to reduce P discharge to the canals of the EAA (Sievers et al. 2002; Daroub et al. 2009; Daroub et al. 2011).

For water year 2010, it was estimated that nearly $3 \times$ 10¹² m³ of water and nearly 169 metric tons (mt) of P at a concentration of 127 μ g l⁻¹ discharged from the EAA into the Everglades Protection Area (EPA), consisting of Arthur R. Marshal Loxahatchee Wildlife Refuge, the WCAs, and the ENP (SFER 2011), corresponding to a rainfall adjusted P load reduction of 41 % compared to a base period from 1978 to 1988. While a major source of P to the EAA canals is from farm drainage waters, a significant portion is attributed to internal loading from the canal sediments (Bostrom et al. 1982; Diaz et al. 2006). Other sources of P in the EAA are from fertilizer application in farms, inflow water from Lake Okeechobee, and mineralization of the organic soil (Stuck 1996). Historic P loading to the EAA canals and subsequent P flux from accumulated sediments to the water column have been identified as a potential source of P to the water column and downstream ecosystems. Stuck et al. (2001) showed that farm canals alone can have a significant impact on total P (TP) loads discharged from agricultural farms and that up to 70 % of the exported P was particulate in nature. A large percentage of particulate P (PP) is derived from aquatic vegetation growing in the canals (Stuck et al. 2001; Daroub et al. 2003). Particulate P in agricultural drainage waters of the EAA was highly variable with landuse and management practices (CH2M Hill 1978). 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, and can be easily transported to downstream ecosystems (Dierberg and DeBusk 2008). Particulate P can also arise from erosion of canal banks. While it is still the individual farming practices that ultimately control the amount of nutrients introduced to the canal systems, canal management strategies such as optimum pumping velocity for draining water off farms and good aquatic weed control programs have been shown to reduce P loads exiting the canals (Daroub et al. 2003). In addition, different crops have different P loads according to fertilizer requirements and water management practices.

Phosphorus fractionation procedures have been successfully used to explain P movement and transformation in upland soils (Tiessen et al. 1983; Beck and Sanchez 1996), organic wetland soils (Ivanoff et al. 1998; Bhadha and Jawitz 2010), and calcareous lake sediments (Hielties and Liklema 1980). In South Florida, White et al. (2004) performed inorganic P fractionation (KCl-NaOH-HCl) on sediments from STA-1 W and found that the Ca phosphates and residual-P comprised more than 75 % of TP. Newman et al. (1997) showed that almost 70 % of TP in the sediments from WCA-1 was organically derived. Diaz et al. (2006) used the KCl-NaOH-HCl fractionation scheme on canal sediments to evaluate the amount of inorganic and organic P in perimeter canals of the WCAs. They found that Ca- and Mg-bound P, along with residual-P, were the dominant forms in the WCA perimeter canals.

The implementation of BMPs in the EAA since 1995 has resulted in >50 % annual P load reduction compared to baseline levels (SFER 2009; Daroub et al. 2011). Those reductions, in addition to further treatment of the water in constructed stormwater treatment areas, have improved water quality in the Everglades (SFER 2009). However, current efforts have yet to achieve the water quality criterion of 10 ppb required by law. Further reduction of P concentrations and loads from the EAA is critical to achieve Everglades restoration and protect downstream ecosystems. Despite management practices employed on farm canals (for example, control of floating aquatic vegetation and dredging of canal sediments), a large percentage of the P load exported from the EAA is found in particulate form due to suspended sediments from farm canals (Stuck et al. 2001). Conversely, main canals receive few management practices. We wanted to answer two questions: (1) How much of the P stored in the canals is in labile forms that can potentially become biologically available on short-term and long-term bases, and (2) do sediment properties differ between farm and main canals? Determining the physical and chemical properties of both farm and main canal sediments is a crucial first step to understanding their potential impact on downstream ecosystems.

The objectives of this study were to (1) determine the physicochemical properties of three main conveyance and three farm canals sediments within the EAA, (2) evaluate clay mineralogy of sediment in the main canals, and (3) use a fractionation scheme to evaluate the nature of P storage in the sediments and its potential role in internal loading of P. An overall understanding of sediment physicochemical

characteristics and P bioavailability can help plan future restoration work and implement sound management strategies.

2 Materials and methods

2.1 Site description

The three conveyance canals sampled were Miami, West Palm Beach (WPB), and Ocean canals (Fig. 1). The canals are managed by the South Florida Water Management District and are also called Main or District canals. The role of these conveyance canals within the EAA is to facilitate drainage and also supply irrigation water to the farms. The Miami canal, also known as the C-6 canal, originates at S-3 pump station on Lake Okeechobee and is approximately 136 km in length (SDAMP 2001). In the EAA, the Miami canal length is approximately 30 km. Miami canal overlies the Fort Thomson bedrock formation and drains into the Miami River that ultimately discharges into Biscayne Bay to the south. The Fort Thomson bedrock formation is made of dense, hard limestone, shells, and sand. The WPB canal, also known as the C-51 canal, overlies the Fort Thomson formation and stretches approximately 68 km southeast from Lake Okeechobee to the Atlantic Ocean. In the EAA, the WPB canal is approximately 32 km. The Ocean canal is approximately 21 km long and is a main canal that connects Hillsboro canal and WPB canals. The Ocean canal stretches east-west and overlies the Fort



Fig. 1 Study site showing the sediment sampling locations along Miami, West Palm Beach, and Ocean canals (*open circles*) and location of farm canals 00A, 09A, and 06AB (*open star*)

Thomson and the Anastasia bedrock formation (SFER 2009). The Anastasia formation is composed of shell-rich limestone, sedimentary rocks, and sand, and is much more permeable compared to the Fort Thomson formation (SFER 2009).

Three farm canal sediments were sampled: 09A, 00A, and 06AB (see Fig. 1). Farm canal 09A drains a large (12.4 km²) sugarcane monoculture farm facilitated by three high capacity diesel pumps (6–37 m³ min⁻¹) that are operated manually. Located within the S8 farm basin, farm 09A consists of Terra Ceia (Typic Haplosaprists) and Pahokee (Lithic Haplosaprists) soil series with depth to bedrock ranging from 51 to 91 cm (Soil Survey Staff 2007). Farm canal 09A represents a large farm with a large canal relative to pump capacity, and the farm canal has a low velocity. Due to low flow velocity, farm canal 09A sediments are slow to mobilize. Particulate P averages about 70 % of TP from this farm (SFER 2004) due to accumulation of sediments, but TP concentration in drainage water is low. Farm canal 09A ultimately drains into the Miami canal.

Farm canal 00A is located in the eastern part of EAA, draining a medium-sized (5.2 km²) sugarcane monoculture farm. The farm is drained by two high-capacity (9–29 m³ min⁻¹) and one lower capacity (5–9 m³ min⁻¹) single-speed electrical pumps. Farm canal 00A receives irrigation water and ultimately drains into the WPB canal. Soils in Farm 00A are classified as Terra Ceia (Typic Haplosaprists) and Pahokee (Lithic Haplosaprists) soil series with depths to bedrock <90 cm.

Farm canal 06AB drains a medium-sized (7.1 km²) mixed-crop farm located in the S-5A subbasin in the eastern part of the EAA. Farm 06AB comprises Terra Ceia (Typic Haplosaprists) and Pahokee (Lithic Haplosaprists) soil series with depth to bedrock <90 cm. It has two pump stations, each with two high-capacity diesel pumps. Farm 06AB includes multiple control structures that allow an aggressive water management program preventing build-up of PP in the farm canal (SFER 2004). Water in farm canal 06AB is shallower, and drainage water flows faster than canals 00A and 09A (SFER 2004); this causes the settled particulates in the canal to be mobilized faster. Thus, 06AB canal sediment is prone to having a higher mineral matter content than 09A and 00A canal sediments, as the light and flocculent particulates are transported off farm, leaving behind denser mineral matter. Farm canal 06AB ultimately discharges into the Ocean canal.

2.2 Sediment sampling and analyses

Intact sediment cores were collected from four transects (T1, T2, T3, and T4) within the Miami, WPB, and Ocean canals (see Fig. 1). The first transect (T1) for Miami and WPB canal was closest to Lake Okeechobee, while the other transects (T2, T3, and T4) were taken progressively southward into the EAA. The average distance between the

sampling locations was ~11 km, which covered the entire length of these two canals within the EAA boundaries. The first sampling location (T1) in the Ocean canal was closest to the WPB canal, and the fourth transect (T4) was closest to the Hillsboro canal. The average distance between transects in the Ocean canal was ~2 km for approximately 6 km of the canal being sampled. Triplicate sediment cores were collected at each transect within the middle two-thirds of the canal cross-sectional area for a total of 36 sediment cores. For farm canals, intact sediment cores were collected in triplicates from five transects along the length of these canals (T1 nearest to pump station and T5 farthest away from pump station) for a total of 45 sediment cores. Sediment cores were collected using a piston sediment core sampler comprised of a 7.2-cm inner diameter polycarbonate core tube that was inserted into the sediment bed. Approximately 20 cm of sediment was collected in the cores, along with 10 cm of water column. After retrieval from the canal, both ends of the core were sealed. Water from the cores was suctioned off using a pump. Sediment cores were sectioned at 5-cm depth increments (surface 0-5 cm and subsurface 5-10 cm). Samples were stored in plastic containers at 4 °C until analyses.

Samples were analyzed for pH, bulk density ($\rho_{\rm b}$), organic matter (OM), and TP. Sediment pH was determined by weighing 10 g of sediment and adding deionized (DI) water to it in a 1:2 (mass:volume) ratio (Thomas 1996). The wet weight of each layer sampled was measured, and dry weight was calculated after determining the water content of the layer by placing 10 g of sediment in an oven at 105 °C for 24 h. Bulk density was calculated by dividing the dry mass of the sediment sample by the volume of the sampling core (Blake and Hartge 1986). Organic matter content was determined using the loss-on-ignition (LOI) method, where 5 g of wet sediment was combusted at 550 °C for 4 h in a muffle furnace (Andersen 1976). Thermogravimetric (TG) analyses was conducted on the main canal surface (0-5 cm) sediments due to the assumption that these sediments contain hydrated clay minerals that can interfere with the actual measure of OM when analyzed using the LOI method (Harris et al. 2007). Estimating OM using the TG method involved using a computer-controlled thermal analysis system that analyzed loss in sediment mass between 300 °C and 600 °C depending on the weight loss curves (Earnest 1988). The residue ash following LOI for all sediments was acid digested and analyzed for TP using the ascorbic acid method (USEPA 1993: Method 365.4). Surface sediments from the three main canals were also analyzed for clay mineralogy by X-ray diffraction (XRD, Nicolet Corporation, Madison, WI, USA) using a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Oriented mounts were prepared by sedimentation on unglazed ceramic tiles under suction. Diagnostic cation saturation with MgCl₂ and glycerol was performed to aid in the identification of phyllosilicate minerals (Harris and White 2008). XRD analyses of the samples were done at a scan rate of 2 °2 θ per minute using Cu anode and K α radiation. The concentrations of calcite and dolomite were determined by TG based on weight loss from CO₂ evolution in the temperature range of their thermal decomposition reaction and the stoichiometry of the reaction (e.g., CaCO₃ (s) \rightarrow CaO(s)+CO₂ (g) \uparrow) (Karathanasis and Harris 1994).

The characterization of P fractions in all sediment canals was performed for each of the three replicates using a sequential fractionation procedure developed by Reddy et al. (1995, 1998). Inorganic P (Pi) fractions extracted were KCl, NaOH, and HCl. Organic P (Po) fraction in NaOH was also determined. Residual-P in the soil was finally determined with no distinction made between Pi and Po. A 0.3-g dry sediment equivalent of wet sediments was sequentially extracted with 1-M KCl, 0.1-M NaOH, and 0.5-M HCl solutions, followed by digestion. Inorganic P was analyzed in all fractions colorimetrically (Murphy and Riley 1962) using Spectronic[®] 20 GenesysTM spectrophotometer. The TP in the NaOH fraction was determined by digesting the NaOH extract in an autoclave with ammonium persulfate and sulfuric acid for 30 min at 121 °C, 15-20 psi (USEPA 1993), and analyzed with the same methods as previously discussed. NaOH-Po was determined by the difference between total and inorganic P in that fraction. To determine residue-P, the contents were digested in a muffle furnace at 550 °C for 4 h and redigested on a hot plate by adding 20 ml 6.0-M HCl. The digestion in hot plate was repeated for a second time with 2.25 ml of 6.0-M HCl. The contents were cooled, filtered, and analyzed using the same method as previously discussed.

The KCl–Pi fraction represents the labile-Pi that is water soluble and exchangeable (loosely adsorbed); NaOH–Pi represents Fe- and Al-bound inorganic P, while NaOH–Po is associated with humic and fulvic acids. The HCl–Pi fraction includes Ca- and Mg-bound P, while residue-P represents recalcitrant organic P compounds and P bound to minerals. Quality assurance/quality control was strictly followed with calibration, standards, spikes, and blanks routinely included in the analysis.

2.3 Statistical data analysis

Descriptive statistics of means, standard deviations, 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 fractionation 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 physicochemical properties and P fractions between transects in each canal. Summary statistics and Tukey's test were conducted (SAS Institute 2003) to assess significant (p<0.05) differences between transects and depths within individual canals. Pearson correlation analysis was used to correlate TP versus OM content of canal sediments.

3 Results and discussion

3.1 Physicochemical properties

Both Miami and WPB canal sediments had similar mean pH values of 7.4 ± 0.2 and 7.4 ± 0.1 , respectively (Table 1). The pH of the Ocean canal sediments was slightly higher at 7.9± 0.1. The average pH values of canals 09A, 00A, and 06AB surface layer were 7.5 \pm 0.1, 7.1 \pm 0.3, and 7.7 \pm 0.1, respectively. Sediment pH values between different transects within the farm canals were significantly different in the surface (0-5 cm) layer of 06AB canal and subsurface (5-10 cm) layers of 00A and 06AB canals (Table 2). A difference in pH between sediment layers in EAA canals can arise with the accumulation of organic particulates on top of predominantly mineral carbonatic sediments, which can have higher pH values than the former. 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).

Bulk density values for Miami canal sediments varied from 0.14 g cm⁻³ at T3 to 0.54 g cm⁻³ at T4 in the surface layer (see Table 1). Bulk densities of WPB canal varied from 0.12 g cm⁻³ at T2 to 0.29 g cm⁻³ at T3 in the surface layer. Bulk density values of Ocean canal did not vary significantly between the different transects, and the mean value was 0.35 ± 0.06 g cm⁻³ in the surface layer. Farm canal sediments 00A had mean $\rho_{\rm b}$ values of 0.12±0.03 and 0.23±0.16 g cm⁻³ in the surface and subsurface layers, respectively (see Table 2). Farm canal sediments 09A had mean $\rho_{\rm b}$ values of 0.18 ± 0.05 and 0.36 ± 0.13 g cm⁻³ in surface and subsurface layers, while farm canal sediments 06AB had mean $\rho_{\rm b}$ values of 0.37 ± 0.12 and 0.41 ± 0.08 g cm⁻³ in surface and subsurface layers, respectively. There is a slight increase in mean $\rho_{\rm b}$ between the surface and subsurface layers within the farm canal sediments for 09A and 00A, although the individual transects did not show any statistical differences. The changes in composition between the two layers may be partly due to compaction of sediments within the deeper zones and lower OM content at the subsurface layer. The increased OM in the surface layer allows the soil to remain porous, thereby decreasing $\rho_{\rm b}$ (Brady and Weil 1999). Similar range of $\rho_{\rm b}$ values $(0.1 \text{ to } 0.6 \text{ g cm}^{-3})$ was observed 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 reported an average bulk density of 0.42 g cm⁻³. The $\rho_{\rm b}$ values in the sediments of both the farm and main canals are lower than typical bulk density values of mineral soils and thus are susceptible to be transported in the EAA drainage waters as suspended solids (along with P) distributed throughout the water column.

Table 1 Mean pH, bulk density (ρ_b), organic matter (OM), and total phosphorus (TP) values of Miami, West Palm Beach (WPB), and Ocean canal sediments from T1 to T4 observed in the surface (0–5 cm) and subsurface (5–10 cm) layers (n=3)

Transect	pН			$\rho_{\rm b} \ ({\rm g \ cm}^{-3})$			OM (%)			TP (mg kg ⁻¹)		
	Miami	WPB	Ocean	Miami	WPB	Ocean	Miami	WPB	Ocean	Miami	WPB	Ocean
0–5 cm												
T1	7.2 b	7.4 ns	7.9 ns	0.18 b	0.22 a	0.37 ns	30 a	29 ns	23 ab	1,140 bc	1,300 ns	480 ab
T2	7.3 b	7.4	7.9	0.18 b	0.12 b	0.36	43 a	33	20 ab	910 c	1,190	430 b
Т3	7.4 b	7.4	7.9	0.14 b	0.29 a	0.40	24 a	18	17 bA	1,730 ab	1,010	510 ab
T4	7.7 a	7.3	7.8	0.54 a	0.26 a	0.26	7.2 b	26	38 a	1,940 aA	1,050	930 a
5-10 cm												
T1	7.3 b	7.4 ns	8.0 a	0.18 b	0.30 ab	0.45 a	27 a	41 ns	29 ns	1,240 a	950 ns	390 ns
T2	7.4 b	7.5	8.0 a	0.21 b	0.38 a	0.5 a	37 a	24	17	870 b	930	450
Т3	7.6 b	7.3	7.9 a	0.19 b	0.23 b	0.37 ab	27 a	25	43 B	2,050 a	1,070	360
T4	7.9 a	7.5	7.8 b	0.50 a	0.25 ab	0.20 b	7.2 b	29	54	890 bB	1,010	450

Treatment means within the same column followed by the same small case letter are not different by Tukey's test between transects for each canal at p < 0.05. Treatment means within the same column followed by the same upper case letter are not different by Tukey's test between same transects for two depth horizons and for each canal p < 0.05

ns not significant

Table 2 Mean pH, bulk density (ρ_b), organic matter (OM), and total phosphorus (TP) values of farm 09A, 00A, and 06AB canal sediments from T1 to T5 observed in the surface and subsurface layers (n=3)

Transect	рН			$\rho_{\rm b} \ ({\rm g \ cm}^{-3})$			OM (%)			TP (mg kg ⁻¹)		
	09A	00A	06AB	09A	00A	06AB	09A	00A	06AB	09A	00A	06AB
0–5 cm												
T1	7.5 ns	6.8 ns	7.8 a	0.12 ns	0.12 ab	0.54 a	38 ns	42 cA	14 c	1,110 a	1,120 bA	340 c
T2	7.5	7.3	7.6 b	0.16	0.13 ab	0.36 abc	37	42 c	24abc	870 ab	1,520 abA	520 b
T3	7.5	7.0	7.6 ab	0.19	0.16 a	0.44 ab	29	74 a	24 bc	760 ab	2,460 a	560 ab
T4	7.5	7.3	7.6 b	0.23	0.11 bc	0.27 bc	25	50 b	40 ab	570 c	1,590 ab	740 a
T5	7.6	7.3	7.7 ab	0.22	0.08 c	0.24 c	32	57 b	42 a	670 b	930 b	720 a
5-10 cm												
T1	7.4 ns	7.2 ab	7.8 a	0.36 ab	0.50 a	0.44 a	22 ns	16 cB	21 ns	750 ns	480 cB	490 ns
T2	7.6	7.4 a	7.7 ab	0.33 ab	0.21 b	0.50 a	28	41 b	25	640	920 bB	570
Т3	7.6	7.0 b	7.7 ab	0.56 a	0.20 b	0.47 a	22	74 a	24	590	2,220 a	520
T4	7.6	7.4 a	7.7 b	0.36 ab	0.14 bc	0.37 ab	21	44 b	38	550	1,170 b	610
T5	7.5	7.4 a	7.8 ab	0.19 b	0.10 c	0.29 b	33	52 ab	40	650	870 b	650

Treatment means within the same column followed by the same small case letter are not different by Tukey's test between transects for each canal at p < 0.05. Treatment means within the same column followed by the same upper case letter are not different by Tukey's test between same transects for two depth horizons and for each canal p < 0.05

ns not significant

While the mean measure of percent OM (based on LOI) was similar between the main canal sediments, it was variable within individual canals (see Table 1). For example, T4 in Miami canal had a significantly lower OM content compared to the other transects in both depths. The Ocean canal had OM ranging from a low of 17 % at T3 at 0-5 cm to a high of 54 % at T4 at the 5-10 cm depth. Percent OM of farm canal sediments varied between different canals. Canal sediments from farm 00A, 09A, and 06AB had mean OM content at the 0–5-cm surface layer of 53 ± 13 %, 32 ± 5 %, and 29±12 %, respectively. The OM content decreased with depth for 00A canal at T1, while for 09A and 06AB, the values were not significantly different between the surface and subsurface layers in any of the transects. Farm canals 00A and 06AB had lowest OM content at T1 closest to the pump. This is probably due to greater water velocity associated with pumping near T1 that can effectively mobilize the light, flocculent sediment surface layer. In comparison, farm canal sediments had greater OM content than the main canal sediments. A possible reason is that farm canal sediments directly receive drainage water from the farmlands. Even though the main canals drain a much larger area in the region, the concentration of particulate matter flowing through the main canals is lower compared to the farm canals (SFER 2009).

In the surface layer, the mean TP concentration from Miami canal sediments was $1,430\pm480$ mg kg⁻¹, and the highest concentration was observed in location T4 at the 0–5 cm depth (1,940 mg kg⁻¹) (see Table 1). In the surface layer, for WPB canal sediments, the mean TP concentration

was $1,140\pm130$ mg kg⁻¹; the highest concentration was observed at location T1 at 0–5 cm (1,300 mg kg⁻¹). In the surface layer, Ocean canal sediments had the lowest mean TP concentrations compared to the other two canals (590±231 mg kg⁻¹).

In general, the farm canal sediments had lower TP concentrations than the main canals. Possible explanation includes the fact that main canals receive water from Lake Okeechobee in addition to farmland drainage. Water P concentration in Lake Okeechobee is typically high (Reddy et al. 1999) and can contribute to higher P levels in the water which translates to higher sediment P content. In addition, farm canals are often cleaned, while main canals are not. Canal sediments of 00A, 09A, and 06AB had mean TP concentrations at the 0-5-cm layer of $1,520\pm590, 790\pm$ 210, and 580±160 mg kg⁻¹, respectively. Similar TP concentrations were observed at the 5-10-cm layer with some exceptions. Total P concentration of sediments decreased with depth in farm canal 00A at T1 and T2, likely due to the significant decrease in OM with depth. Similar trends of decreasing TP with depth have been found in sediments of the Everglades region (Reddy et al. 1993; Newman et al. 1997; White and Reddy 2000, 2003). There was no significant change in TP values with depth for 06AB canal sediments similar to the OM content. This could be attributed to the aggressive aquatic weed control and canal cleanup operations that may have helped in reducing deposition of detrital matter high in P content. Overall, there was a positive correlation ($R^2=0.69$) between sediment TP and OM content from farm canals, suggesting that a significant fraction

% OM

of TP was organically derived (Fig. 2), while the main canals showed a slight negative correlation possibly due to the higher inorganic nature of the canal sediments.

3.2 Mineralogical assessment

Mineralogical composition of the main canal sediments was evaluated based on TG and XRD analyses on the clay-sized fraction of the three main canal sediments. Thermogravimetric analysis on surface sediments from transects T1, T2, and T3 in the Miami canal as well as all transects from WPB and Ocean canal indicated three inflections corresponding to concentration of OM, dolomite, and calcite (Fig. 3). Organic matter content measured by the TG method was slightly lower than measured by LOI. Partial weight loss in LOI could be due to loss of volatile salts, structural water of clay minerals or metal oxides, or inorganic carbon. The TG curve from T4 of Miami canal resulted in only two inflections corresponding to weight loss due to OM and calcite. The presence of dolomite [(CaMg $(CO_3)_2$ from sediments in the Miami canal sediments T1, T2, and T3 was also confirmed using XRD analysis, however, lacking in T4. Other minerals identified using XRD in the % OM

Miami canal were sepiolite, quartz, calcite, and aragonite (Fig. 4). Based on the relative peaks of calcite and aragonite from the Miami canal, T4 suggested that both of these minerals were abundant. Mineralogically, all four locations within the WPB canal were similar, showing the presence of dolomite, calcite, sepiolite, and quartz (see Figs. 3 and 4). The XRD data of Ocean canal sediments indicated the presence of palygorskite in addition to sepiolite, calcite, dolomite, quartz, and aragonite. The presence of sepiolite in WPB and Ocean canals was further substantiated by XRD after selective dissolution of OM and carbonates (see Fig. 4). Selective dissolution also revealed the presence of kaolinite and smectite. Smectite is an expandable secondary phyllosilicate, with a relatively high density of permanent negative charge than kaolinite. Hence, it imparts a higher cation exchange capacity than kaolinite, in addition to its lower edge to face ratio than kaolinite which would not favor retention of anionic species such as orthophosphate (Pant et al. 2002). A more weathered mineral suite, consisting of minerals such as metal oxides and kaolinite, would tend to impart higher P retention capacity per gram of clay than would smectite. In contrast, sediments with high OM content may interfere with the P sorption properties





Fig. 4 Sequences of X-ray diffraction (XRD) patterns for surface sediments collected from Miami, West Palm Beach (WPB), and Ocean canals from all four locations scanned at 25 °C after cation saturation with MgCl₂ and glycerol. The XRD patterns inserts of WPB and Ocean canals are after selective dissolution of organic matter and carbonates scanned at 25 °C after cation saturation with MgCl₂ and glycerol. *SP* sepiolite-magnesium Silicate [Mg₄Si₆O₁₅(OH)₂•6H₂O)], *OZ* quartz-

silicon dioxide (SiO₂), *CA* calcite-calcium carbonate (CaCO₃), *DO* dolomite-calcium magnesium carbonate [CaMg(CO₃)₂], *AR* aragonite-polymorph of calcium carbonate (CaCO₃), *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)₂Si₄O₁₀(OH)•4(H₂O) (determined by removing carbonate and organic matter)

of the mineral phases. Olila et al. (1995) and Harris et al. (2007) identified similar mineral phases from the mud of Lake Okeechobee, suggesting that some of the mineral matter is being transported from Lake Okeechobee with irrigation water and deposited in the main canals. Crystalline form of Ca–P minerals, if present, was too low in concentration to be detected by XRD. Particles of Ca–P composition were detected in Lake Okeechobee mud sediment using energy-dispersive X-ray fluorescence elemental microanalysis (Harris et al. 2007). The lack of any 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), or insufficient time for mineral formation. Phosphate is known to be adsorbed on calcite and aragonite surfaces (Kitano et al. 1978; Millero et al. 2001). Thus, it is possible that P in Miami, WPB, and Ocean canals does not exist as discrete phosphatic minerals; instead, it is adsorbed on carbonate minerals. This is supported by the fact that P-related mineral deposits usually occur in central and northern Florida, and have not been found in South Florida (Zhou and Li 2001; Chambers and Pederson 2006).

3.3 Phosphorus fractionation

3.3.1 Main canal sediments

Within the main canals, the labile KCl–Pi fraction represented 0.6 % to 1.2 % of TP in surface and subsurface sediments at all of the locations (Fig. 5a). The KCl–Pi did not vary significantly between the different locations in each canal and ranged from 4.5 to 14.2 mg kg⁻¹. The inorganic NaOH–Pi fraction ranged from 3 % to 8 % of TP in all three main canal sediments. The concentration of NaOH–Pi did not vary significantly among the different locations of the main canals, and the mean concentrations were $106\pm$ 82 mg kg⁻¹ (7.9±5.9 %), 93±31 mg kg⁻¹ (8.7±1.5 %), and 18±1 mg kg⁻¹ (3.4±0.9 %) for Miami, WPB, and Ocean canals, respectively. The NaOH–Pi fraction represents the Fe and Al bound P. Phosphorus bound to Fe is highly redox sensitive. This would mean that short-term fluctuations in the water level or seasonal changes between wet and dry

Fig. 5 Percent fractions of various forms of phosphorus (P) within the surface (0–5 cm) (a) and subsurface (5–10 cm) (b) horizons collected from four locations within the Miami, West Palm Beach (WPB), and Ocean canals. T1 is nearest to Lake Okeechobee, while T4 is farthest away from the Lake periods have the potential to slowly release P to the water column. Phosphorus release from sediments is normally greater under anaerobic conditions than aerobic due to reduction of Fe oxides (Pautler and Sims 2000; Pierzvnski et al. 2005; Bhadha et al. 2010a). The NaOH-Po fraction represented 1 % to 6 % of TP in all canal sediments with the highest percentage in Miami T1 and T2 transects. Typically, under anaerobic conditions, the NaOH-Po pool is relatively stable as the rate of OM decomposition is regulated by the availability of oxygen in the system. However, under aerobic conditions, this fraction of P may be susceptible to mineralization, consequently releasing P to the water column. Both Miami and WPB canal sediments, due to the higher NaOH-Pi and Po concentrations than the Ocean canal, would be more susceptible to this sort of P release under alternating redox conditions. Organic P in the NaOH pool can be humic-sesquioxide complexed P (e.g., Gerke 1992). In humic-Fe-P complexes, P might be mobile at anaerobic conditions. Das et al. (2012) have shown that



canal sediments in the EAA have nearly a five-fold surplus of oxalate extractable Fe (529 mg kg⁻¹) than oxalate extractable Al (110 mg kg⁻¹). Since Al constituted only a small fraction of metals in these sediments compared to Fe, anaerobic conditions could significantly affect the NaOH–Pi within the system.

The HCl-P fraction within the sediments of the main canals was the largest and accounted for 60 % to 73 % of TP in the surface horizon (see Fig. 5a). The HCl-P concentrations for Miami canal ranged from 653 mg kg⁻¹ at T1 to 1,530 mg kg⁻¹ at T4, with a mean of 525 ± 461 mg kg⁻¹. Sediment HCl-P concentrations did not vary significantly between the locations of the WPB canal, and the mean concentration was 649±100 mg kg⁻¹. Ocean canal HCl-P concentrations ranged from 316 to 735 mg kg⁻¹, and the mean concentration was 424 ± 207 mg kg⁻¹. With the exception of WCA-1, the Everglades soils are dominated by Ca-P and Mg-P (Reddy et al. 1998). The residue-P fraction is considered as the most stable (recalcitrant), and it was the second largest storage pool of the three main canal sediments comprising 17 % to 26 % of TP. The concentration of residue-P did not vary significantly between locations in the Miami and Ocean canals. The mean concentration of residue-P from the Miami, WPB, and Ocean canal sediments was 234 ± 30 , 233 ± 109 , and 127 ± 30 mg kg⁻¹, respectively. From a P-management standpoint, while it may be promising that the majority (>80 %) of the P within the surface sediments of the main canals is present in relatively stable form (HCl) and very stable form (residue-P), the remaining fractions (KCl- and NaOH-P) can pose serious concerns for internal loading of P. In addition, HCl-P can become available over a long period of time. Reddy et al. (2011) defined NaOH-P and HCl-P as reactive P that are available for release at different time scales. Residual-P is non-reactive P and considered unavailable for biotic or abiotic transformation.

Overall, only Miami canal sediments showed a significant increase in the HCl–P from location T1 to T4 and a decrease in NaOH–Po, NaOH–Pi, KCl–P, and residue-P. No significant changes were observed in P fractionations from WPB and Ocean canal sediments based on the location of sampling sites.

3.3.2 Farm canal sediments

The KCl–Pi fraction of the farm canal sediments comprised less than 2 % of TP (Fig. 6a, b) and was not significantly different between individual locations or between surface and subsurface horizons. Among the three farm canals, canal 00A had the highest mean KCl–Pi concentrations of $17\pm8 \text{ mg kg}^{-1}$ (1.4±0.8 %) and 8.5±5 mg kg⁻¹ (0.9±0.4 %) within the surface and subsurface layers, respectively. KCl– Pi is of concern because it represents the readily available labile-P pool. These KCl–Pi concentration values in the farm canal sediments were in accordance to those reported by various researchers in South Florida: 0.1-2.3 % of TP 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), and 0.01 % of TP in the STA-1 W (White et al. 2006).

The NaOH-Pi fraction comprised 4 % to 7 % of TP in the surface and subsurface horizons of the canal sediments. There was no significant difference in NaOH-Pi concentrations within or between all three farm canals. The mean NaOH-Pi concentrations in the 0-5-cm layer of canal sediments 00A, 09A, and 06AB were 74 ± 18 mg kg⁻¹ (5.7± 1.0 %), $69\pm39 \text{ mg kg}^{-1}$ (6.9±3.1 %), and $15\pm7 \text{ mg kg}^{-1}$ $(2.8\pm1.0 \%)$, respectively. Similar TP concentrations were observed in the 5-10-cm layer. Typically, the NaOH-Pi fraction is 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 (Hieltjes and Lijklema 1980; Olila et al. 1995; Bhadha et al. 2010b). Phosphorus fractionation studies by Diaz et al. (2006) on canal sediments of the STA and the WCA found that the NaOH-Pi fraction varied from 1 % to 13 % of TP. Redox fluctuations are dominant in sediments with high OM or from sediments in canals with low flow velocities or pulse flow (Diaz et al. 2006). The latter is particularly important as water flow in EAA farm canals is not continuous but regulated by pumps resulting in quiescent no-flow period between pumping events. This can result in accumulation of PP and detrital material in the canals which can be easily mobilized during high velocity periods, such as during pumping or storm events.

The NaOH-Po fraction represented about 3 % to 14 % of TP within the surface and subsurface sediments of all three farm canals. The NaOH-Po concentrations did not vary significantly between various locations in farm canals 09A and 00A within both surface and subsurface layers. The highest concentration of NaOH-Po was observed in canal 09A, $121\pm50 \text{ mg kg}^{-1}$ (14±3.4 %) and $83\pm65 \text{ mg kg}^{-1}$ (12± 7.7 %) within the surface and subsurface horizons, respectively. 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 subsequent detrital deposition. Farm 09A does not implement any practices for controlling floating aquatic vegetation or canal sediment dredging which explains the higher concentration of organic-bound P in those sediments. The decomposition of the NaOH-Po pool is dependent on the availability of oxygen and is relatively stable under hypoxic conditions. In the EAA canals, the deposition of detrital matter is not favored by canal management practices such as weed control and removal of floating aquatic vegetation; thus,

Fig. 6 Percent fractions of various forms of phosphorus (P) within the surface (0–5 cm) (a) and subsurface (5–10 cm) (b) horizons collected from five locations within the farm canals, 09A, 00A, and 06AB. T1 is nearest to the pump station, while T5 is farthest away from the pump



the NaOH-Po content is lower than sediments in the Everglades.

The HCl–Pi (Ca–P and Mg–P) fraction at the three farm canals accounted for 51 % to 59 % of TP in the surface horizon and 56 % to 61 % within the subsurface horizon, representing the largest portion of TP, similar to what was found in the main canals. The highest concentrations of HCl–Pi were observed in sediments from 00A, 756± 257 mg kg⁻¹ (52 ± 4.2 %) and 578 ± 339 mg kg⁻¹ (55 ± 3.9 %) within the surface and subsurface horizons, respectively. Mean HCl–Pi concentrations for canals 09A and 06AB at the 0–5-cm surface layer were 442±67 mg kg⁻¹ (52 ± 8.7 %) and 318 ± 58 mg kg⁻¹ (59 ± 7.3 %), respectively. Similar mean values were found at the 5–10-cm subsurface layer.

The residue-P fraction, typically comprising stable lignin and organo-metallic complexes, was the second largest P fraction in all of the three farm canal sediments, representing 25 % to 41 % and 25 % to 39 % of TP within the surface and subsurface horizons, respectively. Similar residue-P concentrations were also reported by Diaz et al. (2006) in canal sediments of North and South Miami canals (21–35 %). In the surface horizon, the residue-P in canal 09A did not show any significant difference between the different locations, and mean concentrations were $225\pm63 \text{ mg kg}^{-1}$ ($26\pm3.6 \%$). The residue-P concentrations at the 0–5-cm layer from canal 00A and 06AB were $446\pm72 \text{ mg kg}^{-1}$ ($34\pm6.0 \%$) and $173\pm54 \text{ mg kg}^{-1}$ ($32\pm6.3 \%$), respectively. Similar mean values were found at the 5–10-cm layer.

3.4 P Storage in main canals

The canals of the EAA can potentially be a source of P to the downstream ecosystems negatively affecting Everglades restoration. This could occur either by P flux from sediments in situ and/or transport of these sediments with drainage water. Although we did not sample all main conveyance canals in the EAA, determining P storage and its reactivity

in the three canals sampled will provide an indication on the potential of long-term impacts. Total P can be divided into non-reactive P (residue-P fraction) and reactive P (mostly NaOH and HCl fractions) (Reddy et al. 2011). The reactive P may be available for release at different time scales. Phosphorus stored at the surface 0-10-cm layer in Miami, WPB, and Ocean canals within the EAA boundary were 34 (± 12) , 26 (± 3) , and 13 (± 5) mt, respectively. Phosphorus storage was calculated by multiplying TP concentration in each canal by the bulk density and area of each canal within the EAA boundaries. The areas of the canals within the EAA were estimated using Google Maps. From the fractionation data, about 78 % of TP was classified as reactive and 22 % as non-reactive. An estimated 57 mt of reactive P is stored in the top 10-cm layer in these three main canals within the EAA boundaries. The long-term P load out of the EAA is estimated to be 170 mt per year (SFER 2010). Reddy et al. (2011) estimated that legacy P in surface soils of the EAA with 8,010 to 20,020 mt of reactive P being potentially released would support the 170 mt per year load to the STAs and WCAs for the next 47 to 118 years. It is obvious that the reactive stored P in the 0-10-cm layer of these canals is a small percentage of what is found in EAA soils, but these canal sediments are prone to being transported with drainage water into the STAs and WCAs. The farm and main canal sediments are also continuously accruing sediments mostly from the growth and death of floating aquatic vegetation. These sediments have a high organic matter content and low bulk density, and may be easily transported with drainage water.

4 Conclusions

The main and farm canal sediments collected from the EAA had a neutral pH with appreciable amounts of OM. The main canals consisted of 24-27 % OM, while the farm canals had slightly greater OM content ranging from 25-53 %. The source of the OM is primarily from growth of floating aquatic vegetation both in the farm and main canals and to a lesser extent from soil erosion. As the main canals receive water directly from Lake Okeechobee, their sediments tend to be slightly more inorganic. This is reflected in the lack of any positive correlation between TP and OM between main canal sediments, unlike that of farm canal sediments. Total P was slightly higher in the main canals compared to the farm canals, although there was variability between the transects. Among the main canals, the Ocean canal had much lower TP than both WPB and Miami canals. Also, Miami canal T4 was different from the other transects, having much lower OM and higher TP. Because of the organic nature and the low bulk density of these sediments, they could be highly mobile under the right conditions of low canal elevations and high drainage velocity.

X-ray diffraction and TG analyses revealed the presence of various Ca-based minerals derived from the underlying calcium carbonate bedrock. Kaolinite and smectite were the two most dominant minerals that were identified within the finer clay-sized fraction of the sediments, and while kaolinite has a high P-sorption capacity, the presence of OM could significantly affect the role of phyllosilicates within the sediment matrix.

The fractionation data revealed that an average of 78 % of TP in main canals was in reactive forms (labile-Pi, NaOH-P, and HCl-Pi) and 22 % in non-reactive forms (residual-P). The labile, KCl-P fraction constituted a very small fraction of the TP, but it has the highest potential of being biologically available. The NaOH-Pi fraction consisted of 1-14 % of TP within all the canal sediments combined. Under fluctuating redox conditions associated with pumping during flow and no-flow events, Fe-bound P has the potential to be released from the sediments, posing concern for internal loading of P from sediments. Ocean canal had a much lower NaOH-Po than the WPB and Miami canals. The majority of the P present in the canal sediments was contained in the HCl-P fraction (Ca-P and Mg-P), which is considered fairly stable but could be released over a long period of time. The residue-P form comprised the second largest fraction of TP within the canal sediments, and it is considered a stable form of P.

Phosphorus stored in the three main canals is a small proportion of what is stored in EAA soils. But, these canals store 73 mt of P in the upper 10-cm layer, and the majority of the stored P is reactive. Since these sediments are highly organic with low ρ_b , they are susceptible to being transported south into the STAs and WCAs. The P stored in the sediments may be released depending on factors that include redox potential in sediments as well as overlying water column P concentrations. Investigation of the potential of P release from these sediments, as well as factors impacting the release, is warranted.

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