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Phosphorus Release and Equilibrium Dynamics of Canal Sediments within the Everglades Agricultural Area, Florida

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Abstract High phosphorus (P) in surface drainage water from agricultural and urban runoff is the main cause of eutrophication within aquatic systems in South Florida, including the Everglades. While primary sources of P in drainage canals in the Everglades Agricultural Area (EAA) are from land use application of agricultural chemicals and oxidation of the organic soils, internal sources from canal sediments can also affect overall P status in the water column. In this paper, we evaluate P release and equilibrium dynamics from three conveyance canals within the EAA. Incubation and flux experiments were conducted on intact sediment cores collected from four locations within the Miami, West Palm Beach (WPB), and Ocean canal. After three continuous exchanges, Miami canal sediments reported the highest P release (66±37 mg m^{-2}) compared to WPB (13±10 mg m^{-2}) and Ocean (17±11 mg m^{-2}) canal over 84 days. Overall, the P flux from all three canal sediments was highest during the first exchange. Miami canal sediments showed the highest P flux (2.4±1.3 mg m^{-2} day^{-1}) compared to WPB (0.83±0.39 mg m^{-2}d^{-1}) and Ocean canal sediments (0.98±0.38 mg m^{-2} day^{-1}). Low P release from WPB canal sediments despite having high TP content could be due to carbonate layers distributed throughout the sediment column inhibiting P release. Equilibrium P concentrations estimated from the sediment core experiment corresponded to 0.12±0.04 mg L^{-1}, 0.06±0.03 mg L^{-1}, and 0.08±0.03 mg L^{-1} for Miami, WPB, and Ocean canal sediments, respectively, indicating Miami canal sediments behave as a source of P, while Ocean and WPB canal sediments are in equilibrium with the water column. Overall, the sediments showed a significant positive correlation between P release and total P (r=0.42), Fe$_{ox}$ (r=0.65), and Al$_{ox}$ (r=0.64) content of sediments. The contribution of P from the three main canals sediments within the EAA boundary corresponded to a very small portion of the total P load exiting the EAA. These estimates, however, only take into consideration diffusive fluxes from sediments and no other factors such as canal flow, bioturbation, resuspension, and anaerobic conditions.

Keywords Everglades Agricultural Area · Sediments · Canal · Phosphorus · Equilibrium · Incubation · Release

1 Introduction

The Everglades Agricultural Area (EAA) consists of a portion (2,833 km^2) of the original Everglades region

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of south Florida, actively drained to sustain an annual \$2 billion agriculture industry within the region. To maintain a high rate of productivity, nutrient and water management are essential. Over the years, phosphorus (P) in drainage water has been purported as a major contributor to the eutrophic state of the downstream Everglades ecosystem. Some of the efforts carried out to reduce P loads out of the EAA involved best management practices (BMPs) that have resulted in an average annual P load reduction of 50% compared to baseline levels since inception in 1995 (Daroub et al. 2011). In an attempt to further reduce P loads, six stormwater treatment areas (STA) were constructed along the outer boundary of the EAA, encompassing an area of approximately 160 km^2 (SFER 2011b). The STAs are used to "filter" water coming from agricultural and urban areas before being discharged into the water conservation areas (WCAs). The main goal of farming BMPs and STAs is to deliver water with low P concentration to downstream ecosystems. However, historic P loading to canals and subsequent P flux from accumulated sediments to the water column is of concern as a potential source of P to canal waters and ultimately downstream aquatic systems.

There are four main canals that are used to deliver irrigation water from Lake Okeechobee in the dry season and act as drainage canals in the wet season within the EAA: the West Palm Beach, Hillsboro, North New River, and the Miami. The Ocean canal is another connecting conveyance canal. The canals are controlled and maintained by the South Florida Water Management District (SFWMD). The canals transport water and P to the WCAs, and can impact the quality of water of these wetlands (Gu et al. 2001). Mechanisms that alter P levels in the canals may also be responsible for the changes in the P levels in the STAs and WCAs (Kadlec and Wallace 2008). While one such mechanism maybe sediment resuspension due to flow, another could involve simple diffusional exchange of P from shallow porewater to the water column. Sediment resuspension from flow may be beneficial to the quality of receiving water by sorbing the ortho-P from the water column (Brezonik et al. 1979); conversely, sediment resuspension may be problematic by releasing nutrients from the suspended material (McPherson et al. 1976). The net effect is that ortho-P is cycled between the suspended sediment and the water in a state of dynamic equilibrium (Gale 1975; Davis 1982).

Typically under aerobic conditions, ortho-P is removed from the water column in the presence of Fe and Al hydroxides (Pierzynski et al. 2005; Bhadha et al. 2010a). This loss also occurs when there is a high concentration of Ca, as is the case in the EAA canals. Such condition favors the precipitation rather than the release of P (McPherson et al. 1976). Reddy (1983) studied P interaction between sediments and overlying water column and found that organic sediments had the lowest ability to remove P from the water column. However, calcareous clay loams have the highest P removal ability, which is similar to the underlying marl deposits in the EAA. Since the main canals are dug into the limestone bedrock, a significant removal of P can be expected until organic sediment deposits accumulate to the point where they limit diffusion. This is in fact expected to be the case in most of the EAA canals resulting from decades of detrital organic matter deposition within the canals from agricultural runoff and growth of aquatic vegetation. Under turbulent flow conditions, the canal sediments may be resuspended and could potentially be a source of soluble nutrients (Stuck et al. 2001). Generally, anaerobic and acidic conditions favor the release of phosphate from sediments. Waller and Earle (1975) supported this, but because of the prevalence of aerobic conditions most of the year they concluded that ortho-P is released from the sediments only infrequently.

The release of P from sediment is chemically dependent upon factors such as mixing (Holden and Armstrong 1980; Boström et al. 1982), pH, bioturbation (Sondergaard 1989), redox potential (Moore et al. 1998), and concentrations of oxygen, Ca, Fe, and Al. Small changes in sediment–water equilibria can have large effects on P levels in the water. Gale (1975) reported the rate of P release from sediments in Lake Okeechobee to be 6.42 g m^{-2} year^{-1}. Similar estimates need to be calculated for the main canal sediments within the EAA. Water flowing out of the EAA contains P in the dissolved form (orthophosphate and soluble organic) and in the particulate form (mineral and organic) (Daroub et al. 2002). Phosphorus transported to canals accumulates in the sediments and the capacity of sediments to retain or release P can affect water quality. Our concern about EAA canals is that the canal sediments can act as potential P source and generate an internal load of P to the overlying water column which is then delivered to the downstream Everglades. Another concern is that the sediments are subject to transport and can act as a P source wherever transported. A Phosphorus-flux incubation study will help us understand the P release characteristics associated with internal loading of the EAA canal sediments.

Equilibrium phosphorus concentration (EPC) measurements of canal sediments can be used to determine if sediments act as sink or source of P. The EPC is defined as the aqueous P concentration in the water column at which zero net flux occurs between the sediments and the water, i.e., the P in solution is in equilibrium with P in the solid phase (Reddy et al. 1999). When soluble reactive P (SRP) in the 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 is less than the EPC (Reddy et al. 1995; Pant and Reddy 2001). Determining the EPC values within EAA main canals will allow us to identify the direction of SRP fluxes across the sediment–water interface.

Equilibrium P concentration (EPC) values can be determined from incubation of intact sediment cores. The EPC_w is the floodwater P concentration in intact sediment columns when there is no net P release/retention from the sediments. 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 high animal density areas soils in a watershed north of Lake Okeechobee. These active dairy soils had EPC values ranging from 5.3 to 10.6 mg L^{-1} whereas the EPC value for the native soils was 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}.

The main conveyance canals in the EAA are structurally and ecologically connected to the rest of the Everglades. Dynamics of P release/retention, its magnitude, and interaction with other parameters in these canals is of prime importance as it indicates the potential of canal sediments to release P and adversely affect downstream water bodies. We hypothesized that canal sediments high in organic matter and total P content are more likely to release P into the water column and have a higher EPC. Evaluating the interactions between P release and sediment physicochemical parameters such as organic matter (OM), pH, P species, and metals can be important information necessary to diagnose present water quality conditions. This information can be utilized to forecast water quality conditions, build water quality models, and develop effective long-term management strategies. Results from Das et al. (2012) indicated that majority of P in the canal sediments was contained in the HCl–P fraction (Ca–P and Mg–P), comprising >50% of total P in the main and farm canal sediments. An estimated 73 mt of P was stored in the 0–10cm layer of the three main canals within the EAA boundaries of which 57 mt P is reactive and available for release at different time scales (Das et al. 2012). Concerns generated from these results have prompted the need to investigate potential P release from the main canal sediments.

The objectives of this study were to (1) evaluate the potential P release from Miami, West Palm Beach (WPB), and Ocean canal sediments; (2) determine the EPC of the three canals to determine if the sediments act as a source or sink of P; and (3) correlate factors such as OM, total P, extractable Ca and Mg, and Fe–Al oxides content with P release from these canal sediments.

2 Materials and Methods

2.1 Sediment Sampling and Analyses

Intact sediment cores were collected from four different transects (T1, T2, T3, and T4) within the Miami, WPB, and Ocean canals EAA boundary (Fig. 1). The intact cores were collected using a piston sediment corer comprised of a 7.0-cm inner diameter polycarbonate core tube that was inserted into the sediment bed (Fisher et al. 1992). At each of the four transects in each canal, about 20 cm of intact sediments was collected in triplicates along the width of the transect leading to 12 cores per canal. The first location (T1) for Miami and WPB canal was closest to the Lake Okeechobee while the other transects (T2, T3, and T4) were taken progressively southward into EAA. The average distance between the sampling locations was ~11 km. The first sampling location (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 transects in Ocean canal was ~2 km. In total, 36 intact sediment cores along with two blank cores (no sediment) were used for the incubation experiment.

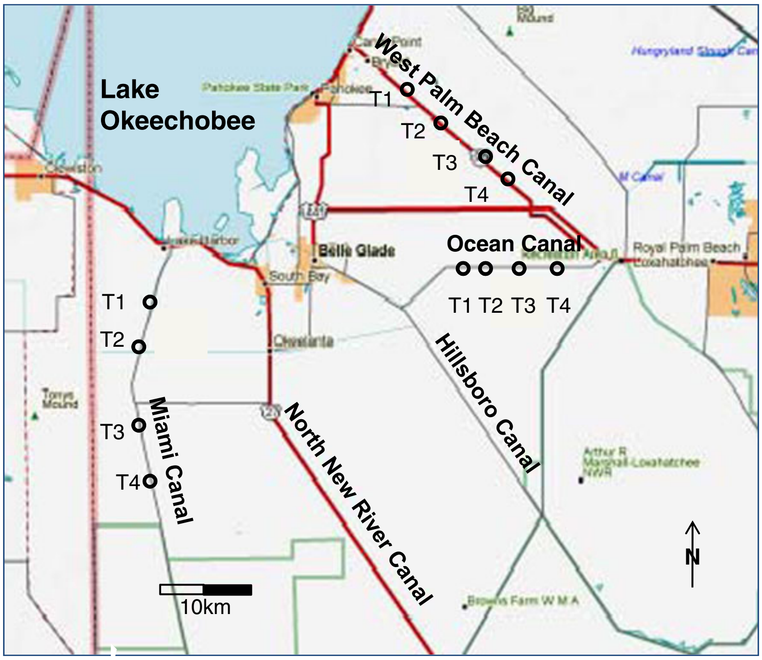


Fig. 1 Study site showing the sediment sampling locations along Miami, West Palm Beach, and Ocean canal. T1 is the closest to the pump station while T4 was the furthest away

Another set of 36 sediment cores from same locations was sampled earlier (Das et al. 2012). Sediments were analyzed for OM, pH, bulk density (D_b), and total phosphorus (TP). Organic matter content was determined using loss on ignition method, where 5 g of dry sediment sample was combusted at 550°C for 4 h in a muffle furnace (Andersen 1974). Sediment pH was determined by weighing 10 g of sediment and adding DI water to it in a 1:2 (mass/volume) ratio (Thomas 1996). Bulk density for each layer was calculated by dividing the dry weight of the sediment sample by the volume of the sampling corer. The dry weight of the sediment was calculated by measuring the gravimetric water content of 10 g of sediment at 105°C for 24 h. The residue ash following loss on ignition for all sediments was dissolved in 6M HCl and analyzed for TP using the ascorbic acid method (US EPA 1983, Method 365.4).

Phosphorus sequential extraction on sediments was performed according to the method of Chang and Jackson (1957) modified for wetland soils (Qualls and Richardson 1995; Reddy et al. 1998, 2007). Oxalate extractable Fe (Fe_{ox}) and Al (Al_{ox}) were extracted using 0.2 M ammonium oxalate and 0.2 M oxalic acid at pH 3.0 in darkness after pre-treating the samples to remove calcium carbonate ($CaCO_3$) (Loeppert and Inskeep 1996; McKeague and Day 1966) and the extracts analyzed using an inductively coupled plasma spectrophotometer. Extractable Ca and Mg were determined by 0.5 mol L^{-1} acetic acid extracting solution (Sanchez 1990) and analyzed using an atomic absorption spectrophotometer (Varian Inc., Palo Alto, CA, USA).

2.2 Sediment Core Incubation

After the cores were collected, canal water from the sediment cores was siphoned off and the cores were refilled with stock water collected from the Arthur R. Marshall Loxahatchee Wildlife Refuge (Refuge). A 20-cm (Malecki et al. 2004) water column was maintained above the sediment layer in the cores which was accomplished by adding ~275 mL of the stock water. The water columns in the cores were maintained under aerobic conditions by bubbling air using aquarium pumps via tubing inserted into the water columns. Water was sampled from each core using a syringe fitted with tubing. The floodwater dissolved O_2 concentration was maintained between 5 and 8 mg L^{-1} by bubbling air through the upper portion of the water column. Bubbling air through the water column ensured aerobic conditions in the water column (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 a water bath to maintain a constant temperature (21±2°C).

Three floodwater exchanges were performed at an interval of 28 days each. The stock water SRP concentration used during the three exchanges was 0.008, 0.004, and 0.007 mg L^{-1}, respectively. During exchanges, water from the sediment cores was suctioned with minimum disturbance to the sediment column. The cores were then refilled with ~275 mL of stock water and incubated for another 28 days. Throughout individual exchanges, water samples were collected at time 0, 1, 2, 4, 7, 14, 21, and 28 days, respectively. Prior to sampling, the aerator was turned off to minimize disturbance. Dissolved oxygen (DO) and pH of the water column from each core were measured before sampling. A 20-mL sample was pipetted from the water column, filtered through a 0.45-μm filter, and analyzed for SRP using ascorbic acid colorimetric method (US EPA 1983, Method 365.1).

2.3 P-Flux Estimation

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 core over unit time (days). Sediment P flux was calculated as linear change 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. 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 et al. 2004), while the P flux was calculated as SRP released/retained per unit surface area per unit time:

$$J = \sum \frac{(C_t - C_{t-1}) \times V_t + (C_t - C_s) \times V_s}{A \times t} \qquad (1)$$

where

J	phosphorus flux (mg m^{-2} day^{-1})
C_t	final SRP concentration (mg L^{-1}) of the overlying water
C_{t-1}	initial SRP concentration (mg L^{-1}) of the overlying water
V_t	total volume (mL) of the water column overlying the sediment
C_s	SRP concentration (mg L^{-1}) of the water replaced for sampling
V_s	volume of water taken for sampling (mL)
A	cross-sectional area of the sediment core (m^2)
t	duration of study (days)

2.4 Estimation of EPC_w Using 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. Water collected from the Refuge with a P concentration of 0.007 mg L^{-1} was used for the first exchange. The rest of the spikes were prepared by adding appropriate P standard solution (KH_2PO_4) to water collected from the Refuge. Similar to the earlier sediment core incubation experiment used to estimate P flux, a 20-cm water column was maintained above the sediment layer in the cores which was accomplished by adding ~275 mL of the desired spiked water. During exchanges, water from the sediment cores were suctioned with minimum disturbance to the sediment column. The cores were then refilled with ~275mL of the next higher spike concentration and incubated for another 7 days. For each exchange, samples were collected at time 0-, 2-, 4-, and 7-day intervals. Prior to sampling, the aerator was turned off to minimize disturbance. A 20-mL sample was pipetted from the water column, filtered (0.45 μm), and analyzed for SRP. Sediment P release was calculated using Eq. (1). The EPC_w values were determined as the intersection of P release (*y*-axis) with initial spike P concentration (*x*-axis). The equation of the straight line was equated to zero and solved for the value of *x*, or the P concentration (Reddy et al. 1999; Leeds 2006).

Determination of the relationship between P release and soil physicochemical properties, P fractions and Fe_{ox}, Al_{ox}, Ca, and Mg were performed using SAS statistical program (proc CORR) (SAS Institute 2003).

3 Results and Discussion

3.1 Phosphorus Release from Canal Sediments

Phosphorus release from Miami, WPB, and Ocean canal sediments varied extensively between individual canals, locations within each canal, and floodwater exchanges (Fig. 2). In general, P release was highest

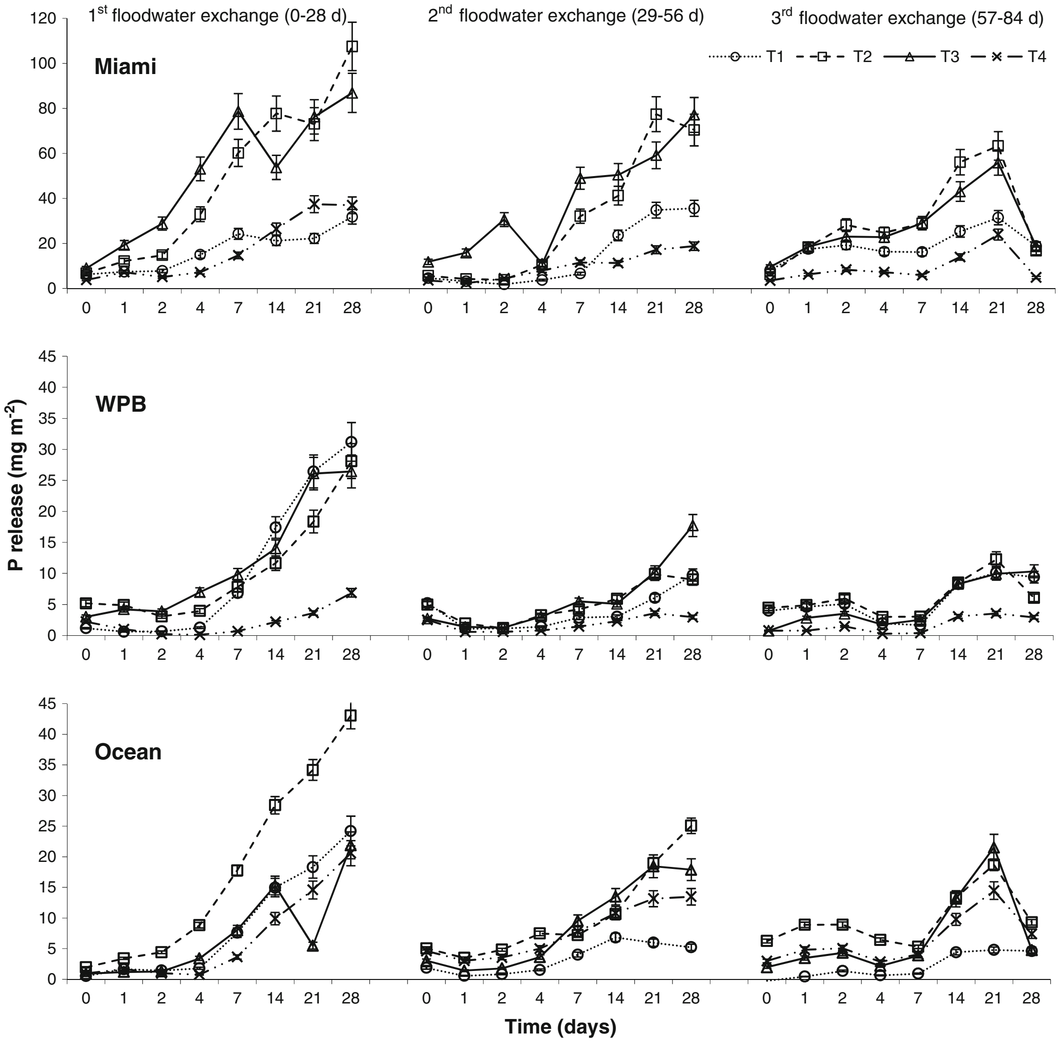


Fig. 2 Cumulative phosphorus release (mg m^{-2}) from Miami, WPB, and Ocean canal sediments from four locations within the canals. Three floodwater exchanges of 0.008, 0.004, and 0.007 mg L^{-1}, and water analyzed at 0, 1, 2, 4, 7, 14, 21, and 28 days, respectively. *Error bars* represent standard deviation

from Miami canal sediments compared to the other two canals, although there were differences between transects. During exchange 1, sediments from Miami canal T1 and T4 showed lower cumulative P release rates of 31.9 and 37.0 mg m^{-2}, respectively, than T2 and T3 with 107.5 and 86.9 mg m^{-2} released, respectively. The S8 sub-basin of the EAA (in which the Miami canal is located) had a TP load of 16.3 mt $year^{-1}$ in 2008 (DBhydro database—http://www.sfwmd.gov/dbhydroplsql). Multiplying measured cumulative P release in this study by the area of the Miami canal gives a total P release ranging from 0.4 to 1.2 mt $year^{-1}$. Phosphorus release from Miami canal was estimated to contribute 2% to 7% of the total P load of the S8 basin.

Phosphorus release from WPB canal sediments was lower than that of Miami canal at all locations and exchanges. Within the WPB canal, T4 had the least cumulative P release values for all the three exchanges. During exchange 1, cumulative P release from T1, T2, and T3 were 31.2, 28.1, and 26.5 mg m^{-2}, respectively. Similar to Miami canal, during consecutive exchanges P release values decreased at all locations at WPB canal. The WPB canal is situated in the S5A basin which has an annual P load of 50.0 mt $year^{-1}$ in 2008

(DBhydro database—http://www.sfwmd.gov/dbhydroplsql). Multiplying cumulative P release by WPB canal area gives a P release ranging from 0.17 to 0.76 mt year^{-1}, contributing approximately 0.3% to 1.5% of the total P load for the entire S5A sub-basin.

Ocean canal sediment P release values were lower than Miami canal sediments for all floodwater exchanges, but were comparable to P release values of WPB canal sediments. Within Ocean canal, the highest cumulative P release was observed at T2 that decreased in subsequent exchanges from 43.1 to 25.1, and 9.3 mg m^{-2} during exchanges 1, 2, and 3. Similar to Miami canal and WPB canal sediments, cumulative P release decreased at all locations during exchanges 2 and 3. The Ocean canal is also located in the S5A basin with a P load of 50.0 mt year^{-1} in 2008. Multiplying cumulative P release by Ocean canal area gives a total estimated P release ranging from 0.17 to 0.36 mt year^{-1}. Combined, WPB and Ocean canals have an estimated P release ranging from 0.40 to 1.1 mt year^{-1} and comprise about 0.7% to 2% of the total P load of the S5A basin.

3.2 Phosphorus Flux

Phosphorus flux from the sediments was typically highest during exchange 1 (first 28-day floodwater exchange) (Fig. 3). During exchange 1, Miami canal sediments showed the highest P flux (2.4±1.3 mg m^{-2} day^{-1}) compared to WPB (0.83±0.39 mg m^{-2} day^{-1}) and Ocean canal sediments (0.98±0.38 mg m^{-2} day^{-1}). This trend was observed during the second and third floodwater exchanges. The average P flux from Miami canal sediments during the second floodwater exchange was 1.8±1.0 mg m^{-2} day^{-1}, compared to WPB (0.35±0.22 mg m^{-2} day^{-1}) and Ocean canal sediments (0.55±0.3 mg m^{-2} day^{-1}). Lower flux rates

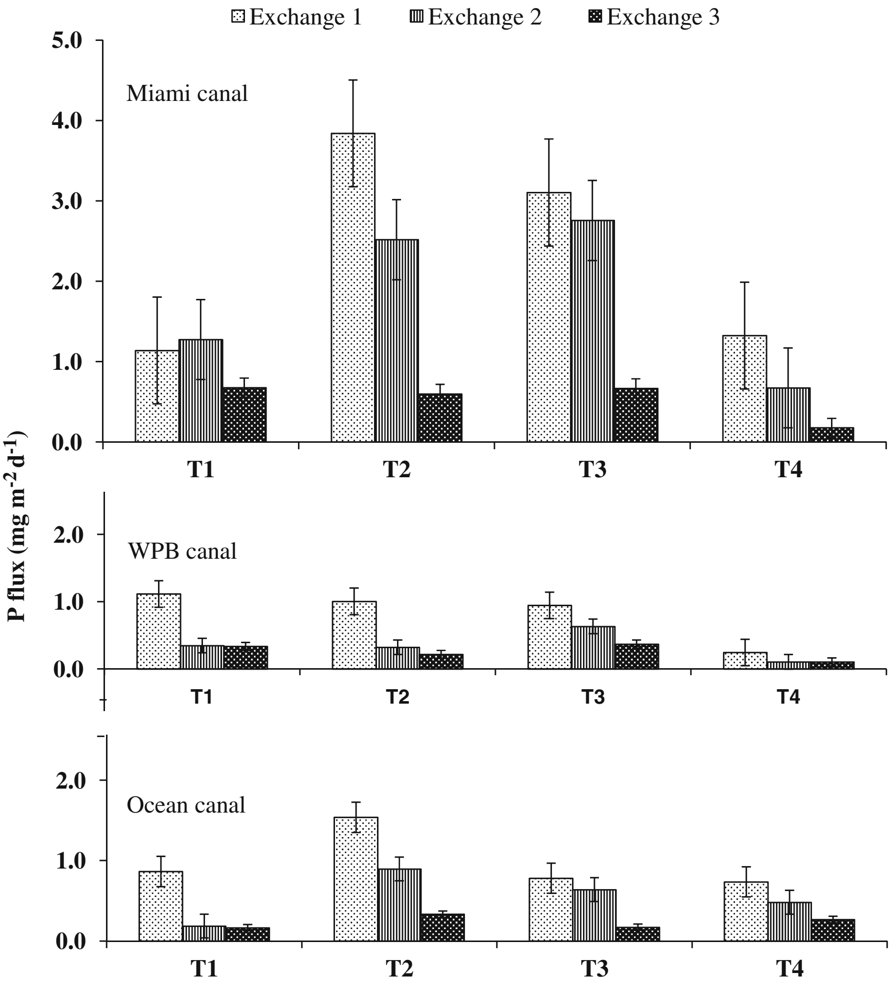


Fig. 3 Phosphorus fluxes (mg m^{-2} d^{-1}) estimated for three 28-day floodwater exchanges based on the sediment core incubation experiment for Miami, WPB, and Ocean canal sediments at four different locations. *Error bars* indicate the standard deviation of P flux based on the triplicate sediment cores collected from individual locations

were observed during exchange 3. The fluxes reported here are up to an order of magnitude lower than those estimated from the peat soils within the Everglades WCA-2A (1.5 to 6.5 mg m^{-2} day^{-1}) (Fisher and Reddy 2001), but are consistent with those from within the sandy zones from within Lake Okeechobee (0.1 to 0.5 mg m^{-2} day^{-1}) (Moore at al. 1998). This is not unusual since large volumes of Lake sediments get transported to the main canals during instances when water from Lake Okeechobee is drained via the canals. It should be noted that there are variations in Miami canal sediments with T2 and T3 exhibiting higher flux rates during exchanges 1 and 2. While the accretion of P-rich material at the sediment–water interface could increase the diffusive flux from the sediment to the water column, an increase in surface water concentrations from agriculture runoff inputs could potentially reduce diffusive flux from shallow sediments to the water column, as the P concentration gradient between the two also reduces (Bhadha et al. 2010b). This type of quasi-equilibrium between the water column P and sediment P content is a common phenomenon in lotic systems such as streams and canals. Malecki et al. (2004) and Sen et al. (2007) showed that the flux of soluble P from sediments under anaerobic conditions was significantly greater than under aerobic conditions. During this study, the sediments were monitored only under aerobic conditions; however, the canal sediments frequently experience both aerobic and anaerobic conditions depending on the time of year. Also, fluxes associated to advective modes such as mixing and bioturbation are not incorporated in core study experiment such as this one. This would imply that the P fluxes reported here provide a conservative estimate compared to the overall potential P flux from the Miami, WPB, and Ocean canal sediments.

Total P stored in the canal sediments up to a depth of 10cm was determined by multiplying TP content by D_b and canal area estimated using Google map, 2010 (Das et al. 2012). Average TP stored in Miami, WPB, and Ocean canal sediments up to 10 cm were 34 (±12), 26 (±3), and 13 (±5) mt, respectively. Total P was divided into non-reactive P (residue P fraction) and reactive P (KCL, NaOH, and HCl fractions) (Reddy et al. 2011). Less than 22% of the TP was contained in the residue-P fraction, a recalcitrant form of P but susceptible to microbial breakdown over time. Reactive P comprised 78% of TP and is potentially available for release at different time scales. Phosphorus storage values indicated that appreciable quantities of P are stored in EAA canals that could function as a P source to the system. A comparison of EAA canal internal P load to the overall P loads from the EAA of 169 mt $year^{-1}$ in water year 2010 (SFER 2011a) indicate that internal P load from the three main canals is a very small portion of the entire P load from EAA. Internal P load calculated here simulates no flow conditions as in the Everglades and takes into account diffusive P flux only under aerobic conditions. In reality, P flux from EAA canals may be much higher than the calculated value due to seasonal anaerobic conditions, sediment transport, and resuspension. Water flow in EAA canals can undergo rapid fluctuations from stagnant conditions to 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).

3.3 Equilibrium Phosphorus Concentration (EPC_W)

Phosphorus release/retention during exchanges 1 to 5 from the four transects of each canal to determine EPC is presented in Fig. 4. Each exchange represents a different initial P spike concentration (0.007, 0.05, 0.13, 0.27, and 0.35 mg L^{-1}). Phosphorus release from Miami canal sediments shows that sediments released P during exchanges 1 and 2 and retained P during exchanges 4 and 5 (Fig. 4). Phosphorus release from WPB canal sediments shows all transects released P during exchange 1. 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 retained P.

Ocean canal sediments show all locations released P during exchange 1 with P spike concentration of 0.007 mg L^{-1}. During exchange 2, with P spike concentration of 0.05 mg L^{-1}, T2–T4 were releasing P while the P release curve for T1 intersects the horizontal axis which indicates equilibrium concentration. During exchange 3, with P spike concentration 0.12 mg L^{-1}, all transects retained P except T2 which briefly released P before finally starting to retain it.

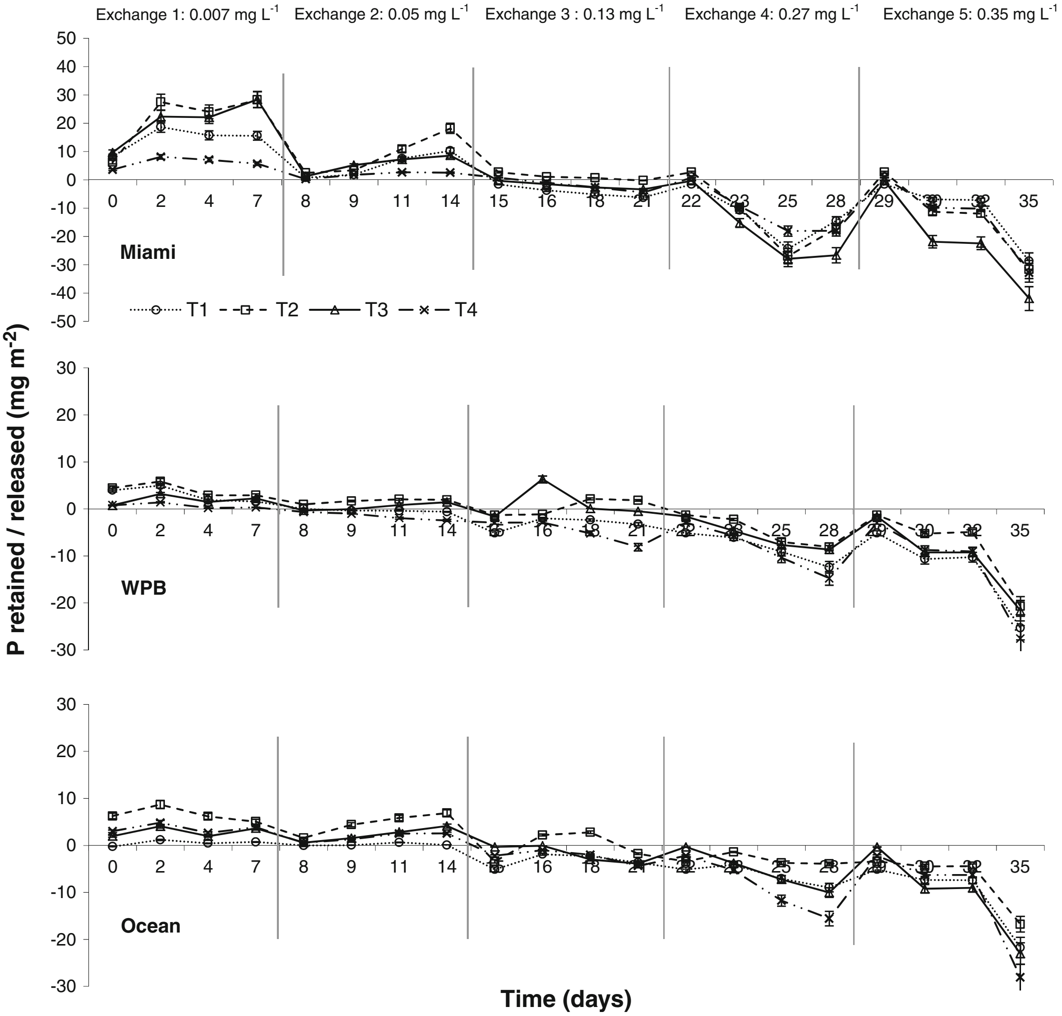
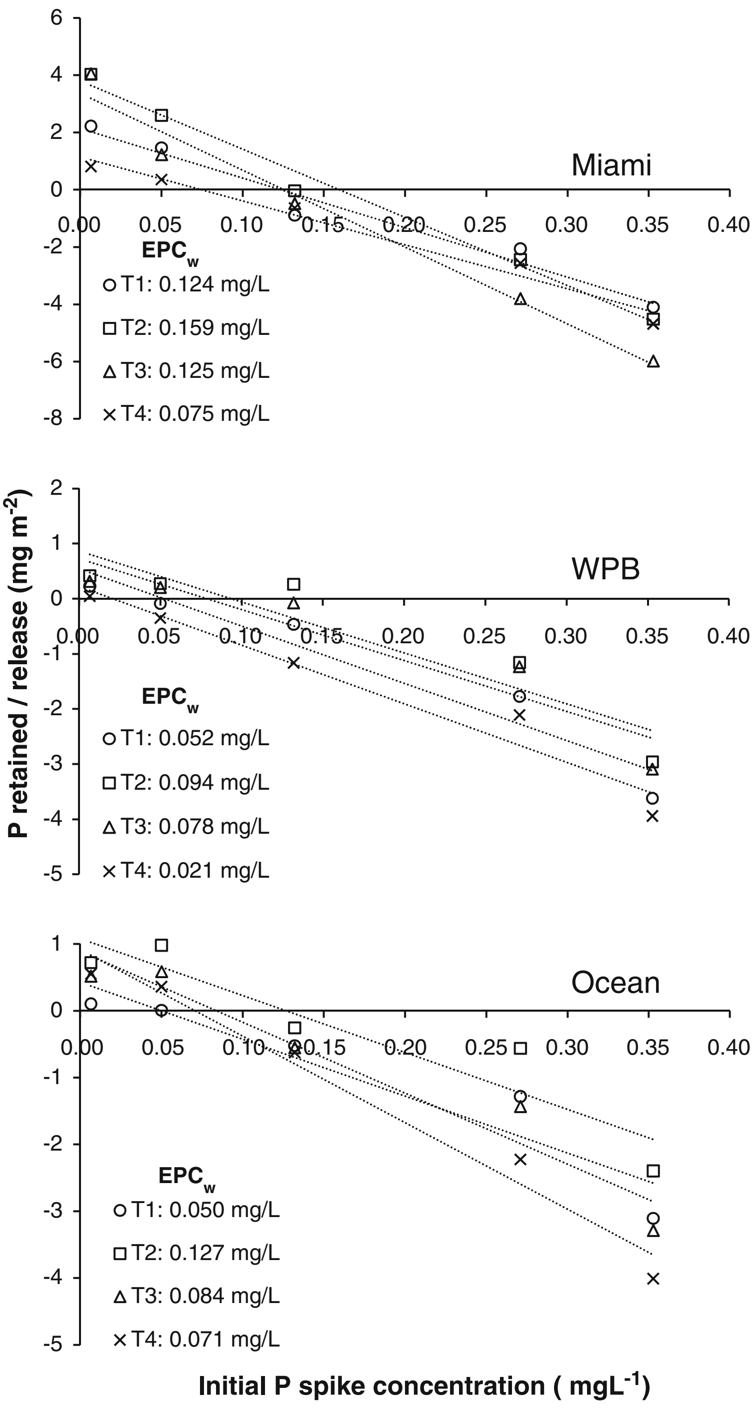


Fig. 4 Phosphorus released (+) or retained (−) from Miami, WPB, and Ocean canal sediments during the application of five floodwater exchanges of concentrations ranging from 0.007 to 0.35 mg L^{-1}. *Error bars* represent standard deviation

Based on the 7-day sediment core incubation experiment using five different initial concentrations, EPC$_W$ was estimated for all four locations within the Miami, WPB, and Ocean canal (Fig. 5). For the Miami canal, the mean EPC$_W$ value was 0.12±0.04 mg L^{-1}, with the highest value observed at T2 (0.159 mg L^{-1}) and the lowest at T4 (0.075 mg L^{-1}). In WPB canal, the mean EPC$_W$ was 0.06±0.03 mg L^{-1}, with the highest values observed at T2 (0.094 mg L^{-1}) and the lowest value at T4 (0.021 mg L^{-1}). The EPC$_W$ values in Ocean canal was 0.08±0.03 mg L^{-1}, with the highest value observed at T2 (0.127 mg L^{-1}) and the lowest value at T1 (0.050 mg L^{-1}). In general, locations with low EPC$_W$ values were the ones that showed low P release as well. This would suggest that available P sorption sites is just as important in estimating EPC$_W$ as is the TP content of the sediment.

The ambient canal water SRP concentration for Miami, WPB, and Ocean canal at the time of sediment collection was 0.035±0.008, 0.060±0.005, and 0.066±0.003 mg L^{-1}, respectively. Based on the range of EPC$_W$ values, this would imply that Miami canal sediments could potentially behave as a source of P since water column SRP was much lower than the EPC$_W$ of 0.12 mg L^{-1}. Pump station C3 is the inflow structure that supplies water from Lake Okeechobee to the Miami canal. A 5-year average of SRP concentration monitored at C3 is 0.027±0.02 mg L^{-1} (DBhydro database—http://www.sfwmd.gov/dbhydroplsql), similar to those measured in this study. The WPB and Ocean canal sediments

Fig. 5 Equilibrium P concentration (EPC_w) estimated for the Miami, WPB, and Ocean canal sediments at four location based on a 7-day sediment core study. *X*-axis corresponds to the initial P spike concentrations (0.007, 0.05, 0.13, 0.27, and 0.35 mg L^{-1}); *Y*-axis corresponds to the amount of P released (+) or retained (−) (mg m^{-2})



appear to be in a state of equilibrium with the overlying water column as water column SRP concentration was close to the EPC_W in both canals. Individual transects do vary for example T4 in WPB canal with an EPC_W of 0.021 mg L^{-1} is probably a sink of P with overlying water column concentration of 0.060±0.005 mg L^{-1}. Whether sediments behave as a sink or source of P will depend on P concentrations in the overlying water column, which changes with season, cropping practices, and water release from Lake Okeechobee.

3.4 Sediment Physico-Chemical Properties and P Release

Overall, the physicochemical properties of Miami and WPB canal sediments were similar in terms of OM, pH, D_b, and TP (Table 1). In addition to high TP, both Miami and WPB canal sediments had low D_b, which make them susceptible to resuspension and downstream transport. This is a cause of concern due to the high TP content of these sediments. Physico-chemical properties of Ocean canal sediments were different from Miami and WPB canal sediments. Ocean canal sediments had lower total P, and slightly higher D_b and pH compared to the Miami and WPB canals. Miami and WPB canals had higher concentrations of Fe oxides and Mg compared to the ocean canal. However, the ocean canal had the highest concentrations of Ca compared to the other two canals that would explain the slightly higher pH. Both WPB and Ocean canal sediments consisted of varying amounts of calcareous shell horizons dispersed within the sediment profile.

Phosphorus released from EAA main canal sediments was not significantly correlated with sediment physico-chemical properties including OM, pH, and D_b (Table 2). But the low D_b of the EAA canal sediments has multiple implications. Low D_b values of the sediments tend to make sediments easily transportable to downstream ecosystems. Low D_b can also cause increased P flux to the water column by sediment resuspension and maintaining a P concentration gradient in the water column. High P release rates due to wind induced turbulence and flushing in lakes have been reported by Andersen (1974), Ryding and Forsberg (1977), Ahlgren (1980), and Poon (1977). Organic matter cannot bind phosphate by itself; it is dependent on associated metals such as Fe and Al (Boström et al. 1982). Indirect interactions between OM and Fe and Al oxides can inhibit crystallization and thereby increase P sorption (Kang et al. 2009). Direct interactions occur where OM and P compete for same sorption sites. Janardhnan and Daroub (2010) showed a negative correlation between P sorption and OM in EAA soils as competition between P and organic anions for sorption sites is likely to be high in soils with >75% OM (Giesler et al. 2005). In our system, the correlation between OM content in the sediment and P release was not significant (r=0.29), implying that other factors such as sediment mixing, redox, or presence of carbonate layers may have an overriding effect on P release from these sediments compared to just OM content. In addition, there was high correlation of TP with SRP (r=0.96, n=20), and nearly 81% of TP was SRP in the water column, suggesting that most of the water column P was predominantly inorganic.

Phosphorus release from Miami, WPB, and Ocean canal sediments was significantly correlated to TP, but not with individual P fractions (Table 2). The influence TP on P release is indicated by the lower P release from Ocean canal sediments, which had low sediment TP values, and higher P release from Miami canal sediments that had greater TP values. 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, and that P transformation within different fractions does not necessarily result in P release (Boström et al. 1982). The low P release from WPB canal sediments despite having similar properties as Miami canal sediments including high TP content could be due to alternating carbonate layers distributed throughout the sediment column inhibiting P release from sediments. Alternating climatic conditions favoring peat and calcite formation

Table 1 Mean OM, pH, D_b, TP, Fe_{ox}, Al_{ox}, and extractable Ca and Mg values of Miami, WPB, and Ocean canal sediments from all four locations at 0–5 cm depth

Canal	OM (g kg^{-1})	pH	D_b (g cm^{-3})	TP (mg kg^{-1})	Fe_{ox}^{b} (mg kg^{-1})	Al_{ox}^{b} (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})
Miami	260ns	7.4b	0.26b	1,430a	713a	153a	19,190a	758a[a]
WPB	270	7.4b	0.22b	1,130a	592a	92b	8,500b	751a
Ocean	245	7.9a	0.35a	590b	283b	85b	26,700c	595b

ns not significant

[a] Treatment means within the same column followed by the same lowercase letter are not different by Tukey's test between transects for each canal at $p<0.05$

[b] Fe and Al extracted by ammonium oxalate

Table 2 Correlation of P release from canal sediments with physico-chemical parameters, TP, P fractions, and metals (n=36)

Parameter		P release
OM		0.29 ns
pH		−0.30 ns
D_b		−0.28 ns
TP		0.41**
	P fractions[a]	
	KCl-P	0.33 ns
	NaOH-Pi	0.004 ns
	NaOH-Po	0.25 ns
	HCl-P	0.25 ns
	Residue-P	0.04 ns
Fe_{ox}[b]		0.65*
Al_{ox}[b]		0.64*
Ca		0.42 ns
Mg		0.47 ns

ns not significant

*Significant at the 0.05 probability level, **significant at the 0.01 probability level

[a] P fractions: sequential fractionation using KCl, NaOH, HCl, and residue P

[b] Fe and Al extracted by ammonium oxalate

have been documented by Gleason and Spackman (1974) leading to inter-bedding of peat and carbonate layers in parts of EAA. Ocean canal sediments also had a layer of calcareous shells on the sediment surface and well distributed throughout the sediment column. 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. 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.

Sediment P release was significantly correlated with both Fe_{ox} and Al_{ox} concentrations, but not with Ca and Mg concentrations (Table 2). This signifies that even though present in lower concentrations than Ca and Mg, active Fe_{ox} and Al_{ox} concentrations significantly affect P release in EAA canals. Janardhanan and Daroub (2010) found P sorption capacities of the EAA Histosols were affected by active Fe_{ox} and Al_{ox} concentrations, rather than the $CaCO_3$ concentrations. Hayes (1964) and Lijklema (1977) found that sorption efficiencies for Fe oxides and hydroxides are greatest around pH 6 and decreases with increase in pH. The EAA canal sediment pHs are circumneutral (Das et al. 2012) which may have led to reduced sorption capacity leading to P release. Though present in lower concentrations than Fe_{ox}, the correlation of P release with Al_{ox} signifies the sensitivity of Al–phosphate complexes to undergo release in EAA canal sediments. Calcium in EAA canal sediments can exist as calcium carbonates/calcites (Das et al. 2012). Phosphorus associated with Ca may 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).

4 Conclusions

Phosphorus release from EAA main canal sediments have been found to vary among the three main canals and also among transects of the same canal. We accept the hypothesis that sediments with high TP will have higher P release and flux rates compared to sediments with low TP. But P release was found to be affected by presence of carbonate layers within the sediments. Miami canal sediments had higher TP compared to Ocean canal, and P release from Miami canal sediments was much higher than Ocean canal sediments which supported the correlation of P release with TP. But WPB canal which is similar to Miami canal in physico-chemical properties and high TP content had lower P release that were comparable to Ocean canal sediments P release. Although WPB canal sediments have the potential to release P, the distributions of carbonate layers in those sediments may have limited P release to water column. The presence of surface shell layers observed in the Ocean and WPB sediments was thought to inhibit P release by reducing the effective surface area.

The role of OM in P release was not well defined as there was no significant correlation of P release with OM in the EAA canals. Organic matter can play an important role in facilitating P release by direct competition for sorption sites or increase P sorption by inhibiting crystallization of associated Fe and Al oxides. But other factors may have an overriding effect on P release such as redox and presence of carbonate layers. Support for this conclusion can be seen in the fourth transect in Miami canal which was more mineral in nature compared to the other three transects (only 7.2% OM compared to 26% average) and had lower P release similar to Ocean canal sediments with high OM content. Therefore, organic-rich, high TP sediments in EAA canals which are expected to have high P release can in fact behave in the opposite way if sediment bed is not in contact with the water column due to presence of a shell horizon.

Phosphorus release over the 84-day incubation period from Miami canal is estimated to potentially contribute 2–7% of the TP load from Miami canal basin (S8), while WPB and Ocean canals combined are estimated to contribute approximately 0.7–2% of the TP load in the WPB–Ocean (S5A) sub-basin, respectively. This in situ flux from these canal sediments comprised a small percentage of the total P load exiting the EAA basin every year. These estimates, however, only take into consideration diffusive fluxes from the sediments under aerobic conditions. In actuality within canals, factors such as canal flow, bioturbation, resuspension, anaerobic conditions, and continuous addition of P can increase the magnitude as well as prolong the time of the P release.

The $\mathrm{EPC_W}$ of the sediments showed under the conditions during sampling time, the Miami canal is a potential source for P while the Ocean and WPC canals are closer to a state of equilibrium neither releasing or assimilating P. The $\mathrm{EPC_W}$ of individual transects was variable though. Whether these sediments act as a sink or source of P depends on water column P concentrations that can vary tremendously with season and other factors.

We conclude that the canal sediments sampled have the potential of P release, and under the prevalent water column P concentrations are either releasing P to the water column or in a state of equilibrium. Further studies should focus on the flux rates under anaerobic conditions as well as the potential transport of sediment into very sensitive ecosystems. Water column P concentrations in WCA can be much lower than EAA canals and these same sediments then would be a source of P to the water column. It is also noteworthy to further investigate the chemical characteristics of organic matter and relationship to P release.

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