Phosphorus fractionation and distribution in sediments from wetlands and canals of a water conservation area in the Florida Everglades

Qingren Wang, Yuncong Li, and Ying Ouyang

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1 Phosphorus (P) fractionation and distribution in sediments are of great concern in the Florida Everglades ecosystem because potential eutrophication of surface waters usually results from P external loading and stability. Intact core sediment samples were collected to a depth of 35 cm from wetlands and canals across Water Conservation Area 3 (WCA-3) of the Florida Everglades. These sediment cores were sliced into 5 cm increments and analyzed for P contents in different fractions by sequential extraction. These fractions mainly included total P (TP), readily available P (Pi), Ca/Mg-bound P (Pi-NaOH), Fe/Al-bound P (Pi-KCl), organic P (Po-NaOH), and residual P (PoResidue). Results showed that the canal sediments had the highest concentrations of TP, with about 87% in the form of Ca/Mg-bound fraction, and the concentrations of TP in these sediments increased with depth. In contrast, the wetland sediments contained the lowest concentrations of TP (predominantly in the organic fraction), with 43% residual P and 27% Po-NaOH, and the concentrations of TP in these sediments decreased with depth. In addition, a large amount of the readily available P (up to 1500 mg kg⁻¹) in the canal sediments was accumulated at the top layer of 0–5 cm. This study suggests that any disturbance and/or environmental alterations, such as high canal flow and dredging in canal sediments, could pose a potential risk of a P increase in the water column and, consequently, in the wetlands because of the release of readily available P despite the relatively stable nature of such P fractions in these sediments.


1. Introduction

2 Phosphorus (P) fractionation in sediments from aquatic and wetland ecosystems plays a critical role in determining P mobility and exchanges with the overlying water [Chalar and Tundisi, 2001; Shilla et al., 2009]. It provides information on P reactivity, bioavailability, and potential contamination of water bodies [Richardson, 1985; Reddy et al., 1995]. Bostrom et al. [1982] reported that the release of a small amount of P from sediments significantly increases P concentrations in the overlying water. Some P fractions, such as the readily available P in sediments, are crucial to the increase of P concentrations in surface waters. Phosphorus fractionation analysis with a sequential extraction was initially used in soils [Chang and Jackson, 1957; Hieljes and Lijklema, 1980; Psenner et al., 1988] and has been adapted to sediments in wetlands and canals [Qualls and Richardson, 1995; Corstanje et al., 2006; White et al., 2006]. In recent years, scientists have made numerous attempts to elucidate the P fractions and their distributions in surface water bodies [Bruland and Richardson, 2006] of natural and constructed wetlands [Lueteritz et al., 2001; Koskiaho et al., 2003; Lai and Lam, 2009]. These studies have provided very useful insights into the P dynamics of certain ecosystems, but insufficient effort has been devoted to investigating such dynamics in the Florida Everglades.

3 The Florida Everglades are subtropical wetlands extending from the lakes and marshes of central Florida southward to the Florida Bay at the southern tip of the peninsula. They comprise a 1.6 × 10⁶ ha shallow and sluggish “river of grass” replete with numerous teardrop-shaped hardwood hammocks. Three water conservation areas (WCAs), created during the 1950s, are mainly used for water storage to meet demands during the dry season, for flood control to retain excess water during periods of heavy rainfall, and for wildlife habitat and recreation activities [South Florida Water Management District (SFWMD), 1992; Bruland et al., 2006]. Among the three WCAs, WCA-3 is considered to be an oligotrophic ecounvironmental system rarely affected by anthropogenic activities because it is distant from the Everglades Agricultural Area (EAA) [Reddy et al., 1998]. For instance, the total P in sediment samples (0–10 cm) collected from WCA-3 ranges from 29 to 1200 mg kg⁻¹ [Bruland et al., 2006], while that from WCA-2 in the same year ranges from 155 to 1300 mg kg⁻¹ [Rivero et al., 2007]. However, a recent
study of this area revealed that the portion with >500 mg kg\(^{-1}\) total phosphorus (TP) in the soil and sediment increased from 21% to 53% during the period 1992–2003 [Bruland et al., 2006]. In response to controlling the Everglades’ eutrophication and the wetland shrinkage, the U.S. federal government and the state of Florida launched a Comprehensive Everglades Restoration Plan in 1997, intended to be implemented over 30 years with a budget of $7.8 billion to focus on water level recovery and nutrient reduction. One of the goals of this restoration plan [SFWMD, 2007] is to attain a target of 10 \(\mu\)g L\(^{-1}\) TP in surface water of the Everglades Protection Area by 2016 [Payne and Weaver, 2004] in order to maintain the oligotrophic ecosystems of the Everglades. To accomplish such a plan and reach such a target, WCA-3 has become the centerpiece of such an effort [U.S. Department of the Interior, 2005].

4 To control the water level in the Everglades, canals play an important role in transporting water from upstream to downstream locations. The amount of P stored in canal and wetland sediments, especially in the canal sediments, is greater than that in the water column. Diaz et al. [2006] estimated that the total sediment volume in WCA-3 is about 6.8 \(\times\) 10\(^8\) m\(^3\), with a TP mass of over 1800 Mg stored within major WCA canals, including the Miami Canal, which was originally constructed to drain the EAA into the Miami River. Phosphorus forms and concentrations in the other canals, such as L-28 and S-140, which are associated with less affected levees and wetlands in WCA-3 (Figure 1), have been reported only rarely. However, the quantities and forms of P stored in these sediments may play an important role in determining the P content of the water column and therefore of sediments of adjacent oligotrophic wetlands. Previous studies in other areas of the Everglades have found that the highest P concentration is in the inflow water, and distinct gradients of dissolved and other bioavailable P forms occur over distance [Reddy et al., 1998; Noe et al., 2001; Payne and Weaver, 2004]. Therefore, it is of great importance to quantify wetland and canal total P and its major forms in sediments to elucidate the potential risk of increasing P concentrations in the water column and associated wetlands if any disturbance to the canal sediments occurs. Historic canal P loading and the resulting P flux from sediments to the water column can be a potential source (internal loading) of P contamination of the water and marsh ecosystem [Diaz et al., 2006].

5 A number of studies on the distribution of major sediment P forms in either the Everglades wetlands or main canals have been conducted over the past decade [Reddy et al., 1998; Diaz et al., 2006; Corstanje et al., 2006]. However, almost all of these studies dealt with the anthropogenic impacts from EAA and/or TP changes over a certain period of time [Bruland et al., 2006]. For example, in previous studies, an area close to the northern boundary of WCA-3, including canal L-5 and its affected area, and the Miami Canal directly connected to EAA have been investigated [Reddy et al., 1998; Diaz et al., 2006]. In the least affected area, from the middle west adjacent to the Big Cypress National Preserve to the southeast across the major wetland area of WCA-3, an evaluation of and comparison between wetland and canal sediment P concentrations, fractionations, characteristics, and potential bioavailability are needed to successfully reach the restoration goals for the Everglades.
The replicate analyses.

The dominant native vegetation in the sampling area was saw grass (\textit{Cladium} spp.), although it could be completely dry from March to May. The transect offset to the east by 3′ in the middle Everglades (26°14′ W) and returned by a parallel – 3′ in the middle Everglades.

Chemical Determination

Geochemical Forms Associated With Precise Values in the Chemical Determination

<table>
<thead>
<tr>
<th>P Fraction</th>
<th>Geochemical Form</th>
<th>MDL* (µg L⁻¹)</th>
<th>RSDb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pi-KCl</td>
<td>readily available P</td>
<td>2</td>
<td>3.5</td>
</tr>
<tr>
<td>Pi-NaOH</td>
<td>Fe/Al-bound P</td>
<td>2</td>
<td>5.8</td>
</tr>
<tr>
<td>Pi-HCl</td>
<td>Ca/Mg-bound P</td>
<td>2</td>
<td>6.2</td>
</tr>
<tr>
<td>Pi_total</td>
<td>total inorganic P</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>Po-NaOH</td>
<td>organic P</td>
<td>2</td>
<td>4.6</td>
</tr>
<tr>
<td>PoResidue</td>
<td>organic residual P</td>
<td>2</td>
<td>6.5</td>
</tr>
<tr>
<td>PoTot</td>
<td>total organic P</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>PiLabile</td>
<td>labile inorganic P</td>
<td>2</td>
<td>4.2</td>
</tr>
<tr>
<td>PoLabile</td>
<td>labile organic P</td>
<td>2</td>
<td>5.3</td>
</tr>
</tbody>
</table>

*MDL = \(t \times S\), where MDL is method detection limit, \(t\) is the Student’s \(t\) value for a 99% confidence interval, and \(S\) is the standard deviation of the replicate analyses.

RSD = \(SD/X \times 100\), where RSD is relative standard deviation, SD is standard deviation of recoveries, and \(X\) is mean of sample recoveries.

The objectives of this study were (1) to document the P fractions and distributions in sediments and water across the canals and wetlands from the least affected WCA-3 and (2) to assess the chemical stability of these sediments in both canals and wetlands. The sediment stability can affect potential P loading of the overlying water columns of the canals and thereby lead to the eutrophication of the least anthropogenically affected WCA-3 wetland ecosystem of the Everglades.

2. Materials and Methods

2.1. Sampling Site Description

The WCA-3 (Figure 1) in the Everglades consists of 232,600 ha dominated by saw grass (\textit{Cladium} spp.) marsh, tree islands, wet prairies, and aquatic sloughs. Phosphorus inputs into this area are mainly from runoff through rainfall (42%) and water control structures (58%), resulting in an annual P load of approximately 269 Mg P [SPWMD, 1992; Reddy et al., 1998].

Two transects with extra sampling sites identified by GPS coordinates across WCA-3 in the middle Everglades were selected (Figure 1). For sampling in the middle of the Everglades, a helicopter, navigated by GPS, followed the southeast transect (25°39′37″N, 80°34′40″W) to the northwest (26°14′32″N, 80°48′28″W) and returned by a parallel transect offset to the east by 3–5 km. Depending on rainfall events, the wetland water depth varied from several centimeters up to 1.5 m, typically from June to the next February, although it could be completely dry from March to May. The dominant native vegetation in the sampling area was saw grass (\textit{Cladium jamaicense} Crantz) and bulrush (\textit{Scirpus} spp.), which are particularly adapted to the nutrient-poor environment, with sparse patches of water hyacinth (\textit{Eichhornia crassipes}), cattail (\textit{Typha domingensis} Pers.), and other wetland plants that require high P concentrations. At the canal sites, the water level varied from about 2.5 m (winter) to 3.5 m (summer). Water hyacinth presented as the dominant aquatic plant along canal banks. Water flow rates varied from almost zero to a maximum of 12,000 m³ h⁻¹ on the basis of long-term water quality monitoring data [Wang et al., 2004], but the flow rates during the sampling period in this study varied from 80 to 200 m³ h⁻¹.

2.2. Sediment Sample Core Collection and Preparation

From December 2005 through May 2006, intact sediment cores were collected with a polycarbonate piston corer sampler with a 7.0 cm internal diameter and 60 cm length with a sharpened end to collect a 35 cm deep core [Fisher et al., 1992]. A total of 142 samples were taken (102 from wetlands and 40 from canals) along two transects and some additional sampling sites (Figure 1). For wetland sampling, a helicopter was used to reach the sites across the WCA-3 area and transport samples to the laboratory. A fiberglass motor boat was used for sampling the L-28, L-28 Intercept, S-140, and I-75 canals along the northwestern WCA-3 (Figure 1). All samples were transported to the laboratory and stored at 4°C until analyzed.

2.3. Sequential Extraction and Chemical Analysis

The sediment cores were each sliced into 5 cm increments, air-dried, and ground to pass a 1 mm diameter sieve prior to chemical analysis. The fractioning extraction procedure of Reddy et al. [1998] was adopted, which included sequential extractions in 1 M KCl for readily available P (Pi-KCl), 0.1 M NaOH for Fe/Al-bound P (Pi-NaOH) and for organic P (Po-NaOH) associated with fulvic and humic acids, 0.5 M HCl for Ca/Mg-bound P (Pi-HCl), and 6 M HCl in ash residue for organic residual P (PoResidue). Subsamples were fractionated with 0.5 M NaHCO₃ (pH = 8.5) for labile inorganic P (PiLabile). The labile organic P (PoLabile) was calculated as the difference between P extracted with NaHCO₃ from sediments fumigated by chloroform to lyse microbial cells for 72 h and that extracted from the same sediment samples without fumigation [Hedley and Stewart, 1982; Ivanoiff et al., 1998]. Total P was determined after combustion of subsamples (550°C) and dissolution in 6 M HCl. The ammonium molybdate colorimetric method (U.S. Environmental Protection Agency (EPA) method 365.4 [EPA, 1993]) was used for P determination in all of the above extracts with an autoanalyzer (AA-3, BRAN+LUEBBE, GmbH, Norderstedt, Germany). This instrument was calibrated with six standard solutions and a blank prior to analysis. The corresponding dilution factors had to be applied to calculate different fractions of P because the maximum concentration for a linear curve was 1.0 mg L⁻¹. The method detection limit was 0.002 mg L⁻¹, and the relative standard deviation ranged from 3.5% to 6.5% (Table 1) for all the samples tested in our laboratory (Soil and Water Research), which is certified by the National Environmental Laboratory Accreditation Conference (NELAC). Geometric mean P concentrations (defined as nth root of the value of n numbers) were calculated for the different fractions. Unlike the arithmetic mean, the geometric mean is less affected by extreme values in skewed data and is considered to be appropriate for environmental data such as those in the current experiment. Total inorganic P (PiTot) and total organic P (PoTot) were calculated as follows:

\[
\text{PiTot} = \sum (\text{Pi-KCl}, \text{Pi-NaOH}, \text{Pi-HCl}),
\]

\[
\text{PoTot} = \sum (\text{Po-NaOH}, \text{PoResidue}).
\]

A sample from each sediment depth was weighed and dried to determine moisture and bulk density in a certain volume. The pH and electrical conductivity (EC) in a ratio of 1:2.5
sediment to water were determined with a pH meter at 25°C. Organic carbon was determined by loss on ignition at 550°C for 12 h [Wang et al., 2011], and N was analyzed using a CNS autoanalyzer (Vario Max Elementar, Hanau, Germany).

2.4. Surface Water Collection and Chemical Analysis

[11] Canal water was grab sampled with a bailer, and wetland water was collected with sampling bottles. Canal water samples were simultaneously collected at 20 cm depth increments down to 100 cm using an array of bailers bound together. All water samples were preserved in a cooler with wet ice prior to transport to the laboratory. The P forms in water were determined as follows: Total P was determined in digested water samples following EPA method 365.4 [EPA, 1993], reactive P (ortho-P) was measured in filtered water samples (Whatman 42), particulate P was obtained as the difference in P concentrations between filtered and unfiltered water samples, inorganic P was the sum of reactive and particulate P, and organic P was calculated by subtracting unfiltered water samples, inorganic P was the sum of reactive 

2.5. Core Column Leaching

[12] Intact cores (three replicates) selected from both canal and wetland sites were arranged in a randomized block design in a wooden stand with a double shelf to hold them upright. The bottom end of each column was covered by filter paper (Whatman 42) and a piece of fine-nylon screen to prevent loss of sediment particles. Once a week, 100 mL distilled deionized (DDI) water was added to each column, and the leachate was collected with a funnel into a polyethylene bottle. All the columns were kept at 25°C during leaching for 9 weeks, followed by leaching with DDI water adjusted to a series of pH values (4, 5, 6, 7, 8, and 9 ± 0.2, respectively) with 0.1 M HCl or NaOH associated with P-free buffer solutions (such as sodium citrate, NaHCO₃, etc.) for another 9 weeks. All leachates were collected for P analysis as described in section 2.4.

2.6. Statistical Analysis

[13] Descriptive statistics of means, standard errors, and standard deviation (PROC MAENS), regression (PROC REG), and analysis of variation (ANOVA) appropriate for a randomized complete block design with a general linear model were calculated with mean values separated by Duncan’s test with p ≤ 0.05 as a significance level in the SAS software [SAS Institute, 2004].

3. Results

3.1. Fractionation of P in Sediment

[14] Total P concentrations at the top 5 cm of wetland sediments varied from 100 to 706 mg kg⁻¹, while those at the same depth of canal sediments were more than twofold larger (Table 2). The geometric mean values of TP were 240 and 375 mg kg⁻¹ in wetland and canal sediments, respectively. Organic P forms accounted for more than 66% of TP in the wetland sediments, being composed mainly of highly resistant PoResidue. In canal sediments, the total inorganic form was dominant (i.e., 75% of the TP), occurring mainly in the form of Ca/Mg-bound P, which contributed 67% of TP. The fact that wetland sediments contained a high content of organic matter and were less compacted compared to those of the canal sediments might be due to the vigorous growth of vegetation and then rapid nutrient cycling.

[15] Among total inorganic P fractions, the readily available form, Pi-KCl, also called soluble reactive P, accounted for 4.7% and 1.1% of the TP on the basis of the geometric means in the wetland and canal sediments, respectively. Organic P forms accounted for more than 66% of TP in the wetland sediments, being composed mainly of highly resistant PoResidue. In canal sediments, the total inorganic form was dominant (i.e., 75% of the TP), occurring mainly in the form of Ca/Mg-bound P, which contributed 67% of TP. The fact that wetland sediments contained a high content of organic matter and were less compacted compared to those of the canal sediments might be due to the vigorous growth of vegetation and then rapid nutrient cycling.

[16] In wetland and canal sediments, the labile inorganic P fraction of the total P was greater (14%–19%) than that of the labile organic P (0.3%–4.5%). The organic labile P was approximately 20% of the total labile P in the wetland sediments.
ments, while it was only about 2% in the canal sediments (Table 2).

[17] Some distinct differences in physiochemical properties were observed in sediments from wetlands and canals on the basis of the mean values over all depths. The pH, bulk density, EC, and total and extractable P concentrations were greater in canal sediments than those in wetland sediments. The converse was true for organic C and total N concentrations (Table 3).

3.2. Distribution of P Fraction in Sediment Profile

[18] Total P concentrations in the wetland and canal sediments decreased and increased, respectively, with depth (Figure 2). The proportion of labile inorganic P in both the wetland and canal sediments was larger in the upper layer (0–5 or 0–10 cm) than that in the middle or bottom layers.

3.3. Concentrations of P in Surface Water and Leachate

[19] The inorganic P fractions, including readily available P and Fe/Al-bound P, decreased with depth in wetland and canal sediments (Figure 3). However, the concentrations of Ca/Mg-bound P in the wetland sediments were lower compared to those in the canal sediments, which increased considerably with depth.

[20] The residual organic P decreased with depth in the wetland sediments, but no clear trend was observed for the case of canals, except for an exceptionally high value at 15–20 cm depth (Figure 4). Figure 4 further reveals that the P fraction associated with humic and fulvic acids in both the wetland and canal sediments decreased with depth, although the concentrations in the wetland sediments were greater than those in the canal sediments.

3.4. Concentrations of P in Surface Water and Leachate

[21] Total P concentrations in the surface water of wetlands and canals were about 4–18 and 19–208 µg L\(^{-1}\), respectively, during the dry season when the sediment samples were collected (Table 4). However, concentrations of P in the canal water were generally high during the summer rainy season, i.e., June to September, which may be attributed to runoff, but such a seasonal change was not so obvious in the interior wetlands [Wang et al., 2004]. During the sediment sampling period, reactive P concentrations were in the range of 2–7 µg L\(^{-1}\) in the wetlands and 2–180 µg L\(^{-1}\) in the canals. Organic P accounted for up to 67% of the TP in the wetland water, while inorganic P was the dominant form (69%) in the canal water.

Table 3. Selected Physical and Chemical Characteristics of Sediments (0–5 cm) From Wetlands and Canals in Water Conservation Area 3\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>Wetlands (n = 102)</th>
<th>Canals (n = 40)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.8 (0.2)</td>
<td>7.1 (0.6)</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-1}))</td>
<td>0.13 (0.02)</td>
<td>0.42 (0.21)</td>
</tr>
<tr>
<td>Electrical conductivity (µS cm(^{-1}))</td>
<td>280 (89)</td>
<td>2500 (330)</td>
</tr>
<tr>
<td>Total P (mg kg(^{-1}))</td>
<td>290 (83)</td>
<td>570 (150)</td>
</tr>
<tr>
<td>1 M HCl extractable P (mg kg(^{-1}))</td>
<td>52 (26)</td>
<td>440 (59)</td>
</tr>
<tr>
<td>Organic C (g kg(^{-1}))</td>
<td>430 (81)</td>
<td>110 (36)</td>
</tr>
<tr>
<td>Total N (g kg(^{-1}))</td>
<td>32 (5.8)</td>
<td>13 (4.6)</td>
</tr>
</tbody>
</table>

\(^a\)Given are mean values with standard deviation in parentheses.

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\[\text{Figure 2.} \quad \text{Profile distribution of total P and labile inorganic P (P}_{\text{labile}}\text{) as arithmetic means in the wetland and canal sediments of WCA-3. Error bars represent standard deviation of means (wetland, n = 102; canal, n = 40).}\]
Figure 3. Profile distribution of various inorganic P fractions in the wetland and canal sediments of WCA-3. Error bars represent standard deviation of means (wetland, n = 102; canal, n = 40).
Concentrations of total P and ortho-P in canal water varied \((p \leq 0.05)\) among sampling locations, but there were no significant differences across sampling depths, except at the S-140 canal (Table 5). Water flow rate was much faster in that canal than in others. High water velocity usually carries more particles or debris than low velocity. The tendency for more particles to settle out in deeper water may explain the greater total P concentration in the deeper rather than the shallow water column.

Phosphorus concentrations in sediment column leachate represent soluble P fractions. No significant differences \((p \leq 0.05)\) were found in water-soluble P (ortho-P) from the column leachate between the marsh and canal sediment samples \((3.4-4.0 \, \mu g \, L^{-1})\). The total P concentration was significantly larger in the leachate from wetland sediment \((13.7 \, \mu g \, L^{-1})\) compared to that from canal sediment \((10.9 \, \mu g \, L^{-1})\). High leaching water pH \((pH \, 8.0-9.0)\) increased total P and ortho-P concentrations in the leachate (Figure 5).

### 4. Discussion

Variations of P fractionation in the canal and wetland sediments of the Florida Everglades occurred primarily because of the differences of the physicochemical characteristics, biological environments, and hydrological conditions in the two distinct sediments. The larger fractions of organic P in the wetland sediments and inorganic P in the canal sediments indicated that organic matter and vegetation could play a critical role in recycling bioavailable P from either water or sediments in the wetlands of this area (WCA-3).

Vegetation and microbes take up and accumulate P in their biomass or detritus tissues [Richardson and Marshall, 1986], which are the main contributors to sediment organic P. Waterlogged conditions for most, if not all, of the year in the wetlands decreased biomass decomposition and subsequent mineralization of organic matters in the sediments, which might be the main reason why organic P was predominant. This finding was in agreement with that in stream sediments in Argentina [García and de Iorio, 2003]. García and de Iorio found that increasing the organic matter load results in an increase in organic P and that bacterial activity under anoxic conditions releases P from organic matter. In canals, the influence of vegetation is rather minimal, although some aquatic plants, such as duckweed (Lemna minor) or water hyacinth, can grow during summer in the shallow water or close to canal banks. Because of the sporadic distribution of the aquatic plants in canals, their influence on P concentrations in canal sediments was trivial in the studied area. Canal

### Table 4. Range and Mean Concentrations of Major P Forms (\(\mu g \, L^{-1}\)) in Surface Water From Canals and Wetlands in Water Conservation Area 3

<table>
<thead>
<tr>
<th></th>
<th>Wetlands (n = 81)</th>
<th>Canals (n = 126)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Total P</td>
<td>4.2–18</td>
<td>9.2</td>
</tr>
<tr>
<td>Reactive P</td>
<td>2.1–7.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Particulate P</td>
<td>0.7–3.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Organic P</td>
<td>2.5–11</td>
<td>6.2</td>
</tr>
<tr>
<td>Inorganic P</td>
<td>1.7–7.4</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Figure 4. Profile distribution of organic P fractions in the wetland and canal sediments of WCA-3. Error bars represent standard deviation of means (wetland, \(n = 102\); canal, \(n = 40\)).
fauna influence recycling of water P, but such cycling is relatively small compared to that in wetland ecosystems. [25] Among the three inorganic P forms, the readily available P is considered the most important form in controlling the P concentrations in the overlying water column [Reddy et al., 1998]. However, through all sampling points and depths (0–35 cm) in the wetland sediments, residual organic P was the dominant form and accounted for 43% of TP, followed by the P associated with humic and fulvic acids, which accounted for 27% (Table 6). In the canal sediments, the Ca/Mg-bound P fraction represented 87% of the total P, while the residual organic P accounted for only 10%. Low proportions of readily available P in the canal (0.2%) and wetland (3.8%) sediments in the current study were comparable with those reported by Diaz et al. [2006], who found that readily available P accounts for <1% of TP in canals and 0.3%–3.1% of TP in wetlands. However, the proportions of readily available P in both canal and wetland sediments in the current study were larger than those in the lake sediments of northern Greece (<0.1% of the total) [Fytianos and Kotzakioti, 2005] but much lower than those of drainage canal sediments in India (2.2%–13%) [Moturi et al., 2005]. [26] A major portion of TP in the wetland sediments was in the organic form, whereas the dominant portion of TP in the canal sediments was in the inorganic form. However, the proportion of labile inorganic P in this study (14%–19% of total P, Table 2) was much larger than in the previously reported data (<2% from the northern area) [Reddy et al., 1998], possibly because of differences in spatial distribution or a substantial increase over time. In the latter case, such an increase in this pool over the past decade might be a cause for concern because labile inorganic P is more reactive and can participate in nutrient cycling in the ecosystem more readily and quickly than organic forms. [27] The overall proportion of Ca/Mg-bound P (87% of TP) in the current studied canal sediments was larger than that in other canals (41%–64%), including the Miami Canal in WCA-3 [Diaz et al., 2006], but was comparable to that in lake sediments in Greece (72%–82%) [Fytianos and Kotzakioti, 2005]. Long periods of precipitation of P by Ca/Mg with less impact from agriculture in the current study area may explain such dominance since canals close to the EAA (such as L-40 in WCA-1) appear to have lower Ca/Mg-bound P than those farther away from the EAA (e.g., Miami Canal) [Diaz et al., 2006]. [28] The large proportion of Fe/Al-bound P, such as bound by soluble Fe(II) or adsorbed by insoluble FeS under anaerobic conditions [Wang and Li, 2010], in the wetland sediments may constitute an important potential source of P to the water column and vegetation under waterlogged conditions [Hietjes and Lijklema, 1980; Ollila et al., 1995]. The high concentrations of 1 M HCl extractable Fe (>2300 mg

### Table 5. Mean Total P Concentrations (μg L⁻¹) in Canal Water at Various Depths in Water Conservation Area 3

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Ortho-P</th>
<th>Total P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–20</td>
<td>83</td>
<td>108</td>
</tr>
<tr>
<td>20–40</td>
<td>85</td>
<td>110</td>
</tr>
<tr>
<td>40–60</td>
<td>86</td>
<td>109</td>
</tr>
<tr>
<td>60–80</td>
<td>87</td>
<td>110</td>
</tr>
<tr>
<td>80–100</td>
<td>87</td>
<td>112</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>S-140 (n = 10)</th>
<th>L-28 (n = 8)</th>
<th>L-28 Intercept (n = 12)</th>
<th>I-75 (n = 9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho-P</td>
<td>Total P</td>
<td>Ortho-P</td>
<td>Total P</td>
</tr>
<tr>
<td>86</td>
<td>109</td>
<td>19</td>
<td>32</td>
</tr>
<tr>
<td>87</td>
<td>108</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>87</td>
<td>108</td>
<td>20</td>
<td>32</td>
</tr>
<tr>
<td>86</td>
<td>108</td>
<td>20</td>
<td>33</td>
</tr>
</tbody>
</table>

Significance*: p < 0.05

*NS, no significant difference at p ≤ 0.05.

### Table 6. Overall Proportion of Each Fraction and Parameters in a Zero-Order Linear Model Between Selected Fractions and the Total P Concentrations in Different Sediments*

<table>
<thead>
<tr>
<th>P Fraction</th>
<th>Percent of Total P</th>
<th>a (mg kg⁻¹)</th>
<th>b (mg kg⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands (n = 178)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pi-KCl</td>
<td>3.8</td>
<td>-5.82</td>
<td>0.0794</td>
<td>0.70</td>
</tr>
<tr>
<td>Pi-NaOH</td>
<td>13</td>
<td>-7.14</td>
<td>0.180</td>
<td>0.54</td>
</tr>
<tr>
<td>Pi-HCl</td>
<td>13</td>
<td>-0.033</td>
<td>0.134</td>
<td>0.56</td>
</tr>
<tr>
<td>Po-NaOH</td>
<td>27</td>
<td>5.06</td>
<td>0.222</td>
<td>0.50</td>
</tr>
<tr>
<td>PoResidue</td>
<td>43</td>
<td>7.94</td>
<td>0.384</td>
<td>0.77</td>
</tr>
<tr>
<td>Canals (n = 144)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pi-KCl</td>
<td>0.2</td>
<td>2.95</td>
<td>-0.00051</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Pi-NaOH</td>
<td>1.4</td>
<td>23.0</td>
<td>-0.0025</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Pi-HCl</td>
<td>87</td>
<td>-194</td>
<td>1.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Po-NaOH</td>
<td>1.5</td>
<td>25.2</td>
<td>-0.0031</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>PoResidue</td>
<td>10</td>
<td>143</td>
<td>0.0010</td>
<td>&lt;0.10</td>
</tr>
</tbody>
</table>

*P fraction = a + b × total P.

### Figure 5. Total P and ortho-P in the leachate using different pH solutions from sediment core columns from wetlands in WCA-3. Error bars represent standard error of means with three replicates.
kg$^{-1}$) and Al (3000 mg kg$^{-1}$) in a slightly acidic system [SFWMD, 1992; Reddy et al., 1998; Corstanje et al., 2006] in the sediments of the studied area might be considered as evidence in support of the Fe/Al-bound P fraction.

[29] Precipitation of mineral particles containing P by Ca and Mg in surface water through long-term deposition might be the main process responsible for P accumulation in canal sediments, especially where there is an abundance of Ca, such as in the Florida Everglades. As reported by Diaz et al. [1994], high concentrations of Ca (116 mg L$^{-1}$) and Mg (42 mg L$^{-1}$) in EAA drainage water combined with pH > 8.2 caused precipitation of soluble P as Ca phosphate minerals. A high proportion of inorganic labile P in the surface of canal sediments implies that inorganic P could be bound to the abundant Ca already present or could result from recently precipitated, amorphous monocalcium phosphate due to high drainage water Ca concentration in the Everglades WCA [Reddy et al., 1998].

[30] To establish a relationship between the TP and selected P fractions, Reddy et al. [1998] proposed a model ($Y = \alpha X^b$) between total (X) and selected P fractions (Y), where $\alpha$ and $b$ are empirical constants in wetland sediments, but this was not satisfactory for the current data. Instead, a zero-order linear model (P fraction = $a + b \times$ total P) adequately described the relationship between each P fraction and TP content in wetland sediments ($R^2 = 0.50$–0.77) but only Ca/Mg-bound P in canal sediments ($R^2 = 0.98$) of the study area (Table 6). Using this model and corresponding parameters, various P fractions can be predicted in wetland sediments and Ca/Mg-bound P in canal sediments under similar environmental conditions by determining total P, which will save much time and effort in chemical analysis.

[31] The high total P content observed in the upper layer of wetland sediments might be due to P sequestration and recycling by vegetation and microbes. Microbial and algal storage of P is relatively small, but rapid cycling of this pool may provide a steady supply of bioavailable P to increase its accumulation [Richardson and Marshall, 1986]. In addition, fires that occur naturally during the dry season can also result in P enrichment in the surface layers [Reddy et al., 1998]. In WCA-3, the dominant vegetation is saw grass associated with other native plant communities, such as bulrush, water hyacinth, etc. Saw grass adapted to a low-nutrient environment usually has a low decomposition rate. For example, Davis [1991] reported that after 2 years, most saw grass leaf litter mass was still intact, which may explain why the organic P forms in the wetlands of the current study were dominant. In addition, periphyton, freshwater algae, and cyanobacteria attached to substrates are ubiquitous on the water surface [Gaiser et al., 2006] in this natural environment, and at the low P concentrations they aid in recycling P more efficiently. Benthic periphyton has high productivity and accumulates more biomass than plankton, making nutrients more available from the substrates than from water and form large surfaces for colonization, thereby increasing the efficiency of nutrient cycling [Gaiser et al., 2006; Gaiser, 2008]. Therefore, almost all P forms (total, organic, and inorganic forms, readily available P, and Fe/Al-bound P) were greater in the surface than middle or bottom layers of the wetland sediments in the studied area.

[32] The increase in total and Ca/Mg-bound P with depth in the canal sediments suggests time-dependent progress in P precipitation with the abundant Ca present in the water column [Reddy et al., 1998]. Furthermore, the decreased P release as a result of the recent implementation of best management practices (BMPs) and the operation of the storm water treatment areas before discharge to these WCA canals [White et al., 2006] might explain the lower P accumulation at the surface of the canal sediments. The BMP implementation, which began in 1995 in the EAA, has contributed to >50% reduction in annual P load [Daroub et al., 2003; Sievers et al., 2003; Diaz et al., 2006], resulting in reduced P deposition in the canal sediments.

[33] The presence of a rather high labile inorganic P concentration (up to 180 mg kg$^{-1}$) in the 0–5 cm sediment layer indicates a significant potential for water contamination even if only a small portion of P were released from the sediment [Bostrom et al., 1982; Diaz et al., 2006]. The results of this study suggest that water flow should be maintained below a certain rate to minimize disturbance of the canal surface sediment, thus minimizing the release of P into the overlying water column.

[34] The concentrations of Fe/Al-bound P appeared to be greater in the surface than middle or bottom layers of the canal sediment. However, compared to total P, the Fe/Al-bound P fraction was relatively small and even similar to or smaller than that in the wetland sediments (Figure 3). Although Al-bound P was relatively stable, the stability of Fe-bound P is strongly influenced by redox, and therefore the anaerobic environment can considerably decrease the potential for P release from the sediments [Moore and Reddy, 1994].

[35] On the other hand, Ca/Mg-bound P is much more stable than Fe/Al-bound P and is hardly available for biological assimilation under most circumstances [Sonzogni et al., 1982]. Overall, the Ca/Mg-bound P is the dominant fraction in canal sediments and may play a significant role in P storage. Diaz et al. [2006] reported that this fraction, which accounted for 41%–64% of the total P, was found in the greatest concentrations in the Miami Canal sediments in WCA-3, but most of it occurred at the bottom of the profile (25–35 cm). This is in agreement with the present finding that the concentration at the bottom layer exceeded 4500 mg kg$^{-1}$ (Figure 3).

[36] Phosphorus in the overlying water may or may not be correlated with that in the corresponding sediment since the latter is the result of long-term deposition and accumulation. Historical impacts, rather than instantly ambient P associated with physicochemical and biological interactions in the overlying water, often play a critical role in P accumulation in sediments. However, canal water P concentrations were much greater than in the wetland waters in the present study (Table 3).

[37] No significant differences were found in the amounts of P in leachates from sediment cores between wetland and canal core columns. Abundant Ca in canal water together with alkaline sediments (pH > 8.2) [Diaz et al., 1994] played an important role in retaining P. Significantly larger P concentrations in leachate from both high- or low-pH solutions further confirmed that Fe/Al-bound P and Ca/Mg-bound P were the dominant forms in these sediments because changes in pH may cause Fe/Al-bound or Ca/Mg-bound P to become partially soluble. Although both of these forms are relatively stable, they do have a potential to become reactive under certain conditions. At low pH, P will be insoluble from the Ca/Mg-bound form, while at elevated pH,
dissolution of Fe/Al-bound P might be a considerable contribution. Similar results have been obtained by other researchers [Koski–Vähälä and Hartikainen, 2001], who found that substantial quantities of P were mobilized from sediments between a pH of 6.6 and 9.5, suggesting that environmental changes, such as a change in pH, may cause P release from these sediments into the overlying water via a sediment-supplied increase in the internal loading.

5. Conclusion

[38] Total P in canal sediments was much larger than that in wetland sediments in the least anthropogenically affected WCA of the Florida Everglades, WCA-3. Although most P fractions in the canal sediments were relatively stable (Ca/Mg-bound), a large proportion of P in the readily available fractions in the surface layer (0–5 cm) of the canal sediments has the potential to contaminate the overlying water and subsequently the wetlands if the canal sediments are disturbed and accidently loaded to the oligotrophic wetlands. This is a primary concern in achieving the target of 10 μg L⁻¹ for total P in wetland water, which has been mandated by the Everglades Forever Act. When the wetland water level is raised by the passage of water through these canals, the upper sediment layer, which is very reactive, is likely to be disturbed. On the other hand, in wetland sediments, organic P, which is slowly recycled by vegetation and microbes, is the dominant form. Organic P results in slow P recycling over the long term, thus preventing internal loading of the overlying water column. To meet the objective of restoring historic water levels and seasonal flows in the wetland ecosystem, which is an important target goal in the Comprehensive Everglades Restoration Plan, it is essential to substantially reduce external loading of P in canal water and to avoid the disturbance of canal sediments because such sediments contain high concentrations of total and labile P. Indeed, even minor mechanical disturbances or changes in chemical characteristics (e.g., pH) of the canal sediments may cause a surge of internal loading of P in the water column and consequently threaten the oligotrophic wetland ecosystems by extensive displacement of native plant species with highly undesirable exotic species within the wetlands of the Everglades.

[39] Acknowledgments. The study was supported by the Institute of Food and Agricultural Sciences, Florida Agricultural Experimental Station, Soil and Water Science Department, University of Florida, as a part of Everglades Restoration Project. The authors thank G. Yu, L. Rosado, and N. Campbell for their great assistance in sediment sampling, processing, and analyses. We also thank A. Alva (USDA ARS), M. E. Sumner (agricultural and environmental consultant), and W. Klassen (University of Florida) for their critical review and comments of the manuscript.

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