Effect of Aluminum-Containing Amendments on Phosphorus Sequestration of Wastewater Treatment Wetland Soil

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Little research has been conducted on methods to restore the P removal capacity of older constructed wetlands, as P treatment capacity can decrease with time. We investigated the capacity of alum and three Al-containing alternatives (alum residual, polyaluminum chloride [PAC], and partially neutralized aluminum sulfate [PNAS]), at three rates (9, 18, and 36 g Al m^{-2}) to reduce P concentrations. Water column pH of the alum treatment was significantly less than all other treatments, averaging 3.65 ± 1.12, while PAC (4.85 ± 0.96) and PNAS (4.21 ± 0.93) treatments had pH values significantly less than the alum residual and controls. Soluble reactive P decreased in the water column of all the treatments (–60.41 to –2.11 mg m^{-2} d^{-1}). At all dosage rates, alum and PNAS were most effective at binding P, followed by PAC, while the alum residual was least effective. Significantly less P removal occurred in the 9 g Al m^{-2} alum, PNAS, and PAC treatments than the higher Al dosages. Dosage was inversely related to microbial biomass and activity in the surface soil, suggesting short-term negative effects of chemical additions. Results suggest that a low-dosage Al amendment application to wetland soil can, in the short term, prevent release of P from organic soil into the water column as well as remove P from the water column. Long-term studies are needed, however, to verify P removal efficacy with time and the effects of continued applications on nutrient availability.

Abbreviations: LOI, loss-on-ignition; MBP, microbial biomass phosphorus; OEW, Orlando Easterly Wetland; PAC, polyaluminum chloride; PMP, potentially mineralizable phosphorus; PNAS, partially neutralized aluminum sulfate; SOD, soil oxygen demand; SRP, soluble reactive phosphorus; TP, total phosphorus.

WETLAND SOILS

There is a paucity of research focused on methods to restore the treatment capacity of older constructed wetlands since most treatment wetlands in use today are relatively young, and treatment effectiveness has not declined until recently. Additionally, treatment wetlands are less efficient during the winter months, which can promote nutrient releases from soil and ultimately lead to discharges in excess of permit limits. Hydrologic fluctuations can also promote nutrient releases from wetland soils (White et al., 2004, 2006b; DeLaune and Smith, 1985). A recent study has shown that up to 6% of wetland soil total P can be released from a single drawdown–reflood event (Bostic and White, 2007). One potential management option for dealing with these nutrient releases is the use of chemical amendments for nutrient inactivation; however, the effectiveness of these chemical amendments in wetlands to inactivate P, the longevity of treatment, and the potential effects on flora and fauna are issues that need to be investigated.

The chemical amendment used most often for P inactivation in lakes and coagulation in the wastewater treatment industry is $Al_2(SO_4)_3 \cdot 14H_2O$ (alum). When added to the water column, alum dissociates, forming Al^{3+} ions that are immediately hydrated. Through several rapid hydrolytic reactions, an insoluble gelatinous poorly crystalline $Al(OH)_3$ floc is formed (Ebeling et al., 2003), directly related to the alum dose (Chakraborti et al., 2003). Immobilization of 1 mg of PO_4^{3-} theoretically requires 0.28 mg of Al^{3+}; however, the $Al(OH)_3$ floc also binds with organic matter, typically abundant in treatment wetlands, reducing P treatment efficiency and requiring an increased alum dosage (Van Hullebusch et al., 2002).

The pH of the system is the controlling factor for both the effectiveness of P binding and Al toxicity. Liquid alum itself has a pH of approximately 2.4 (Beecroft et al., 1995; Lind, 2003) and therefore tends to decrease the pH of the system to which it is added. As long as the pH of the system remains between 6 and 8, insoluble polymeric $Al(OH)_3$ will dominate (May et al., 1979) and P inactivation results. If the pH decreases to between 4 and 6, however, soluble intermediates will occur, potentially releasing bound P. Below pH 4, soluble Al^{3+} dominates, and above pH 8 the aluminate ion $[Al(OH)_4^-]$ dominates due to the amphoteric nature of Al, releasing bound P and increasing soluble Al, which may result in Al toxicity (Cooke et al., 1993). The buffering capacity of treatment wetlands is typically high (alkalinity >100 mg L^{-1} as $CaCO_3$) and should buffer alterations in the water column pH due to the addition of Al-containing materials.

There are also several Al-containing alternatives to alum, including PAC, which was developed for water treatment use (Viraraghavan and Wimmer, 1988). Polyaluminum chloride $[Al_n(OH)_mCl_{(3n-m)}]$ is a partially hydrolyzed aluminum chloride solution that has recently been found to provide stronger, faster settling flocs than alum (Boisvert and Jolicoeur, 1999). In the PAC manufacturing process, Al becomes further polymerized, partially eliminating the polymerization process that occurs when it is added to water (Boisvert and Jolicoeur, 1999). This results in greater cation charge, thus increasing its P binding capacity such that lower doses can achieve equivalent treatment efficiency (Jiang and Graham, 1998). Another important benefit of PAC is that it does not decrease the pH as much as alum (Lind, 2003) and is effective across a wider pH range (Jiang and Graham, 1998). Despite the benefits, PAC has not yet been used for environmental restoration due to its high cost, 2.5 times more than alum (Viraraghavan and Wimmer, 1988).

A low-cost alternative to alum is PNAS, developed by Koether et al. (1993, 1997). Partially neutralized aluminum sulfate is a solution formed by adding powdered $CaCO_3$ to concentrated alum, increasing the cost by only 10% above that of liquid alum (Beecroft et al., 1995; Koether et al., 1997). It is similar to PAC in that it contains several preformed Al polymers and is less acidic than alum. The pH of PNAS is 3.3 or greater depending on whether a concentrated or dilute solution is used (Beecroft et al., 1995), and thus would be preferred as an addition to a natural system with low buffering capacity, such as many Florida lakes.

A final alternative to alum investigated in this study is alum residual. Alum residual is a solid formed as a byproduct in many potable water treatment plants that use alum in the treatment process (Butkus et al., 1998). This dried sludge can often be obtained free of charge as Al-based water treatment plant residual (WTR) and has a high P sorption capacity due to the Al oxides that make up a significant fraction of the WTR (Dayton and Basta, 2005). Application of alum residual has little risk for pH changes compared with the addition of alum (Dao et al., 2001); however, a much larger quantity of WTR is required to equal the sorption capacity of alum (Zvomuya et al., 2006), since intraparticle diffusion is required for some P sorption (Makris et al., 2004).

There is no previous published research on the utilization of Al-containing amendments in a constructed wastewater treatment wetland for reducing P concentrations. Additionally, little research has been done on the effect of alum on the microbial populations in the bottom sediment of lakes or wetland soils. Both the size and activity of the microbial pool influences the ability of a wetland to remove nutrients (White and Reddy, 1999, 2003) and other contaminants (White et al., 2006a; Conkle et al., 2008). Microbes are generally sensitive to soil acidity (Degens et al., 2001) and soluble Al (Robert, 1995). The microbial biomass has the potential of being a sensitive indicator of the impact to soil nutrient dynamics (Powlson and Jenkinson, 1981; White and Reddy, 2000) in response to Al amendment chemical applications. The size and activity of the microbial pool, therefore, needs to be assessed in response to Al amendments to fully understand the effects on biogeochemical cycling of nutrients within a treatment wetland.

The hypotheses of this study were that all Al-containing amendments would reduce water column P, with alum alternatives affecting the pH less. Second, pH differences attributed to chemical amendments would decrease the microbial biomass pool size and activity and increase Al availability with increasing dosage rate. The specific objectives of this study were to determine: (i) an effective low dose of the Al-containing amendments (alum, PAC, alum residual, and PNAS) as determined by the P flux at the soil–water interface; (ii) the effect of each Al amendment on soluble Al and the microbial biomass and activity of the amended soils; (iii) the ability of each amendment to remove P from the water column; and (iv) associated changes in the soil P pool related to each amendment.

MATERIALS AND METHODS
Site Description

The Orlando Easterly Wetlands (OEW) Reclamation Project in Orange County, Florida, is one of the oldest and largest constructed treatment wetlands in the United States. The wetland was built in 1986, designed by Post, Buckley, Schuh & Jernigan, Inc., for the City of Orlando's Iron Bridge Regional Water Pollution Control Facility, which needed an alternative discharge point for its wastewater effluent (Burney et al., 1989). The main goal in designing the system was to use macrophytes to facilitate additional nutrient removal for an average daily flow of up to 132,000 m^3 d^{-1} of effluent from the Iron Bridge Water Pollution Control Facility before discharge into the St. Johns River (Black and Wise, 2003).

The 494-ha wetland rests on a 664-ha piece of land 3.2 km west of the main channel of the St. Johns River. Historically, the land had been part of the riparian wetland adjacent to the St. Johns River, but was drained for cattle pasture around the turn of the last century (Burney et al., 1989). The pastureland was underlain by sandy, poorly drained soils of the Malabar (loamy, siliceous, active, hyperthermic Grossarenic Endoaqualfs) and Smyrna (sandy, siliceous, hyperthermic Aeric Alaquods) series. The OEW has a natural topographic gradient of 0.2% downward from west to east, allowing water to flow by gravity through a series of cells with an average elevation drop across each cell of approximately 1 m (Wang and Jawitz, 2006). Water exits the wetland through a weir control structure and flows into a receiving ditch. From there, the water can flow directly to the St. Johns River or travel by sheet flow through Seminole Ranch, a natural marsh adjacent to the OEW owned by the St. Johns River Water Management District (Martinez and Wise, 2003).

The average influent total P (TP) concentration from 1988 to 2006 was 0.22 mg L^{-1}; however, annual inflow TP concentrations ranged from 0.02 to 3.30 mg L^{-1} during the same time period. Since its inception, the OEW has exceeded performance expectations. The TP discharge permit limit established by the Florida Department of Environmental Protection is 0.2 mg L^{-1} (Wang et al., 2006). From 1988 to 1995, the average TP discharged was 0.07 mg L^{-1} (Black and Wise, 2003); however, TP values have been considerably greater from December to February in recent years (Wang et al., 2006).

Field Sampling, Laboratory Setup, and Analyses

Seventy-eight push cores (7-cm i.d.) were collected within a 10-m^2 area from a *Typha* spp. dominated cell (Cell 10) within the OEW. Six replicates were collected for each chemical amendment (alum, PAC, alum residual, and PNAS) at three dosage rates (9, 18, and 36 g Al m^{-2}), and six control cores. Dosage rates were selected

based on previous alum research performed on OEW soil by Simon (2003) and D.B. Environmental (2004). The alum and PAC were obtained from General Chemical Corporation (Parsippany, NJ), the alum residual originated from the Melbourne, FL, Potable Water Treatment Plant, and the PNAS was synthesized in the laboratory according to Koether et al. (1997). Phosphorus flux rates were determined by measuring changes in water column concentrations of intact sediment cores with time (Malecki et al., 2004; Steinman et al., 2004). Floodwater was replaced with filtered (0.45-µm) site water to maintain a 20-cm water column at initiation of the core flux study. Cores were sealed and allowed to equilibrate overnight while water columns were purged with N_2 gas (with 300 mg L^{-1} CO_2) to maintain anaerobic conditions. Time zero samples were collected from the equilibrated cores followed by the addition of the treatments to the water column. Within 24 h, a visible floc had formed at the soil–water interface of those cores treated with alum and PNAS. Cores were purged daily and redox probes were installed in the water column at mid-depth and at 5-cm depth in the soil of two cores selected randomly from each treatment to confirm anaerobic conditions throughout the study. Cores were incubated in the dark in a water bath maintained at 20°C. Water samples were taken at several time intervals (0, 1, 3, 5, 7, 10, and 14 d) during a 2-wk period, filtered through 0.45-µm syringe filters, and analyzed for soluble Al and soluble reactive P (SRP). The water column pH of each core was measured in triplicate for each treatment throughout the study. Flux calculations were based on the immediate change in water column concentrations of SRP with time. Soil flux rates were calculated using a zero-order rate for the first day since we only had the two data points, Day 0 and Day 1. The rate of P sorption was greatest during this time span.

Three cores of each treatment and dosage (39 cores total) were sectioned into depth increments of 0 to 5 and 5 to 10 cm after the 2-wk incubation to determine microbial biomass and activity as well as the P content and physicochemical characteristics of the soil. Before sectioning, any visible floc was removed from the soil surface to prevent altering the results by incorporating the chemical into the soil. The remaining triplicate cores were spiked once per week for 3 wk to a water column concentration increase of 0.180 mg L^{-1} P as KH_2PO_4 (ACS certified, Fisher Scientific, Fair Lawn, NJ), a concentration equivalent to that entering the OEW, to determine the P uptake capacity of the floc formed.

The following physicochemical parameters were measured on the sectioned soil samples: pH, bulk density (Blake and Hartge, 1986), mass loss-on-ignition (LOI), microbial biomass P (MBP), soil O_2 demand (SOD), potentially mineralizeable P (PMP), TP, inorganic P fractionation (Reddy et al., 1998), 1 mol L^{-1} HCl extractable metals, and oxalate-extractable Al (McKeague and Day, 1966). Microbial biomass P was determined by a 24-h chloroform fumigation–extraction technique (Brookes et al., 1982; Hedley and Stewart, 1982). The MBP was calculated as the difference between the TP in the extracts from the chloroform-treated and non-chloroform-treated sediments.

Soil O_2 demand was determined by placing 10 g (wet weight) of soil into 250-mL biochemical O_2 demand (BOD) dark bottles and the bottles filled with O_2–saturated distilled, deionized water (American Public Health Association, 1992). The initial dissolved O_2 (DO) concentrations were recorded using a YSI Model 58 DO meter (Yellow Springs Instrument Co., Yellow Springs, OH) equipped with a YSI Model 5905 BOD stirring probe. The BOD bottles were incubated in the dark for 24 h at 21°C. Following incubation, the final DO concentrations were measured (Fisher and Reddy, 2001, Malecki et al., 2004).

The PMP rate was determined using an anaerobic, waterlogged incubation at 40°C (Chua, 2000). The rate of P release from organic soils is primarily driven by the rate of microbial-mediated decomposition (Chua, 2000). Glass serum bottles (50 mL) were prepared by weighing out field-moist soil (equivalent of 0.5 g dry weight) and adding 5 mL of distilled, deionized water. Bottles were capped with butyl rubber stoppers and sealed with Al crimps. The headspace was evacuated and replaced with O_2–free N_2 gas for incubation in the dark at 40°C for 10 d. A duplicate set of subsamples was weighed into 50-mL centrifuge tubes for the controls. Both the control samples and, 10 d later, the incubated samples were shaken and extracted with 25 mL of 1.0 mol L^{-1} HCl for 3 h on a reciprocal shaker and the supernatant filtered through a 0.45-µm membrane filter. The supernatant was analyzed for total inorganic P (TP_i) using automated, colorimetric analysis (USEPA, 1993, Method 365.1). Potentially mineralizable P (mg kg^{-1} d^{-1}) was calculated as the difference between the incubated and time-zero extractable TP_i on a sediment mass basis, divided by the incubation time.

Total P analysis involved combustion of 0.5-g oven-dried subsamples at 550°C for 4 h in a muffle furnace followed by dissolution of the ash in 6 mol L^{-1} HCl on a hot plate (Andersen, 1976). Total P was analyzed using an automated ascorbic acid method (USEPA, 1993, Method 365.4). Ash content was calculated to determine mass LOI, indicating the organic matter content in the wetland soil (Lim and Jackson, 1982). Total extractable Ca, Mg, Fe, and Al concentrations were determined from 0.5 g of oven-dried soil treated with 25 mL of 1.0 mol L^{-1} HCl and placed on a reciprocal shaker for 3 h. The supernatant was filtered through 0.45-µm membrane filters and analyzed for Ca, Mg, Al, and Fe (DeBusk et al., 1994; Reddy et al., 1998). Metal analyses were determined by inductively coupled argon plasma spectrometry (Vista MPX CCD simultaneous ICP–OES, Varian, Walnut Creek, CA; USEPA, 1993, Method 200.7).

Statistical Analysis

Paired t-tests were used to determine significant differences ($P < 0.05$) between soil properties in the 0- to 5- and 5- to 10-cm sectioned intervals (Microsoft Excel 2000). Additionally, Pearson product-moment correlation coefficients between parameters were calculated (Microsoft Excel 2000). Data normality was determined using the Kolmogorov–Smirnov test (Minitab 13.32, Minitab Inc., State College, PA) and data were transformed iteratively to fit a normal distribution (Microsoft Excel 2000). One-way ANOVAs and multiple comparisons by Tukey's W were used on soil parameters, while repeated-measure ANOVAs followed by multiple comparison determined significant differences ($P < 0.05$) between treatments and dosage rates on water column data (Minitab 13.32). Parameters that did not follow a normal distribution and could not be transformed to fit a normal distribution were analyzed nonparametrically using the Kruskal–Wallis ANOVA on ranks multiple comparisons test (Minitab 13.32). Linear regression analysis was also used (Microsoft Excel 2000).

RESULTS
Soil Physicochemical Characteristics

Total P concentrations were significantly greater ($P < 0.05$) in the surface than the subsurface of the control and alum residual dosed cores, as well as the low-dosage alum cores and high-dosage PNAS cores. There were no significant differences,

however, in the TP concentration between treatments or dosage rates in either layer. The amount of TP in either soil layer was positively correlated ($R^2 = 0.83$, $P < 0.05$) with the LOI percentage, suggesting that much of the P was associated with soil organic matter and detrital plant tissue.

Similarly to TP, the amorphous oxalate-extractable Al was also significantly greater at the surface (Table 1) than in the subsurface layer (Table 2) ($P < 0.001$). The surface layer of the control cores (890 ± 322 mg kg^{-1}) had significantly less ($P < 0.001$) oxalate-extractable Al than the cores treated with alum (3682 ± 1725 mg kg^{-1}), alum residual (3623 ± 1678 mg kg^{-1}), or PNAS (6126 ± 2500 mg kg^{-1}), specifically at the highest Al dosage rate due to alum additions. There was a significant positive correlation ($P < 0.05$) between the Al dosage rate and oxalate Al in the surface of both the alum and alum residual treated cores. There were no significant differences in oxalate-extractable Al in the 5- to 10-cm layer between treatments or dosage rates.

Soil pH did not differ within treatment by depth (Tables 1 and 2); however, there were several significant differences in soil pH between treatments and dosage rates. In the surface layer, the alum residual treated cores (5.8 ± 0.1) had significantly greater soil pH values ($P = 0.001$) than either the alum (5.4 ± 0.2) or PNAS (5.5 ± 0.3) treated cores. At the highest dosage specifically, the alum residual treated cores had significantly greater ($P = 0.02$) pH values than the alum, PAC, or PNAS treated cores, demonstrating that alum residual had the least impact on the soil pH of all amendments. Within a given treatment, ANOVA multiple comparisons indicated that the mean pH of soils treated with 36 g Al m^{-2} as PNAS were significantly lower ($P < 0.001$) than the mean pH values of cores that only received 9 g Al m^{-2} as PNAS. Soil pH and dosage rate were negatively correlated ($P < 0.05$) in both the PNAS and PAC treated cores, thus decreasing pH values were associated with higher dosage rates, as hypothesized.

In the 5- to 10-cm layer (Table 2) the alum treated cores (5.3 ± 0.3) had significantly lower ($P < 0.01$) pH values than not only the alum residual treated cores (5.5 ± 0.1) but also the PNAS (5.6 ± 0.2) and control (5.7 ± 0.1) cores. At the 18 g Al m^{-2} dosage specifically, the alum cores had significantly

Table 1. Mean soil physicochemical characterization data for the 0- to 5-cm depth of cores taken from the Orlando Easterly Wetland, ($n = 3$) ± 1 standard deviation.

Treatment†	Dosage	Bulk density	pH	Loss-on-ignition	Total P	Oxalate-extractable Al
	g Al m^{-2}	g cm^{-3}		%	——mg kg^{-1}——	
Alum	9	0.03 ± 0.01	5.6 ± 0.0 b‡	75.8 ± 6.7	1171 ± 131	2514 ± 710 b
	18	0.05 ± 0.04	5.3 ± 0.3 b	70.0 ± 17.9	1024 ± 378	3188 ± 1296 b
	36	0.05 ± 0.04	5.3 ± 0.3 b	71.3 ± 10.9	1235 ± 177	5344 ± 1779 b
PAC	9	0.02 ± 0.00	5.7 ± 0.1 a	75.8 ± 2.1	973 ± 182	1797 ± 188 b
	18	0.03 ± 0.01	5.7 ± 0.2 a	77.1 ± 6.0	1034 ± 182	2106 ± 184 b
	36	0.09 ± 0.13	5.4 ± 0.1 b	50.3 ± 27.5	699 ± 465	2707 ± 2553 b
Alum residual	9	0.02 ± 0.00	5.8 ± 0.0 a	67.7 ± 8.1	921 ± 216	2416 ± 1108 b
	18	0.06 ± 0.02	5.8 ± 0.1 a	55.9 ± 10.8	686 ± 152	3079 ± 1347 b
	36	0.03 ± 0.02	5.9 ± 0.2 a	80.5 ± 2.0	1006 ± 78	5375 ± 995 b
PNAS	9	0.03 ± 0.01	5.8 ± 0.1 a	74.0 ± 5.7	1004 ± 261	3529 ± 769 b
	18	0.02 ± 0.01	5.4 ± 0.1 b	79.8 ± 4.3	1148 ± 119	7116 ± 619.3 b
	36	0.05 ± 0.03	5.2 ± 0.2 b	68.5 ± 4.5	872 ± 100	7733 ± 2926 b
Control	0	0.06 ± 0.01	5.8 ± 0.0 a	66.3 ± 4.0	720 ± 25	890 ± 322 a

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.

‡ Different letters signify a significant difference at the 0.05 probability level for pH and oxalate-extractable Al across all treatments (down the column).

($P < 0.01$) lower pH values than all other Al-amended cores of the same dosage as well as the controls, proving that the alum amendment has the greatest impact on lowering soil pH.

Soil Microbial Characteristics

Microbial biomass P was significantly greater in the surface than subsurface layer of the control ($P < 0.05$), 18 g Al m^{-2} PAC ($P < 0.05$) and PNAS ($P < 0.01$), as well as the 9 g Al m^{-2} alum residual cores ($P < 0.05$), where recently deposited bioavailable nutrients are accessible (Table 3). Aluminum dosage rates were negatively correlated with MBP in the surface layer for the alum ($R^2 = 0.78$, $P < 0.01$), PAC ($R^2 = 0.94$, $P < 0.01$), and PNAS ($R^2 = 0.96$, $P < 0.01$) treated cores. This same trend was not found in the 5- to 10-cm subsurface layer, suggesting that the influence of added Al amendments on microbial biomass is constrained to the uppermost soil layer in the short term.

Microbial activity, as indicated by PMP and SOD rates, was also greater in the surface than the subsurface layer (Table 3). Similar to MBP, a negative correlation existed between increasing Al dosage rates and decreasing surface layer PMP for the alum (R^2

Table 2. Mean soil physicochemical characterization data for the 5- to 10-cm depth of cores taken from the Orlando Easterly Wetland, ($n = 3$) ± 1 standard deviation.

Treatment†	Dosage	Bulk density	pH	Loss-on-ignition	Total P	Oxalate-extractable Al
	g Al m^{-2}	Mg m^{-3}		%	——mg kg^{-1}——	
	9	0.30 ± 0.19	5.3 ± 0.0	34.5 ± 24.3	244 ± 88	582 ± 348
Alum	18	0.29 ± 0.14	5.0 ± 0.3	34.3 ± 15.9	333 ± 235	451 ± 208
	36	0.27 ± 0.17	5.3 ± 0.3	41.6 ± 16.9	485 ± 187	542 ± 198
	9	0.22 ± 0.03	5.3 ± 0.1	62.4 ± 11.5	660 ± 156	798 ± 59
PAC	18	0.32 ± 0.21	5.5 ± 0.1	39.4 ± 30.1	339 ± 311	493 ± 278
	36	0.38 ± 0.57	5.5 ± 0.0	43.4 ± 42.1	512 ± 559	1496 ± 1837
	9	0.13 ± 0.02	5.6 ± 0.1	53.6 ± 16.1	615 ± 202	952 ± 216
Alum residual	18	0.43 ± 0.29	5.5 ± 0.2	29.6 ± 21.2	288 ± 194	591 ± 468
	36	0.32 ± 0.09	5.4 ± 0.1	37.7 ± 21.3	314 ± 239	653 ± 137
	9	0.19 ± 0.10	5.7 ± 0.1	48.1 ± 23.9	484 ± 238	679 ± 233
PNAS	18	0.23 ± 0.12	5.5 ± 0.2	58.5 ± 23.4	580 ± 276	824 ± 169
	36	0.30 ± 0.14	5.4 ± 0.2	37.3 ± 0.9	367 ± 31	765 ± 73
Control	0	0.54 ± 0.34	5.7 ± 0.1	16.6 ± 5.7	119 ± 72	291 ± 230

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.

Table 3. Mean soil microbial characterization data for soil cores taken from the Orlando Easterly Wetland, (n = 3) ± 1 standard deviation.

Treatment†	Depth	Dosage	Microbial biomass P	Potentially mineralizable P	Sediment O_2 demand
	cm	g Al m^{-2}	mg kg^{-1}	mg kg^{-1} d^{-1}	mg kg^{-1} h^{-1}
Alum	0–5	9	139 ± 57.3	37.1 ± 38.4	74.5 ± 20.2 b‡
		18	93.8 ± 56.7	11.9 ± 22.4	42.7 ± 25.3 b
		36	79.8 ± 50.5	7.48 ± 4.71	66.6 ± 24.3 b
	5–10	9	47.3 ± 35.1	3.13 ± 2.54	18.0 ± 16.2 a
		18	103 ± 53.6	0.65 ± 2.32	12.8 ± 4.22 a
		36	43.0 ± 10.9	1.79 ± 1.53	20.2 ± 17.6 a
PAC	0–5	9	143 ± 27.7	11.1 ± 21.5	98.7 ± 9.60 b
		18	128 ± 39.3	8.44 ± 7.38	77.1 ± 13.1 b
		36	115 ± 89.4	12.2 ± 9.91	66.4 ± 52.0 b
	5–10	9	83.8 ± 65.5	5.13 ± 2.87	16.1 ± 3.98 a
		18	30.2 ± 33.1	16.7 ± 25.3	13.7 ± 9.23 a
		36	79.4 ± 62.7	9.76 ± 7.98	33.3 ± 31.1 a
Alum residual	0–5	9	178 ± 27.8	21.5 ± 3.08	175 ± 49.4 c
		18	63.9 ± 18.5	12.3 ± 10.5	92.1 ± 51.2 c
		36	67.5 ± 38.6	8.65 ± 10.4	155 ± 31.8 c
	5–10	9	52.4 ± 20.3	12.6 ± 7.90	13.2 ± 3.80 a
		18	35.0 ± 21.9	0.94 ± 0.45	12.2 ± 8.79 a
		36	36.0 ± 11.5	2.63 ± 1.52	8.70 ± 4.42 a
PNAS	0–5	9	137 ± 64.7	18.8 ± 10.1	164 ± 32.6 c
		18	88.5 ± 19.5	16.6 ± 3.61	184 ± 62.4 c
		36	42.9 ± 63.1	1.87 ± 8.21	99.0 ± 46.5 c
	5–10	9	62.2 ± 33.8	18.0 ± 24.8	8.49 ± 1.26 a
		18	34.9 ± 16.6	3.36 ± 2.89	20.7 ± 13.6 a
		36	40.8 ± 2.96	5.43 ± 5.42	10.0 ± 0.25 a
Control	0–5	0	70.0 ± 8.28	6.18 ± 4.48	72.9 ± 18.7 b
	5–10	0	23.9 ± 8.33	2.15 ± 2.45	3.85 ± 1.07 a

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.

‡ Different letters signify significant difference at the 0.05 probability level for 0–5 cm depth for soil O_2 demand across all treatments (down column).

= 0.81, $P < 0.01$), alum residual ($R^2 = 0.82$, $P < 0.01$), and PNAS ($R^2 = 0.97$, $P < 0.01$) treated cores. This trend did not persist in the subsurface layer.

Soil O_2 demand rates were significantly greater in the surface than the subsurface of control cores ($P = 0.02$), as well as 9 g Al m^{-2} PAC ($P = 0.006$), alum residual ($P = 0.03$), and

PNAS treated cores ($P = 0.01$), 18 g Al m^{-2} PAC and PNAS treated cores ($P < 0.03$), and 36 g Al m^{-2} alum residual ($P < 0.009$) treated cores (Table 3). While there were no significant differences within treatments by dosage, there were differences between treatments. For the surface layer, the alum and PAC treated cores had significantly lower SOD rates than the alum residual and PNAS treated cores ($P < 0.001$). Aluminum dosage rates were negatively correlated with surface layer SOD rates for the PAC ($R^2 = 0.86$, $P < 0.01$) and PNAS ($R^2 = 0.72$, $P < 0.01$) treated cores.

Soil Phosphorus Forms and Associated Metals

Organic P was the dominant form in all cores, averaging 70% organic P (P_o) and 30% inorganic P (P_i) (Table 4) in the surface layer of all treated cores, and 78% P_o and 22% P_i in the surface layer of the control cores. Generally, all P fractions were greater in the surface layer than in the subsurface, similar to TP. In the surface soil layer, the KCl-extractable P, consisting of labile, readily bioavailable P, made up the significantly smallest portion (0.3–4%) of the total P pool ($P < 0.001$). The HCl-extractable Ca and Mg-bound P comprised 6 to 20% of the total P, while as expected, the NaOH-extractable reactive Al and Fe-bound P were the dominant P_i fraction in the Al treated cores, making up 13 to 22% of the total P pool while only accounting for

Table 4. Mean organic (P_o) and inorganic P (P_i) derived from inorganic P fractionation data for the 0 to 5 cm depth interval of cores taken from the Orlando Easterly Wetland, (n = 3) ± 1 standard deviation.

Treatment†	Dosage	NaOH P_o	Residue P_o	Total P_o	KCl P_i	NaOH P_i	HCl P_i	Total P_i
	g Al m^{-2}				mg kg^{-1}			
Alum	9	283 ± 51.0	349 ± 40.1	632 ± 10.9	17.1 ± 12.6	135 ± 26.8	83.7 ± 24.1	235 ± 34.4
	18	207 ± 152	270 ± 41.3	477 ± 166	4.73 ± 6.97	138 ± 137	75.2 ± 25.5	218 ± 152
	36	322 ± 257	414 ± 179	737 ± 434	3.31 ± 1.75	259 ± 206	249 ± 136	511 ± 77.3
PAC	9	247 ± 20.5	342 ± 30.6	590 ± 50.9	27.6 ± 15.1	97.7 ± 11.3	63.1 ± 15.5	188 ± 39.3
	18	271 ± 68.3	299 ± 31.5	570 ± 66.8	15.3 ± 7.97	140 ± 14.3	76.2 ± 19.5	231 ± 27.5
	36	293 ± 200	334 ± 110	628 ± 305	14.5 ± 12.5	144 ± 106	53.2 ± 27.1	211 ± 146
Alum residual	9	373 ± 35.4	434 ± 100	807 ± 132	35.8 ± 19.0	221 ± 96.0	90.5 ± 14.0	348 ± 64.0
	18	169 ± 40.3	247 ± 69.5	416 ± 109	10.3 ± 8.60	88.3 ± 11.6	67.2 ± 3.61	166 ± 16.3
	36	284 ± 41.4	418 ± 195	702 ± 227	10.3 ± 5.77	145 ± 15.1	69.4 ± 13.4	225 ± 26.6
PNAS	9	299 ± 83.7	374 ± 90.3	673 ± 168	7.55 ± 3.85	185 ± 68.0	104 ± 35.7	297 ± 107
	18	378 ± 52.5	396 ± 153	774 ± 199	3.16 ± 0.95	262 ± 60.7	193 ± 199	458 ± 228
	36	295 ± 127	346 ± 117	640 ± 145	2.31 ± 1.34	195 ± 97.6	57.4 ± 21.6	254 ± 98.7
Control	0	150 ± 18.6	333 ± 33.9	517 ± 96.1	11.6 ± 3.47	57.3 ± 10.9	77.2 ± 24.2	146 ± 35.2

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.

9% of the total P in the control cores. Therefore, the addition of Al did lead to an increase in the Al-bound P pool.

There were no significant differences in 1 mol L^{-1} HCl extractable metals within treatment by dosage rates for the surface (0–5-cm) soils (Table 5). There were no significant differences in metals in the control cores; however, the control cores did have significantly lower Al concentrations than all other treated cores due to no Al additions, corresponding to the low NaOH P$_i$. Generally, Mg made up 3% of the HCl-extractable metals in the surface of Al treated cores, Fe 6%, Al 9 to 26%, and Ca dominated, making up 67 to 82% of the extracted metals, suggesting a well-buffered soil with respect to pH due to the high Ca concentrations.

The subsurface layer was once again dominated by organic P, averaging 69% P$_o$ and 31% P$_i$ (Table 6) for treated cores and 87% P$_o$ and 13% P$_i$ for the control cores. Labile P represented 0.3 to 2% of the total P, followed by the Al and Fe bound P, which only made up 5 to 14% of the subsurface P pool. Generally, Ca made up 88% of the HCl-extractable metals within the 5- to 10-cm layer of all cores, Al 5%, Fe 4%, and Mg 3%. There were no significant differences in extractable metals within treatment by dosage.

Table 5. Mean 1 mol L^{-1} HCl extractable metals for soil cores taken from the Orlando Easterly Wetland, (n = 3) ± 1 standard deviation.

Treatment†	Depth	Dosage	Al	Ca	Fe	Mg
	cm	g Al m^{-2}		mg kg^{-1}		
Alum	0–5	9	3005 ± 581 b‡	23479 ± 481	1766 ± 153	840 ± 36
		18	4401 ± 2803 b	21326 ± 5402	1704 ± 504	657 ± 252
		36	4960 ± 2828 b	21368 ± 1181	1694 ± 154	652 ± 96
	5–10	9	508 ± 251	9319 ± 5120	737 ± 384	313 ± 153
		18	446 ± 159	10611 ± 3927	593 ± 82	296 ± 69
		36	473 ± 156	11379 ± 3914	896 ± 431	354 ± 163
PAC	0–5	9	1684 ± 400 b	21264 ± 1381	1618 ± 166	822 ± 72
		18	3062 ± 681 b	24586 ± 1629	1786 ± 20	876 ± 152
		36	2759 ± 1741 b	18319 ± 8468	1440 ± 730	799 ± 95
	5–10	9	689 ± 24	15752 ± 2374	497 ± 179	512 ± 65
		18	455 ± 250	9276 ± 7789	241 ± 168	350 ± 267
		36	1234 ± 1482	11040 ± 9848	871 ± 798	447 ± 332
Alum residual	0–5	9	2161 ± 850 b	25143 ± 710.6	2072 ± 697	964 ± 122
		18	2727 ± 228 b	20923 ± 5954	1662 ± 450	722 ± 249
		36	5239 ± 2119 b	22847 ± 3577	1889 ± 367	919 ± 182
	5–10	9	756 ± 160	14951 ± 5212	504 ± 232	474 ± 84
		18	496 ± 405	8244 ± 6440	310 ± 245	274 ± 203
		36	580 ± 121	9385 ± 6418	315 ± 141	357 ± 171
PNAS	0–5	9	4804 ± 864 b	25120 ± 600	1800 ± 241	790 ± 31
		18	11267 ± 1400 b	23949 ± 1466	1739 ± 304	722 ± 18
		36	11261 ± 8328 b	20656 ± 5075	1779 ± 178	584 ± 167
	5–10	9	672 ± 419	12675 ± 4617	566 ± 459	499 ± 194
		18	641 ± 154	14603 ± 5534	421 ± 99	515 ± 222
		36	589 ± 44	10298 ± 1072	312 ± 97	358 ± 38
Control	0–5	0	693 ± 233 a	17953 ± 3990	1577 ± 129	640 ± 147
	5–10	0	267 ± 205	3571 ± 2485	122 ± 34	174 ± 91

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.
‡ Different letters signify a significant difference at the 0.05 probability level at the 0- to 5-cm depth for Al across all treatments (down the column).

Water Column Results
Soluble Reactive Phosphorus: Incubation Study

The initial Al application rapidly reduced the SRP concentrations in the water columns of cores treated with alum, PAC, and PNAS, stabilizing by Day 3 (Fig. 1a). The SRP concentration in cores treated with alum residual gradually decreased during the 2-wk time period, while concentrations gradually increased with time in the water column of the control cores. All four treatments resulted in significantly lower water column SRP concentrations than the control at all dosage rates. Therefore, all Al amendments were effective at sequestering P; however, alum and PNAS were more effective at sequestering P than PAC, while alum residual was least effective in terms of time for P removal and the total amount of P sequestered.

Table 6. Mean organic (P$_o$) and inorganic P (P$_i$) derived from inorganic P fractionation data for the 5- to10-cm depth interval of cores taken from the Orlando Easterly Wetland, (n = 3) ± 1 standard deviation.

Treatment†	Dosage	NaOH P$_o$	Residue P$_o$	TP$_o$	KCl P$_i$	NaOH P$_i$	HCl P$_i$	TP$_i$
	g Al m^{-2}			mg kg^{-1}				
Alum	9	77.2 ± 59.3	274 ± 313	351 ± 371	2.98 ± 2.34	27.8 ± 27.7	157 ± 138	188 ± 140
	18	46.6 ± 14.2	166 ± 57.6	213 ± 54.7	7.33 ± 10.1	19.5 ± 11.2	75.6 ± 61.3	102 ± 82.4
	36	52.3 ± 32.6	254 ± 111	211 ± 184	2.36 ± 0.82	19.6 ± 11.5	96.3 ± 65.1	394 ± 436
PAC	9	77.4 ± 7.53	271 ± 114	348 ± 110	2.94 ± 1.96	34.2 ± 11.0	186 ± 223	223 ± 232
	18	58.0 ± 37.0	209 ± 186	267 ± 221	2.88 ± 2.21	22.3 ± 17.1	44.2 ± 30.3	69.4 ± 41.7
	36	139 ± 137	252 ± 234	391 ± 371	9.92 ± 8.50	74.7 ± 89.4	63.3 ± 65.2	148 ± 159
Alum residual	9	92.8 ± 26.7	234 ± 79.7	327 ± 81.7	3.74 ± 0.68	42.1 ± 9.15	96.9 ± 21.7	143 ± 28.4
	18	45.8 ± 37.5	161 ± 223	207 ± 259	2.05 ± 1.52	17.5 ± 19.7	60.3 ± 39.6	81.7 ± 54.6
	36	68.6 ± 21.1	198 ± 101	266 ± 120	1.05 ± 0.33	26.7 ± 7.09	29.3 ± 9.30	57.0 ± 14.5
PNAS	9	84.0 ± 45.1	151 ± 81.7	235 ± 38.5	9.67 ± 7.33	36.5 ± 27.2	109 ± 69.9	155 ± 93.6
	18	74.5 ± 36.5	313 ± 333	387 ± 369	2.61 ± 2.42	29.6 ± 17.7	51.2 ± 30.8	83.4 ± 50.5
	36	52.6 ± 13.3	215 ± 76.6	268 ± 89.9	1.54 ± 1.43	17.8 ± 5.36	39.6 ± 25.2	58.9 ± 31.3
Control	0	32.4 ± 19.5	102 ± 77.8	134 ± 96.9	1.44 ± 0.99	10.4 ± 6.62	7.58 ± 4.16	19.4 ± 11.7

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.
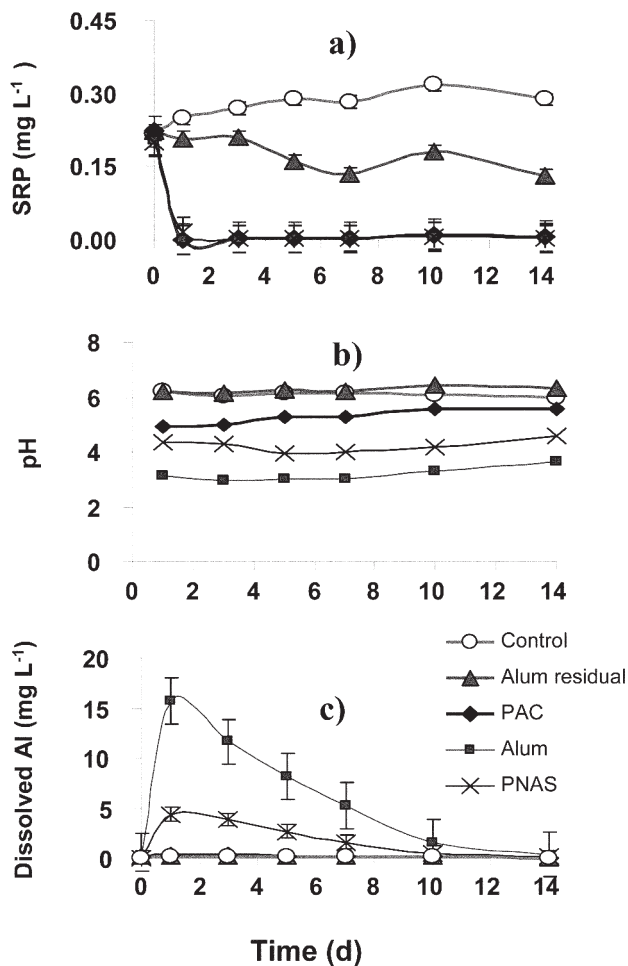
Fig. 1. Changes in water column (a) soluble reactive P (SRP) concentration ($n = 6$), (b) pH ($n = 3$), and (c) soluble Al concentration ($n = 6$) under anaerobic conditions at a treatment dosage of 18 mg Al m^{-2} for soil cores from the Orlando Easterly Wetland; PAC = polyaluminum chloride; PNAS = partially neutralized aluminum sulfate.

Table 7. Mean soluble reactive P flux from constructed wetland soil under anaerobic water column conditions, ($n = 6$) ± 1 standard deviation. A negative flux rate signifies removal from the water column to the sediment.

Treatment†	Dosage	Average P flux
	g Al m^{-2}	mg m^{-2} d^{-1}
Alum	9	−53.3 ± 14.6 a‡
	18	−52.8 ± 23.4 a
	36	−60.4 ± 25.2 a
PAC	9	−49.1 ± 10.7 a
	18	−57.9 ± 17.0 a
	36	−52.4 ± 14.6 a
Alum residual	9	−2.76 ± 3.09 b
	18	−2.61 ± 0.42 b
	36	−2.11 ± 0.71 b
PNAS	9	−50.5 ± 7.94 a
	18	−47.5 ± 11.2 a
	36	−54.9 ± 2.65 a
Control	0	2.27 ± 0.77 c

† PAC, polyaluminum chloride; PNAS, partially neutralized aluminum sulfate.

‡ Different letters signify a significant difference at the 0.05 probability level across all treatments (down the column).

Additionally, there was no significant difference in water column SRP with dosage rate, averaging 0.17 ± 0.06 mg P L^{-1} during the 2-wk time period in the alum residual treatment. For the cores treated with alum, PNAS, and PAC, SRP concentrations were significantly less in the 36 and 18 mg Al m^{-2} treated cores than in the cores treated with 9 mg Al m^{-2}.

The magnitude of the SRP uptake rates of all treatments (−78.9 to −2.75 mg m^{-2} d^{-1}) were equal to or greater than the release rates of the controls (averaging 2.96 mg m^{-2} d^{-1}). At all dosage rates, alum, PNAS, and PAC were more effective at sequestering P than the alum residual (Table 7).

Soluble Reactive Phosphorus: Spiking Study

We repeatedly spiked the water column of each treatment (in triplicate) at Days 0, 8, and 16 after the conclusion of the 15-d flux study to determine the ability of each treatment to sequester P from the water column. After the initial addition of SRP, concentrations rapidly decreased in the water column of cores treated with alum, PNAS, and PAC, stabilizing by the second day at all dosage rates. In the alum residual treated cores, on the other hand, SRP concentrations continued to decrease during the 7-d time period, never fully binding the added P (Fig. 2). Interestingly, the control cores also showed some limited capacity for initial P retention, although these cores had continued to release P during the prior 2-wk incubation study.

Cores treated with alum residual did have a significantly greater sorption capacity than the control cores with time (Fig. 2). Additionally, the sorption capacities of alum, PNAS, and PAC were significantly greater than that of the alum residual at all dosage levels with time, while alum and PNAS had greater sorption capacities than PAC at the 36 and 18 mg Al m^{-2} dosage rates, similar to the results of the incubation study. At the lowest Al dosage, there was a clear separation between all treatment types, with PNAS having a superior P uptake capacity and nearly full recovery to baseline SRP concentrations even after three separate water column spiking events.

Water Column pH

The pH tended to remain relatively stable in the anaerobic water columns, gradually increasing during the 2-wk time period (Fig. 1b). The alum-treated cores always maintained the lowest water column pH values, which were significantly less than all other treatments at the 36 and 18 g Al m^{-2} dosage rates, averaging 2.63 ± 0.19 and 3.19 ± 0.29, respectively. The average pH of the alum treated cores was also significantly less than all other amendments. The PNAS treated cores had the next most acidic water column, with a mean value of 4.12 ± 0.90, significantly lower than that of the PAC, alum residual, and control cores. Finally, the PAC treated cores had significantly lower pH values than the alum residual and control cores at all three Al dosage levels, averaging 4.85 ± 0.96. The alum residual and control cores maintained the highest pH values—at or above 6.0 for the study duration. Additionally, for all treatments, the cores receiving the highest Al dosage had significantly lower water column pH values than the mid- and low-level Al dosages.

Soluble Aluminum

Soluble or dissolved Al concentrations rapidly peaked in the water column after the initial dosing of the cores, and then slowly decreased during the next 10 d (Fig. 1c). Due to the close relationship between pH and Al speciation, the low pH of the water column in cores treated with alum, PNAS, and PAC resulted in a relatively high release of dissolved Al into the water column initially. Overall, alum (12.6 ± 2.38 mg Al L^{-1}) and PNAS (9.32 ± 2.24 mg Al L^{-1}) treated cores had significantly greater water column soluble Al concentrations than the PAC (0.96 ± 0.42 mg Al L^{-1}), alum residual (0.12 ± 0.01 mg Al L^{-1}), and control cores (0.10 ± 0.01 mg Al L^{-1}). The average soluble Al concentration was directly correlated to the dosage rate for alum ($R^2 = 0.98$, $P < 0.05$), alum residual ($R^2 = 0.99$, $P < 0.05$), PAC ($R^2 = 0.92$, $P < 0.05$), and PNAS ($R^2 = 0.97$, $P < 0.05$) treated cores.

DISCUSSION

All amendments tested decreased the flux of P from the soil over the controls. Alum and PNAS were more effective than PAC, however, while the alum residual was the least effective overall. An increased dosage rate led to a lower water column P for the alum, PNAS, and PAC, while the alum residual was insensitive to loading rate. These results suggest that each of the amendments might be valuable management tools in constructed wetlands during times of poor P removal, except for the alum residual. While alum, PAC, and PNAS removed more P with increased dosage, the alum residual did not. It is probable that much of the sorption capacity in alum residual either is inactivated by P or organic matter in the water treatment process or sorption sites are slowly accessible due to diffusion constraints. Consequently, adding alum residual on an "effective Al basis" as the other three amendments would probably physically fill up the wetland, reducing the water treatment volume, which would be counter to the goal of extending the effective nutrient removal of aging wetlands. Results of the spiking experiment have also demonstrated that, in addition to intercepting SRP released from the soil, the chemical amendment treatment can also remove additional P from the water column. This is an additional benefit of chemical amendments application in treatment wetlands during periods of low treatment effectiveness.

It is important to be cognizant of the pH effects in both the water column and the soil related to the use of each of the amendments. As these experiments were conducted in static water columns, the pH of the water column was considerably lower than a flow-through system would produce. We can discern from the results, however, that pH can certainly be a significant problem in adding Al-containing amendments to a wetland system. Where pH drops are experienced in alum lake applications, the effects are generally short lived, usually within hours (Welch and Shrieve, 1994).

There are several consequences for P removal in the low pH of soil and water in constructed wetlands. Pools of P could be mobilized from the soil, in particular, soils with P associated with Ca-bound P. Shifts in soil pH can also affect the microbial pool, which can be very pH sensitive (Malecki-Brown et al., 2007). Finally, a low or high pH can lead to increased Al^{3+} ion availability, which can have toxicological effects on
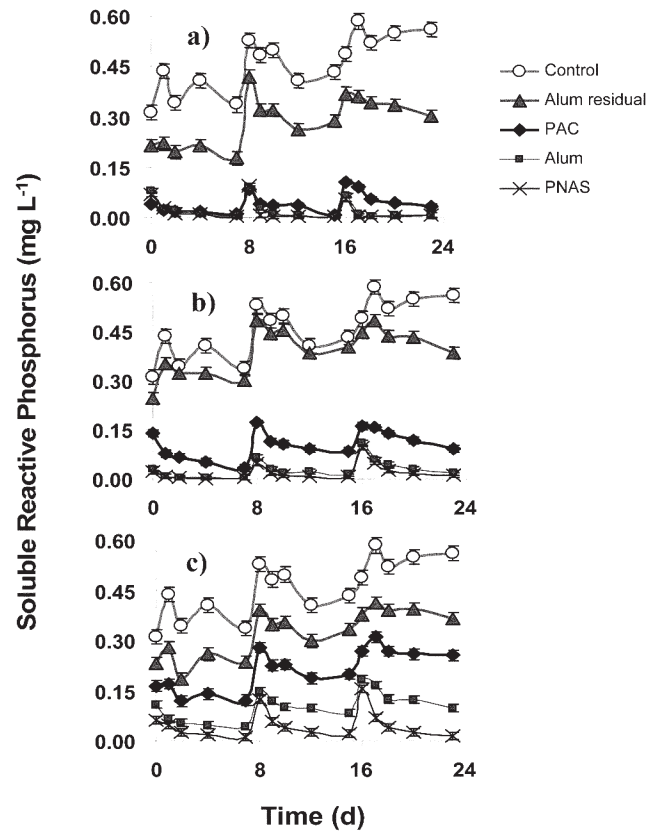

Fig. 2. Changes in soluble reactive P concentration in the water column during weekly P spiking at treatment dosages of (a) 36, (b) 18, and (c) 9 mg Al m^{-2} for soil cores from the Orlando Easterly Wetland (*n* = 3); PAC = polyaluminum chloride; PNAS = partially neutralized aluminum sulfate.

the plant and benthic communities; however, the pH must remain displaced from circumneutral for this to be of concern. This research does support the assertion that the primary benefit of utilizing alternatives such as PNAS and PAC, as indicated by Beecroft et al. (1995) and Jiang and Graham (1998), is that they do not decrease the water column pH to as great an extent as alum, due to their polymerized composition, and therefore have potentially less environmental impact in a wetland system.

While the goal of this research was to investigate short-term sequestration of P, which is generally highest in the surface soil (Grace et al., 2008), there could potentially be an effect of continued chemical amendments on the overall long-term nutrient removal of the wetland. Biogeochemical processes associated with nutrient removal are driven ultimately by the microbial population and activity and by plant uptake. Greater microbial biomass is frequently observed in the surface soil layer due to C availability (DeBusk and Reddy, 1998) and would be in close proximity of the amendments. While not the case in this laboratory study, a 5-mo planted, mesocosm-scale, continuous, slow-drip alum addition experiment found decreased microbial biomass and activity in the surface soil (Malecki-Brown et al., 2007). A potential P limitation could negatively affect the biogeochemical cycling of N, decreasing denitrification and mineralization rates (White and Reddy, 2001, 2003).

With regard to greater biotic effects, Al has been shown to interfere with Ca absorption and transport in terrestrial plants, resulting in reduced Ca concentrations in both the roots and

shoots of Al-stressed plants (Bennet et al., 1987; Thornton et al., 1987). The relationship between Ca availability and Al toxicity is complex, involving a variety of physiological mechanisms that continue to be debated (Matsumoto, 2000; Barcelo and Poschenrieder, 2002; Rengel and Zhang, 2003), while research in the arena of aquatic macrophytes is severely lacking. Aluminum toxicity has been found to be toxic to fish at concentrations as low as 0.1 mg L^{-1} at a pH below 6 or above 10 (Baker, 1982; Neville, 1985; Ramamoorthy, 1988). As long as the pH of the system in question remains above 6, however, typically there should be no negative side effects on fish.

CONCLUSIONS

Alum and the three Al-containing alternatives to alum (PAC and PNAS to a greater extent than the alum residual) were all effective at short-term P sequestration in an organic treatment wetland soil. Under all treatment rates, PAC, PNAS, and alum had the ability to both intercept the P released from the soil and also remove P spiked to the water column, with PNAS performing most effectively at the lowest loading rate. On an Al basis, alum residual underperformed the P sorption capacity of the liquid amendments, with negligible changes in soil and water chemistry. In contrast, surface soil and water column characteristics for alum, PAC, and PNAS showed decreased soil pH and negative impacts on the microbial community, as well as low water column pH and high soluble Al concentrations with increasing application rates. To minimize these negative impacts, the minimum dosage necessary for effective treatment should be applied. The long-term efficacy of a one-time application of these chemical amendments is currently unknown when utilizing alum or its alternatives in a treatment wetland.

Treatment wetland management generally requires monitoring the outflow of the wetland to meet specific discharge criteria. During the winter months, wetlands in the southern United States may become less effective at treating P as plants senesce and microbial activity slows. Application of alum or Al-containing amendments to soil proximal to the outflow regions of the wetland may provide an effective short-term management tool to maintain discharge concentrations within permitted values during these inefficient wetland treatment times. Caution should be exercised, however, about repeated dosages until more long-term data become available.

REFERENCES

American Public Health Association. 1992. Standard methods for the examination of water and wastewater. 18th ed. APHA, Washington, DC.

Andersen, J.M. 1976. An ignition method for determination of total phosphorus in lake sediments. Water Res. 10:329–331.

Baker, J.P. 1982. Effects on fish of metals associated with acidification. p. 165–176. In R.E. Johnson (ed.) Acid rain/fisheries. Am. Fisheries Soc., Bethesda, MD.

Barcelo, J., and C. Poschenrieder. 2002. Fast root growth responses, root exudates, and internal detoxification as clues to the mechanisms of aluminum toxicity and resistance: A review. Environ. Exp. Bot. 48:75–92.

Beecroft, J.R., M.C. Koether, and G.W. vanLoon. 1995. The chemical nature of precipitates formed in solutions of partially neutralized aluminum sulfate. Water Res. 29:1461–1464.

Bennet, R.J., C.M. Breen, and M.V. Fey. 1987. The effects of aluminum on root cap function and root development in Zea mays L. Environ. Exp. Bot. 27:91–104.

Black, C.A., and W.R. Wise. 2003. Evaluation of past and potential phosphorus uptake at the Orlando Easterly Wetland. Ecol. Eng. 21:277–290.

Blake, G.R., and K.H. Hartge. 1986. Bulk density. p. 363–375. In A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Boisvert, J.P., and C. Jolicoeur. 1999. Influences of sulfate and/or silicate present in partially prehydrolyzed Al(III) flocculants on Al(III) speciation in diluted solutions. Colloids Surf. A 155:161–170.

Bostic, E.M., and J.R. White. 2007. Soil phosphorus and vegetation influence on wetland phosphorus release after simulated drought. Soil Sci. Soc. Am. J. 71:238–244.

Brookes, P.C., D.S. Powlson, and D.S. Jenkinson. 1982. Measurement of microbial biomass phosphorus in soil. Soil Biol. Biochem. 14:319–329.

Burney, J.L., S.T. Baccus, and J.B. Lee. 1989. An evaluation of wildlife utilization in a man-made freshwater wetland system in central Florida, USA. p. 24–48. In F.J. Webb, Jr. (ed.) Proc. Annu. Conf. on Wetlands Restoration and Creation, 16th, Plant City, FL. 25–26 May 1989. Hillsborough Community College, Plant City, FL.

Butkus, M.A., D. Grasso, C.P. Schulthess, and H. Wijnja. 1998. Surface complexation modeling of phosphate adsorption by water treatment residual. J. Environ. Qual. 27:1055–1063.

Chakraborti, R.K., K.H. Gardner, J.F. Atkinson, and J.E. Van Benschoten. 2003. Changes in fractal dimension during aggregation. Water Res. 37:873–883.

Chua, T. 2000. Mineralization of organic phosphorus in a subtropical freshwater wetland. Ph.D. diss. Univ. of Florida, Gainesville.

Conkle, J.L., J.R. White, and C.D. Metcalfe. 2008. Reduction of pharmaceutically active compounds by a lagoon wetland wastewater treatment system in southeast Louisiana. Chemosphere 73:1741–1748.

Cooke, G.D., E.B. Welch, S.A. Peterson, and P.R. Newroth. 1993. Phosphorus activation and sediment oxidation. p. 161–209. In Restoration and management of lakes and reservoirs. Lewis Publ., Boca Raton, FL.

Dao, T.H., L.J. Sikora, A. Hamasaki, and R.L. Chaney. 2001. Manure phosphorus extractability as affected by aluminum- and iron by-products and aerobic composting. J. Environ. Qual. 30:1693–1698.

Dayton, E.A., and N.T. Basta. 2005. A method for determining the phosphorus sorption capacity and amorphous aluminum of aluminum-based drinking water treatment residuals. J. Environ. Qual. 34:1112–1118.

D.B. Environmental. 2004. An evaluation of the use of alum to enhance phosphorus removal performance by the Orlando Easterly Wetlands. D.B. Environmental, Rockledge, FL.

DeBusk, W.F., and K.R. Reddy. 1998. Turnover of detrital organic carbon in a nutrient-impacted Everglades marsh. Soil Sci. Soc. Am. J. 62:1460–1468.

DeBusk, W.F., K.R. Reddy, M.S. Koch, and Y. Wang. 1994. Spatial distribution of soil nutrients in a northern Everglades marsh: Water Conservation Area 2A. Soil Sci. Soc. Am. J. 58:543–552.

Degens, B.P., L.A. Schipper, G.P. Sparling, and L.C. Duncan. 2001. Is the microbial community in a soil with reduced catabolic diversity less resistant to stress or disturbance? Soil Biol. Biochem. 33:1143–1153.

DeLaune, R.D., and C.J. Smith. 1985. Release of nutrient and metals following oxidation of freshwater and saline sediment. J. Environ. Qual. 14:164–168.

Ebeling, J.M., P.L. Sibrell, S.R. Ogden, and S.T. Summerfelt. 2003. Evaluation of chemical coagulation–flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge. Aquacult. Eng. 29:23–42.

Fisher, M.M., and K.R. Reddy. 2001. Phosphorus flux from wetland soils affected by long-term nutrient loading. J. Environ. Qual. 30:261–271.

Grace, K.A., F.E. Dierberg, T.A. DeBusk, and J.R. White. 2008. Phosphorus uptake by Typha leaf litter as affected by oxygen availability. Wetlands 28:817–826.

Hedley, M.J., and J.W.B. Stewart. 1982. Method to measure microbial

phosphorus in soils. Soil Biol. Biochem. 14:319–329.

Jiang, J.Q., and N.J.D. Graham. 1998. Pre-polymerised inorganic coagulants and phosphorus removal by coagulation: A review. Water SA 24:237–244.

Koether, M.C., J.E. Deutschman, and G.W. vanLoon. 1993. A bench-scale evaluation of the performance of a polynuclear aluminum coagulent. p. 303–319. *In* W. Robertson et al. (ed.) Disinfection dilemma: Microbiological control versus by-products. Am. Water Works Assoc., Denver, CO.

Koether, M.C., J.E. Deutschman, and G.W. vanLoon. 1997. Low-cost polymeric aluminum coagulent. J. Environ. Eng. 123:859–864.

Lim, C.H., and M.L. Jackson. 1982. Dissolution for total elemental analysis. p. 1–12. *In* A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Lind, C.B. 2003. Alum chemistry, storage and handling in lake treatment applications. p. 89–90. *In* Proc. North Am. Lake Manage. Soc. Southeastern Lakes Management Conf., 12th, Orlando, FL. 2–5 June 2003. North Am. Lake Manage. Soc., Madison, WI.

Makris, K.C., W.G. Harris, G.A. O'Connor, and T.A. Obreza. 2004. Phosphorus immobilization in micropores of drinking-water treatment residuals: Implications for long-term stability. Environ. Sci. Technol. 38:6590–6596.

Malecki, L.M., J.R. White, and K.R. Reddy. 2004. Nitrogen and phosphorus flux rates from sediment in the Lower St. Johns River Estuary. J. Environ. Qual. 33:1545–1555.

Malecki-Brown, L.M., J.R. White, and K.R. Reddy. 2007. Soil biogeochemical characteristics influenced by alum application in a municipal wastewater treatment wetland. J. Environ. Qual. 36:1904–1913.

Martinez, C.J., and W.R. Wise. 2003. Hydraulic analysis of Orlando Easterly Wetland. J. Environ. Eng. 129:553–560.

Matsumoto, H. 2000. Cell biology of aluminum toxicity and tolerance in higher plants. Int. Rev. Cytol. 200:1–46.

May, H.M., P.A. Helmke, and M.L. Jackson. 1979. Gibbsite solubility and thermodynamic properties of hydroxyaluminum ions in aqueous solutions at 25°C. Geochim. Cosmochim. Acta 43:861–868.

McKeague, J.A., and J.H. Day. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46:13–22.

Neville, C.M. 1985. Physiological response of juvenile rainbow trout, *Salmo gairdneri*, to acid and aluminum: Prediction of field responses from laboratory data. Can. J. Fish. Aquat. Sci. 42:2004–2019.

Powlson, D.S., and D.S. Jenkinson. 1981. A comparison of the organic matter, biomass, adenosine triphosphate and mineralizable nitrogen contents of ploughed and direct-drilled soils. J. Agric. Sci. 97:713–721.

Ramamoorthy, S. 1988. Effect of pH on speciation and toxicity of aluminum to rainbow trout (*Salmo gairdneri*). Can. J. Fish. Aquat. Sci. 46:634–642.

Reddy, K.R., Y. Wang, W.F. Debusk, M.M. Fisher, and S. Newman. 1998. Forms of soil phosphorus in selected hydrologic units of the Florida Everglades. Soil Sci. Soc. Am. J. 62:1134–1147.

Rengel, Z., and W.H. Zhang. 2003. Role of dynamics of intracellular calcium in aluminium-toxicity syndrome. New Phytol. 159:295–314.

Robert, M. 1995. Aluminum toxicity: A major stress for microbes in the environment. p. 227–247. *In* P.M. Huang et al. (ed.) Environmental

impact of soil component interactions. Vol. II. Metals, other inorganics, and microbial activities. CRC Press, Boca Raton, FL.

Simon, S.M. 2003. Phosphorus retention and release of soils in a constructed wetland for wastewater treatment. M.S. thesis. Univ. of Florida, Gainesville.

Steinman, A., R. Rediske, and K.R. Reddy. 2004. The reduction of internal phosphorus loading using alum in Spring Lake, Michigan. J. Environ. Qual. 33:2040–2048.

Thornton, F.C., M. Schaedle, and D.J. Raynal. 1987. Effects of aluminum on red spruce seedlings in solution culture. Environ. Exp. Bot. 27:489–498.

USEPA. 1993. Methods of chemical analysis of water and wastes. USEPA 600/R-93/100. Environ. Monit. Support Lab., Cincinnati, OH.

Van Hullebusch, E.V., V. Deluchat, P.M. Chazal, and M. Baudu. 2002. Environmental impact of two successive chemical treatments in a small shallow eutrophied lake: Part I. Case of aluminum sulphate. Environ. Pollut. 120:617–626.

Viraraghavan, T., and C.H. Wimmer. 1988. Polyaluminum chloride as an alternative to alum coagulation: A case study. p. 480–498. *In* Proc. Can. Soc. Civ. Eng. Annu. Conf., Calgary, AB. May 1988. Can. Soc. Civ. Eng., Montreal, QB.

Wang, H., and J.W. Jawitz. 2006. Hydraulic analysis of cell-network treatment wetlands. J. Hydrol. 330:721–734.

Wang, H., J.W. Jawitz, J.R. White, C.J. Martinez, and M. Sees. 2006. Rejuvenating the largest municipal treatment wetland in Florida. Ecol. Eng. 26:132–146.

Welch, E.B., and G.D. Schrieve. 1994. Alum treatment effectiveness and longevity in shallow lakes. Hydrobiologia 275/276:423–431.

White, J.R., M.A. Belmont, and C.D. Metcalfe. 2006a. Pharmaceutical compounds in wastewater: Wetland treatment as a potential solution. Sci. World J. 6:1731–1736.

White, J.R., and K.R. Reddy. 1999. The influence of nitrate and phosphorus loading on denitrification enzyme activity in Everglades wetland soils. Soil Sci. Soc. Am. J. 63:1945–1954.

White, J.R., and K.R. Reddy. 2000. Effects of phosphorus loading on organic nitrogen mineralization of Everglades soils. Soil Sci. Soc. Am. J. 64:1525–1534.

White, J.R., and K.R. Reddy. 2001. Effect of select inorganic electron acceptors on organic nitrogen mineralization in northern Everglades soils. Soil Sci. Soc. Am. J. 65:941–948.

White, J.R., and K.R. Reddy. 2003. Nitrification and denitrification rates of everglades wetland soil along a phosphorus-impacted gradient. J. Environ. Qual. 32:2436–2443.

White, J.R., K.R. Reddy, and M.Z. Moustafa. 2004. Influence of hydrology and vegetation on phosphorus retention in Everglades stormwater treatment wetlands. Hydrol. Processes 18:343–355.

White, J.R., K.R. Reddy, and J.M. Newman. 2006b. Hydrology and vegetation effects on water quality in subtropical constructed wetlands. Soil Sci. Soc. Am. J. 70:1242–1251.

Zvomuya, F., C.J. Rosen, and S.C. Gupta. 2006. Phosphorus sequestration by chemical amendments to reduce leaching from wastewater applications. J. Environ. Qual. 35:201–215.