

Potential Internal Loading of Phosphorus in Constructed Wetlands

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ABSTRACT

Construction of wetlands on agricultural lands, especially those used for dairy operations could result in solubilization of P stored in soils and release to the water column. To study the extent of initial P flux during the start-up period, intact soil-cores from land areas used for dairy operations were obtained and flooded with adjacent creek water. In the first 28-day hydraulic-retention period, P concentration in the water column increased up to 218 times due to P flux from impacted soils. A continuous decrease in P flux to the water column up to third cycle (initial floodwater P concentration 0.2 mg L^{-1}), and constant thereafter (initial floodwater P concentration up to 0.4 mg L^{-1}) suggest that the effect of initial floodwater P upon P flux could be limited. The initial release may be due to high concentration of labile P, however, slow dissolution of relatively stable pools of P could maintain steady flux, well above of that observed from non-impacted soils. The water soluble P along with double acid-extractable magnesium (Mg) could explain up to 76% of the variability in cumulative P flux to the water column. It is apparent that co-occurrence of active adsorption-desorption phenomena due to independent maintenance of P equilibrium by individual P compounds in soils may regulate the P dynamic of the water column.

INTRODUCTION

Phosphorus flux from soils to the overlying water column depends on various factors including physico-chemical characteristics of soils and the P concentration in floodwater used. Construction of wetlands on highly fertilized agricultural lands or manure-impacted lands such as those used for dairy operations could result in solubilization of P stored in soils and release into the water column. A significant portion of the water column P could be removed by biotic (Greenway and Woolley, 1999; Reddy et al., 1999), and abiotic processes (Reddy et al., 1987; Tanner et al., 1998). However, during initial stabilization period, flooded soil conditions could enhance the dissolution of Ca bound P, hydrolysis of Fe/Al bound P, and mineralization of organic P. Several studies have reported on the potential use of wetlands for removal of nutrients including P from wastewater

(Kadlec and Knight, 1996). However, wetland soils could function as source or sink for P (Richardson, 1985) depending on the quality and quantity of native P. During stabilization period, Storm Water treatment Areas (STAs) can potentially export P to the water column until the system reaches equilibrium. The objectives of this study were to (1) measure the extent of P flux from soils of different dairy components to the overlying water column, (2) determine the effect of floodwater P concentration on P flux from soils, and (3) estimate the P sequestration efficiency of the proposed Storm Water Treatment Areas (STAs).

MATERIALS AND METHODS

Site description

The proposed Nubin Slough STAs construction is a part of an effort to reduce P loads to Lake Okeechobee. The proposed STA site (New Palm/Newcomer dairies) is located 2.1 km north of Lake Okeechobee and 10.5 km southeast of the city of Okeechobee, occupies an area of approximately 864 hectares. The soils of the proposed site are primarily Spodosols. The abandoned-intensive (areas that had active dairy operations in the past, but as pastures and/or forages at the time of sampling), active-intensive (areas that had operating dairy), and native (non-impacted, forested area) components occupy 13, 18 and 7% of the total STA, respectively. However, both the forage/pasture and grazing/spray field components account 31% each. The adjacent sites to the STA include intensive agriculture, wetland and upland forests, and urban and reclaimed lands.

Soil-core sampling and analysis

Intact soil cores of 30 cm long x 6.9 cm (internal diameter) were collected from abandoned-intensive, active-intensive, forage/pasture, and native components using polypropylene column. Moreover, to determine selected physico-chemical characteristics, soil samples were collected from A horizon of the respective components.

Soil pH was determined using 1:2 soil to water ratio. Similarly, double acid-extractable ($0.0125 \text{ M H}_2\text{SO}_4 + 0.05 \text{ M HCl}$) calcium (DACa), magnesium (DAMg), and P (DAP) were extracted as described by Mehlich (1953) and analyzed using Inductively Coupled Argon Plasma Spectroscopy (Thermo Jarrell Ash ICAP 61E, Franklin, MA). Amorphous and poorly crystalline Fe and Al (hydr)oxides were determined by oxalate method as described by Loeppert and Inskeep (1996). Soils (1 g) was extracted with 0.175 M ammonium oxalate + 0.1 M oxalic acid at a sediment/solution ratio of 1:60 by shaking on a mechanical

shaker for 4 h. The suspensions were then centrifuged at 5,000 g for 15 min and filtered through a 0.45 μm membrane filter in dark. The filtrates were analyzed for Fe and Al by the Inductively Coupled Argon Plasma Spectrometry.

Water soluble P (WSP) was determined by extracting 5 g soils with 25 mL deionized water for 1 h, and the suspensions were centrifuged at 5,000 g for 15 min and filtered through a 0.45 μm membrane filter. The filtrates were then analyzed for total P (TP) using automated ascorbic acid method following persulfate digestion (Method 365.1, EPA, 1993). For soil total P (TP) determination, 0.5 – 1.0 g finely ground dry soil was combusted at 550 $^{\circ}\text{C}$ in a muffle furnace for 4 h and the ash was dissolved in 6 M HCl (Anderson 1976). The digestate was analyzed for P using an automated ascorbic acid method (Method 365.1, EPA, 1993).

Soil-core flooding and incubation

Each soil core was subjected to initial re-wetting by introducing filtered adjacent (Taylor) Creek water (pH 7.4) (diluted; containing 0.08 mg P L^{-1}) from the bottom of the core to avoid entrapment of air and leaching of P. Once the cores were fully saturated, floodwater depth was raised to 10 cm by slow addition of 450 mL of the diluted filtered site water on to the top of the columns. The columns were kept in the dark at 25 $^{\circ}\text{C}$ to prevent algal growth, and slowly aerated to maintain aerobic conditions. The floodwater was sampled at 0, 1, 3, 7, 14, 21 and 28 days, and filtered through a 0.45 μm membrane filter and analyzed for soluble reactive P (SRP) using automated ascorbic acid method (Method 365.1, EPA 1993). Total dissolved P was also determined in the floodwater by the ascorbic acid method following persulfate digestion as described previously. The sampled floodwater was replenished with equal volume of filtered site water after each sampling, however, the reduction in floodwater level due to evaporation was replenished with distilled water prior to sampling. Three more 28-day hydraulic retention cycle was repeated with diluted or spiked site water of 0.14, 0.20, and 0.4 mg P L^{-1} initial concentrations, and floodwater was sampled intermittently as described above.

Since there was no significant difference among the amounts of TP, TDP and SRP, the potential P flux from soil to the water column was estimated by plotting SRP release per unit surface area of the water column. The slope of P release (mg m^{-2}) vs. flooding period (days) was taken as an average potential P flux ($\text{mg m}^{-2} \text{day}^{-1}$) from soil to the water column and presented separately for each cycle of each component.

Phosphorus release or retention (P_r) was calculated using the following equation:

$$P_r = K_a * C_0 - F_p \quad [1]$$

Where, P_r = net P retention or release per unit surface area of soils (mg m^{-2}), K_a = P assimilation coefficient (L m^{-2}), C_0 = initial floodwater P concentration (mg L^{-1}), and F_p = potential P flux from per unit surface area of soils (mg m^{-2}).

$$\text{Since } P_r = (C_0 - C_t) * V/A \quad [2]$$

Where, C_t = final floodwater P concentration at time (t) 28 days, V = volume of floodwater, and A = surface area of soils.

Experiments were carried out in at least in triplicates, and statistical analysis was performed using Statgraphics plus version 3.1 (Statistical Graphics Corp., 1997). Unless otherwise stated, regression analysis was performed at $p \leq 0.05$ level.

RESULTS AND DISCUSSION

The P flux from soils to the water column was mostly SRP, which indicates the direct increase in available P in the water column consequently, problematic to P sequestration efforts. Phosphorus concentration of the water column increased several folds (up to 218 times) as a result of P flux from soils of abandoned-intensive and active-intensive areas at the end of 28-day hydraulic-retention time of 1st cycle. However, during subsequent cycles, water column P concentration substantially decreased (Fig. 1). Overall increase in water column P was relatively low from soils of forage/pasture areas. In general, final water column P was highest in soil cores obtained from active-intensive area followed by abandoned-intensive, forage/pasture, and native areas, respectively.

In 1st hydraulic-retention cycle, the potential P flux to the water column varied from 15 – 93 $\text{mg P m}^{-2} \text{ day}^{-1}$ in abandoned-intensive area, 27 – 61 $\text{mg P m}^{-2} \text{ day}^{-1}$ in active-intensive area, and 3 – 31 $\text{mg P m}^{-2} \text{ day}^{-1}$ in forage/pasture area. However, the flux was substantially lower in native area, ranging from 3 – 10 $\text{mg P m}^{-2} \text{ day}^{-1}$. As expected, the average P flux to the water column was highest from soils of active-intensive (45 $\text{mg P m}^{-2} \text{ day}^{-1}$) followed by abandoned-intensive (33 $\text{mg P m}^{-2} \text{ day}^{-1}$), forage/pasture (12 $\text{mg P m}^{-2} \text{ day}^{-1}$), and native (7 $\text{mg P m}^{-2} \text{ day}^{-1}$) areas, respectively. Higher P flux from soils of abandoned-intensive and active-intensive areas was expected because of high accumulation of P resulting from intensive dairy operation. Soils of these areas have high concentrations of labile P as shown by Mehlich P (see Table 1). In addition, flooding probably resulted in release of P from solubilization of Fe- and Al-bound P.

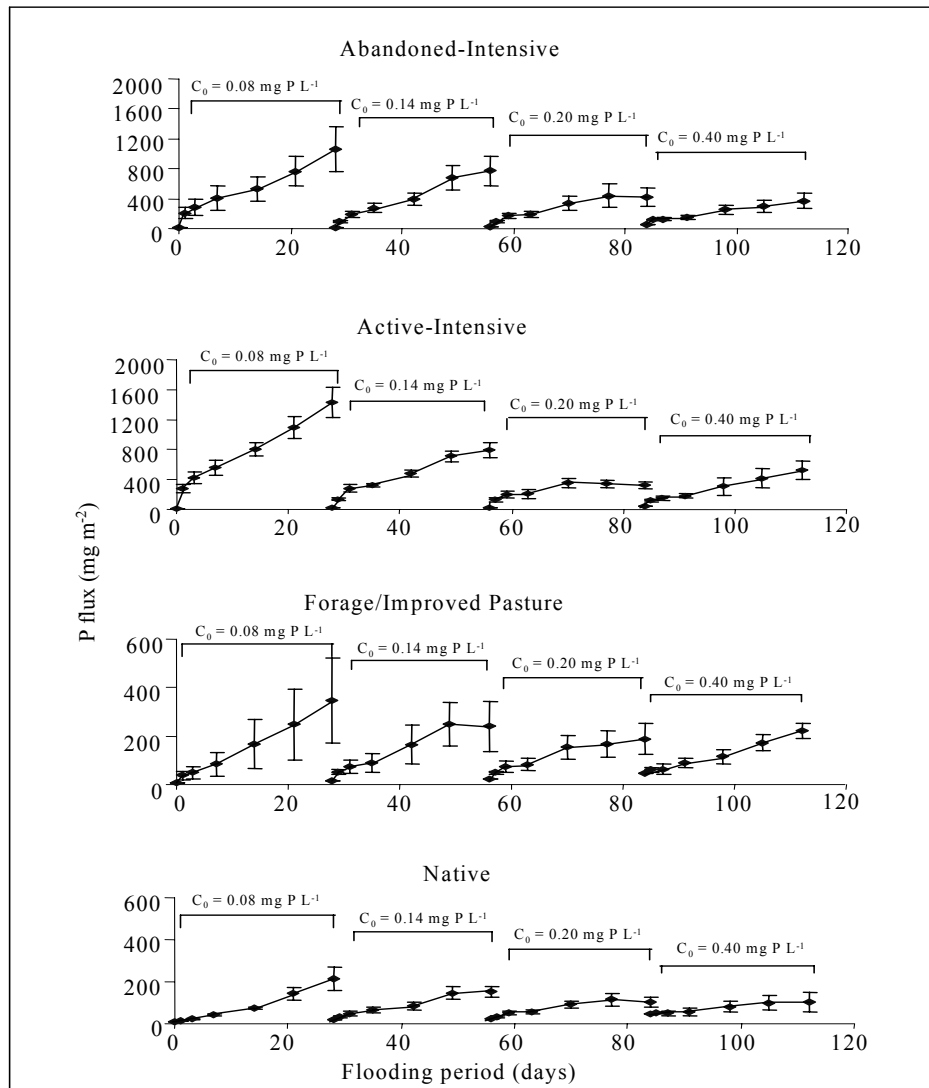


Fig. 1 Phosphorus flux to the water column from different dairy components.

Table 1. Selected physico-chemical characteristics of A-horizon soils (N>3). WSP: water soluble phosphorus, DACa: double acid-extractable Ca, DAMg: double acid-extractable Mg, DAP: double acid-extractable phosphorus, TP: total phosphorus, ox-Fe: oxalate-extractable iron, and ox-Al: oxalate-extractable aluminum.

Site	pH	WSP	DACa	DAMg	DAP	TP	ox-Fe	ox-Al
-----g m ⁻² -----								
Abandon-Intensive	6.2	1.9	193	13.0	20.5	52.4	21.5	79.5
Active-Intensive	6.2	2.1	162	12.2	6.9	20.4	12.5	10.1
Forage/Pasture	5.7	0.5	118	9.0	2.5	15.1	23.2	12.6
Native	5.0	0.7	103	16.3	0.6	19.1	36.9	12.6

As described in the 1st cycle, a high degree of variability was observed in P flux from soils to the water column among replicates of the same component. The difference in potential P flux from soils of abandoned-intensive and active-intensive areas reduced substantially in subsequent cycles (Fig. 2) perhaps, because of the depletion of soluble P. The potential P flux from abandoned-intensive component to the water column decreased steadily up to the last (4th) hydraulic-retention cycle. The overall decrease in P flux in the consecutive hydraulic-retention cycles may have also been affected by the initial concentrations of P in the water used to flood the soil-cores resulting in alteration of P equilibrium status (Mayer and Gloss, 1980; Froelich, 1988).

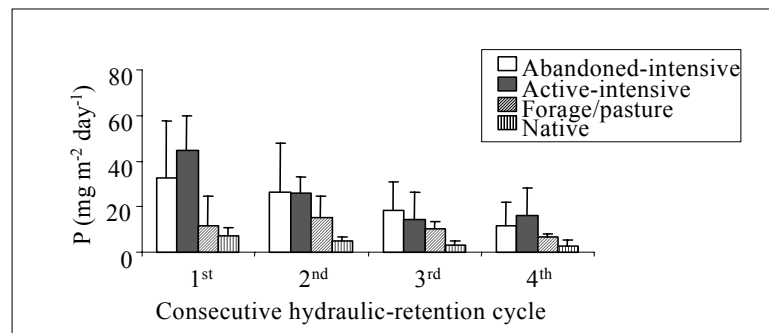


Fig. 2 Potential P flux to the water column from various dairy components in different hydraulic-retention cycles.

Soil cores collected from active-intensive component had maximum cumulative P flux to the water column followed by abandoned-intensive, forage/pasture, and native components, respectively (Table 2). These results from abandoned-intensive and active-intensive components together with higher P released from soils of Bh horizon compared to A horizon of abandon-intensive components (Reddy et al., 2000) suggest that P content of the A horizon is mainly involved in the P exchange processes.

As expected, P flux declined up to the 3rd cycle because of the decrease in solubilization of stored P in soil-cores as well as the increases in initial floodwater P concentrations (Fig. 3), which suppressed the release of P from soils due to changes in the P equilibrium. A continuous decrease in P flux to the water column up to 3rd cycle (initial floodwater P concentration 0.2 mg L⁻¹), and relatively constant thereafter, suggest that initial floodwater P (at <0.2 mg P L⁻¹) may have negative effect on P flux. It is estimated that total P flux from abandoned-intensive, active-intensive, forage/pasture and native areas to the water column could be 4.4, 2.8, 1.6 and 1.9 tons in 1st, 2nd, 3rd and 4th hydraulic-retention cycles,

respectively. The total P flux was slightly higher in the 4th cycle than the 3rd, perhaps due to the slow dissolution of some of the inorganic P compounds, and mineralization of organic P (Sanchez, 1976) from active intensive component. It could be predicted that P flux to the water column could remain constant from 3rd hydraulic-retention cycle until the relatively available (double acid-extractable) P is exhausted from soils given the initial floodwater P concentration remains in the range of 0.2-0.4 mg L⁻¹.

Table 2. Phosphorus flux from different dairy components to the overlying water columns (N>3).

Field component	Area coverage	P flux	
	-----ha-----	---kg ha ⁻¹ ----	---% of TP---
Abandoned-Intensive	112	26	10
Active-Intensive	152	31	17
Forage/Pasture	272	10	6
Native	64	6	3

Using average P flux to the water column, and available P content in A horizon soils (DAP, which was about 46% of TP), it is estimated that soils from abandoned-intensive component could take an average of 3 years to stop releasing P to the water column, whereas, the other components would take less than a year. Though the variability of the data for the estimation of time frame to exhaust available P was quite high due to the heterogeneity within the individual dairy components, the actual time required for STAs to start to sequester P could be quite long under the given conditions.

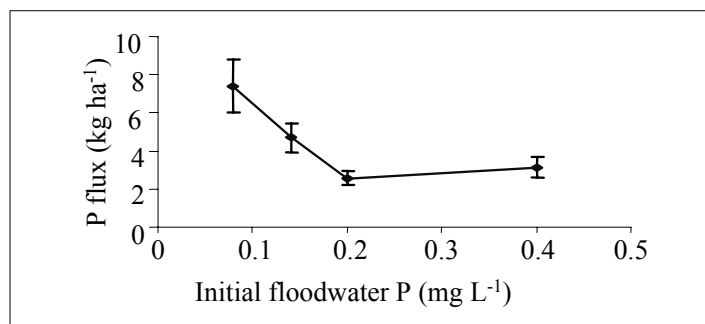


Fig. 3 Effects of initial floodwater P concentration on P flux to the water column.

Water soluble P (WSP) alone could explain 54% of the variability in potential P flux during 2nd and 3rd, and 51% during 4th hydraulic-retention cycles, whereas only 21% of that in the 1st hydraulic-retention cycle (Table 3). The low

predictability for the potential P flux in 1st hydraulic-retention cycle is not known, however, the possible co-occurrence of both active adsorption and desorption phenomena (Barrow, 1983) due to independent maintenance of P equilibrium by individual P compounds (Pant and Reddy, 2000) may have played a major role. Though decrease in potential P flux occurred with the increase in initial P concentration of the water column, no significant correlation was obtained perhaps, because of the confounding of the effect with P depletion.

Table 3. Multiple linear regression analysis of potential phosphorus flux in different hydraulic-retention cycles from soils and selected independent variables. R²: equivalent to variability explain, SE: standard error of estimation, DW: Durbin-Watson statistic (value >1.4 indicates no auto-correlation in residuals), P flux: potential P flux (mg m⁻² day⁻¹), and WSP: water soluble P (mg kg⁻¹).

Hydraulic-retention cycle	Fitted model equation	R ² (%)	SE	DW
1 st	P flux = 17.7 + 0.01[WSP]	21	20.8	1.7
2 nd	P flux = 9.5 + 0.01[WSP]	54	11.4	2.5
3 rd	P flux = 5.6 + 0.01[WSP]	54	7.7	2.1
4 th	P flux = 3.8 + 0.004[WSP]	51	6.9	2.0

Moreover, WSP could also explain 57% and 58% of the variability in cumulative P flux to the water column in 2nd and 4th hydraulic retention cycles (Table 4). Similarly, in 3rd hydraulic retention cycle, water soluble P along with double acid-extractable Mg could explain 76% of variability in cumulative P flux to the water column, whereas in 1st hydraulic retention cycle, water soluble P could only explain 17% of the variability. It is apparent that in initial flooding soluble P release from soils to the water column and adsorb by soil constituents, which have high affinity for P including ox-Fe and ox-Al, thereafter, relatively passive alternate P adsorption-desorption phenomena in soils may regulate the P dynamic of the water column.

Table 4. Multiple linear regression analysis of cumulative phosphorus flux in different hydraulic-retention cycles from soils and selected independent variables. R²: equivalent to variability explain, SE: standard error of estimation, DW: Durbin-Watson statistic (value >1.4 indicates no auto-correlation in residuals), C_p flux: cumulative P flux (total flux in 28-day hydraulic-retention cycle, mg m⁻²), WSP: water soluble P (mg kg⁻¹), and DAMg: double acid-extractable Mg (mg kg⁻¹).

Hydraulic-retention cycle	Fitted model equation	R ² (%)	SE	DW
1 st	C _p flux = 580 + 0.21[WSP]	17	729	1.7
2 nd	C _p flux = 228 + 0.24[WSP]	57	327	2.3
3 rd	C _p flux = 185 + 0.15[WSP] – 0.01[DAMg]	76	138	2.1
4 th	C _p flux = 136 + 0.14[WSP]	58	187	1.9

CONCLUSIONS

This study indicated that highly soluble manure P may be released during first 28 days of flooding, but the slow dissolution of relatively stable pools of P (Fe-, Al-, Ca- and Mg-bound P) could maintain steady flux, well above of that observed from native sites. The study suggests that P flux potential of soils should be given serious consideration prior to STA construction, otherwise massive internal P loading could reduce the effectiveness of the wetlands. By treating soils with chemical amendments, establishing vegetation or flushing the initially released P may potentially stabilize the system, and maintain P removal efficiency.

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