Influence of Flooding on Phosphorus Mobility in Manure-Impacted Soil

H. K. Pant,* V. D. Nair, K. R. Reddy, D. A. Graetz, and R. R. Villapando

ABSTRACT

Agricultural lands are often used for constructing stormwater treatment areas (STAs) to abate nutrient loading to adjacent aquatic systems. Flooding agricultural lands to create STAs could stimulate a significant release of phosphorus (P) from soil to the water column. To assess the suitability of agricultural lands, specifically those impacted by animal operations, for the construction of STAs, soils from different components of the New Palm–Newcomer dairies (Nubbin Slough Basin, Okeechobee, Florida, USA) were collected by horizon and their P retention and release capacities estimated. In general, P released from A-horizon soil under flooded (anaerobic) conditions was greater than under drained (aerobic) conditions due to redox effect on iron (Fe) and consequent P releases. However, the P released from Bh-horizon soil was greater under aerobic conditions than under anaerobic conditions, possibly due to excessive aluminum (Al) content in the horizon. Double acid–extractable calcium (Ca), magnesium (Mg), Al, and P explained 87% of the variability in P release under aerobic conditions, and 80% of that under anaerobic conditions. The P release maxima indicated a high solubility of P in A-horizon soil from both active and abandoned dairies (13 and 8% of the total P, respectively), suggesting that these soils could function as potential sources of P to the overlying water column when used in STA construction. Preestablishment of vegetative communities or chemical amendment, however, could ameliorate high P flux from soil to the water column.

LAND areas used for animal operations are known to accumulate P in soils. Both surface and subsurface discharges from these areas have been detrimental for protecting and restoring adjacent water bodies. Constructed wetlands and retention reservoirs are considered low-cost alternatives for treating wastewater from various sources, including agricultural runoff. A significant portion of the water-column P can be removed by biological (Newbold et al., 1983; Greenway and Woolley, 1999; Reddy et al., 1999) and chemical processes both in natural and constructed wetlands (Diaz et al., 1994; Pant et al., 2001). In many watersheds, land areas previously used for agricultural operations are being converted to wetlands. Flooding these areas can stimulate the dissolution of stored P and increase the P concentrations in the water column (Pant and Reddy, 2000).

Phosphorus runoff from dairies and beef cattle ranches in the Okeechobee Basin, Florida, USA is one of the major sources of P loading to Lake Okeechobee. The soils in the basin are primarily Spodosols; the A and E horizons of the soil profile are sandy and have low P sorption capacities, whereas Bh and Bw horizons have greater P sorption capacities (Mansell et al., 1991) due to greater Al- and Fe-oxide contents (Nair et al., 1998). Although a constructed wetland can be a cost-effective method for removing soluble P from runoff waters, the ambient storage of P in soils, as well as other physico–chemical characteristics of the soils (e.g., pH, Ca, Mg, Fe, and Al contents) are critical for selecting an STA construction site. Studies of P sorption characteristics and release potential of soils of any proposed site should indicate whether the STAs would effectively sequester P. The objectives of this study were to (i) determine the P sorption capacity of soils collected from different horizons and (ii) estimate the P releasing potential of the soils to the water column.

MATERIALS AND METHODS

Site Description

Construction of the Nubbin Slough STA is proposed as a part of the Lake Okeechobee Water Retention/Phosphorus Removal Critical Restoration Project. The project is designed to increase regional water storage north of Lake Okeechobee by on-site wetland restoration and water retention, and to reduce P in surface runoff. The site is located in Newcomer and New Palm dairies, which are 2.1 km north of Lake Okeechobee and 10.5 km southeast of the town of Okeechobee. The site occupies an area of approximately 4.49 km² (Fig. 1).

The site has an abandoned–intensive component, referring to land that had previously been under dairy production for 34 yr, but had been used for pastures or forage production for the last 8 yr. The site also has an active-intensive component, referring to areas with active dairies for the last 20 yr, and a native component, referring to nonimpacted or forested areas. The abandoned–intensive, active-intensive, and native components occupy 13, 18, and 7% of the total land area of the proposed STA, respectively, while the forage–pasture, grazing field, and spray field components account for 31, 15, and 16% of the total, respectively. The adjacent land use of the proposed STA site includes intensive agriculture, wetland and upland forests, and urban and reclaimed lands. Soils from A, E, and Bh horizons of representative locations (from three to nine locations within each component) of the Newcomer–New Palm dairy site were sampled for P retention and release studies. An auger was used to get samples from different depths, and the horizon was identified by visual difference in the soil layer. The average depths were 10, 20, and 11 cm for

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Abbreviations: DA-, double acid–extractable; SRP, soluble reactive phosphorus; STA, stormwater treatment area; TP, total phosphorus; WSP, water-soluble phosphorus.
the A, E, and Bh horizons, respectively. Soils were sieved through 5-mm mesh and air-dried prior to analysis.

Water samples were also collected from Stations 1 and 2 (Fig. 1) each year from 1989 to 1999. The samples were collected throughout the year with a flow-weighted autosampler. In each year we collected at least seven samples.

**Chemical Analysis**

Air-dried soils were extracted with double acids (0.0125 M H$_2$SO$_4$ + 0.05 M HCl) as described by Mehlich (1953). The double-acid extracts were analyzed for aluminum (DA-Al), iron (DA-Fe), calcium (DA-Ca), magnesium (DA-Mg), and
phosphorus (DA-P) with inductively coupled argon plasma emission spectrometry (Thermo Jarrell Ash [Franklin, MA] ICAP 61E). Amorphous and poorly crystalline Fe and Al (hydr)oxides were determined by the oxalate method described by Loepert and Inskeep (1996). Soil (1 g) was extracted with 0.175 M ammonium oxalate + 0.1 M oxalic acid at a soil to solution ratio of 1:60 by shaking on a mechanical shaker in the dark for 4 h. The suspensions were then centrifuged at 5000 × g for 15 min and filtered through a 0.45-μm filter. The filtrates were analyzed for Fe and Al by inductively coupled argon plasma spectrometry. Soil pH was measured by shaking 1:2.5 soil to deionized distilled water in an end-over-end mechanical shaker for 1 h; thereafter, pH was measured in the suspensions using a pH meter.

Water-soluble phosphorus (WSP) was determined by extracting 5 g air dry soil with 25 mL deionized water for 1 h. The suspensions were then centrifuged at 5000 × g for 15 min and filtered through a 0.45-μm filter. The filtrates were analyzed for soluble reactive phosphorus (SRP) using an automated ascorbic acid method (Method 365.1; USEPA, 1993). For soil total phosphorus (TP) determination, 0.5 to 1.0 g finely ground, dry soil was combusted at 550°C in a muffle furnace for 4 h, and the ash was dissolved in 6 M HCl ( Andersen, 1976). The digestate was analyzed for P using the automated ascorbic acid method as described above.

The water samples collected from Stations 1 and 2 (as mentioned previously) were also analyzed for TP with an automated ascorbic acid method following the persulfate digestion method (Method 365.1; USEPA, 1993).

**Phosphorus Retention Maxima**

Diverting water from Taylor Creek, Okeechobee, FL is being considered as a method to flood the proposed STA. Thus, the site water was obtained from Taylor Creek to perform P retention and release studies. The site water was diluted five times to mimic ambient conditions while having low P. The original P content in the site water was 0.4 mg L⁻¹. Two grams of air-dried soil was equilibrated with 20 mL 100 mg P L⁻¹ (prepared in 0.45-μm-filtered site water) for 24 h in an end-over-end shaker at room temperature (25 ± 2°C). The suspensions were then filtered, and the filtrate stored at 4°C until analysis for SRP. The amount of P lost from solution during 24 h of equilibration was considered as the existing and/or remaining P sorption capacity (Sₚₑₑ) of soils. It is usually denoted as P₁₀₀ (i.e., P retention measured at 1000 mg P kg⁻¹ soil), a single-point isotherm at which sorption sites in soils are assumed to be saturated with added P. The term is calculated as follows (Reddy et al., 1998):

\[ P₁₀₀ = \frac{(C₀V - CₚV)}{W} \]

where \( C₀ \) = initial P concentration (100 mg L⁻¹), \( V \) = solution volume (L), \( Cₚ \) = P concentration in solution after 24 h of equilibration (mg L⁻¹), and \( W \) = dry weight of soil (kg).

**Phosphorus Release Maxima**

Highly manure-impacted soil could have a high P release potential. Thus, to estimate the P release potentials of the highly impacted soils, 2 g of A- and Bh-horizon soil from the abandoned- and active-intensive components were extracted with 20 mL diluted and filtered site water (containing 0.08 mg P L⁻¹) for 1 h. The suspensions were centrifuged at 5000 × g and filtered through a 0.45-μm filter, and the supernatants were analyzed for SRP. The residues were extracted repeatedly for five more consecutive cycles, and the supernatants were centrifuged and filtered as described above and analyzed for SRP. To estimate the P release maxima of soils under anaerobic conditions, 2 g soil was weighed in a 50-mL centrifuge tube and flooded with 5 mL diluted and filtered site water (containing 0.08 mg P L⁻¹), capped with air-tight rubber septa, and purged with N₂ gas. The tubes were pre-incubated by submerging in a water bath maintained at room tempera-
Table 2. Estimated storage of different phosphorus forms in the stormwater treatment area (STA) soil profiles. The estimations were based on bulk densities of 1.31, 1.51, and 1.48 g cm$^{-3}$ for A, E, and Bh horizons, respectively, as provided by Graetz and Nair (1995) for the area soils.

<table>
<thead>
<tr>
<th>Dairy component</th>
<th>Area (ha)</th>
<th>Soil depth (cm)</th>
<th>Water-soluble P (Mg)</th>
<th>Double acid-extractable P (Mg)</th>
<th>Total P (Mg)</th>
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</thead>
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<tr>
<td>Abandoned-intensive</td>
<td>58</td>
<td>12.3</td>
<td>1.1</td>
<td>11</td>
<td>43</td>
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<tr>
<td>Active-intensive</td>
<td>79</td>
<td>11.5</td>
<td>1.6</td>
<td>17</td>
<td>43</td>
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<td>Forage and pasture</td>
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<td>2.3</td>
<td>22</td>
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<td>11</td>
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<td>13</td>
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<tr>
<td>Native</td>
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<td>0.1</td>
<td>0.1</td>
<td>3.0</td>
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<tr>
<td>Spray field</td>
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<td>10.2</td>
<td>0.2</td>
<td>0.4</td>
<td>7.0</td>
</tr>
<tr>
<td>Total</td>
<td>449</td>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td>20</td>
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<td>4.0</td>
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<tr>
<td>Active-intensive</td>
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<td>17</td>
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<tr>
<td>Forage and pasture</td>
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<td>2.6</td>
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</tr>
<tr>
<td>Grazing field</td>
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<td>19.2</td>
<td>0.1</td>
<td>0.2</td>
<td>2</td>
</tr>
<tr>
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<td>10</td>
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<td>Forage and pasture</td>
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<tr>
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<td>0.1</td>
<td>2.9</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td>449</td>
<td></td>
<td></td>
<td></td>
<td>67</td>
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</table>

ture (25 ± 2°C) for 30 d, and purged with N$_2$ gas weekly to ensure anaerobic conditions (Pant and Reddy, 2001). At the end of the 30-d incubation, an additional 15 mL de-aerated diluted site water was added, and the suspension shaken for 1 h. The supernatants were separated by centrifugation, acidified with one drop of concentrated H$_2$SO$_4$, and analyzed for SRP. To avoid oxidation, especially of Fe$^{2+}$ to Fe$^{3+}$, and consequent precipitation of P, the filtration was carried out in an N$_2$ atmosphere.

Data Analysis

The data were subjected to two-way analysis of variance (ANOVA) using SAS (SAS Institute, 1996) wherever necessary. Statistical significance was tested using least significant difference (LSD) at the p < 0.05 level. The multiple linear regression analysis of the P release vs. selected variables was performed using Statgraphics Plus Version 3.1 (Statistical Graphics, 1997) at the p ≤ 0.05 significance level.

RESULTS AND DISCUSSION

Soil Chemical Characteristics

The pH of the A-horizon soil ranged from 5.0 in the native area to 6.3 in the active-intensive area (Table 1). The amounts of WSP were 3.7 and 2.7% of soil TP, respectively, from active– and abandoned–intensive areas. This suggests a substantial P flux could occur from the highly manure-impacted areas to the water column during the initial phase of the wetland operation (Pant and Reddy, 2000) if these areas converted to wetlands. The soils from forage–pasture and native areas contained smaller amounts of WSP; however, the relative compositions were 3 and 4% of TP, respectively. Since soil DA-P was relatively high in active– and abandoned–intensive areas, the P flux to the water column could be substantial. The Bh-horizon soil had pH values ranging from 4.7 to 6.5, while E-horizon soil had slightly acidic to near-neutral pH (6.1–7.2). The E horizon is eluted, and generally has low oxalate-extractable Fe and Al, and acid-extractable Ca, Mg, Al, and Fe, resulting in relatively low P sorption capacities compared with other horizons (Nair et al., 1995). Soil from both active–intensive and abandoned–intensive areas had more WSP and TP than forage–pasture, grazing field, spray field, or native areas, reflecting greater manure inputs. Soil collected from the proposed STA contained substantial amounts of readily available P (WSP) and potentially bioavailable P (DA-P) in all three soil horizons (Table 2). Thus, massive internal P loading to the water column could occur due to vertical as well as lateral movement of P through the eluted E horizon of Spodosols. The occurrence of such phenomena can be substantiated by P contained in waters collected at two locations within the proposed STAs over a decade (Fig. 2). Though P concentrations in the runoff from an impacted dairy component (Station 2) and a canal running along various dairies (by Station 1) may vary widely, a continuous substantial P flux from soil to the water column in the proposed STAs had occurred over the decade from the impacted area. The total area of the proposed STAs is estimated to contain 32 and 31 Mg of potentially bioavailable P (DA-P) in A and Bh horizon, respectively. Similarly, the E horizon of the STA area is estimated to contain 16 Mg of potentially bioavailable P. Thus, preestablishment of vegetative communities or chemical amendment are probably necessary for STA effectiveness.
Phosphorus Retention Maxima

The use of the single-point isotherms for determining the maximum retention capacities of soils is well documented for upland soils (Nair et al., 1998), as well as for wetland soils and stream sediments (Reddy et al., 1998). In general, the maximum retention capacity ($P_{1000}$) values varied for A, E, and Bh horizons, with greater retention capacity for the Bh horizon (Fig. 3). A vertical movement of P from the A to Bh horizon could occur as well as horizontal movement from heavily manure-impacted areas to lesser manure-impacted areas through the eluted E horizon. For Okeechobee Basin soil, the P retention capacity is generally related to the Al and Fe content of the soils (Nair et al., 1998; Reddy et al., 1998). Such a significant relationship could not be found for the soils used in this study, perhaps due to high accumulations of soluble P. Moreover, $P_{1000}$ represents only the existing and/or remaining P sorption capacity, unlike maximum sorption capacity ($S_{max}$), which implies total P sorption capacity; thus, such relationship have not been obtained. The P retention capacity of the soils from the A horizon of highly manure-impacted areas were relatively low compared with that of Bj, suggesting the movement through the eluted E horizon could allow P redistribution.

Phosphorus Release Maxima

In the single 1-h extraction, P released from the A horizon of the abandoned-intensive area varied from 2 to 8% and 1 to 12% of TP under aerobic and anaerobic conditions, respectively. However, the P released was greater from the A horizon of the active-intensive area compared with the abandoned-intensive area (2–15% of TP under aerobic and 4–23% of TP under anaerobic conditions). The average P released from the A horizon of the abandoned-intensive area was significantly greater under anaerobic conditions than aerobic (Fig. 4; 7.8 and 5.1% of TP under anaerobic and aerobic conditions, respectively, and significant at $p \leq 0.05$) because of the reduction of Fe(III) to Fe(II) under anaerobic conditions and consequent release of associated P (Froelich, 1988; Pant and Reddy, 2001). Though release from the A horizon of active-intensive areas under anaerobic conditions (8.8% of TP) was greater than release under aerobic conditions (7.2% of TP), they were not significantly different, possibly due to higher variability. Phosphorus released from the Bh horizon of the abandoned-intensive area varied from 2 to 20% of TP under...
Dairy components
Fig. 4. Phosphorus released from active- and abandoned-intensive areas soils in a single 1-h water extraction under aerobic and anaerobic conditions. Error bars represent ± standard error of the means.

aerobic conditions, and from 0.8 to 11% of TP under anaerobic conditions. However, the P released from the Bh horizon of the active–intensive area was less than P release from abandoned–intensive areas under both conditions (0–11% of TP under aerobic and 0–5% of TP under anaerobic conditions). Unlike A-horizon soil, the average P released from the Bh horizon of the abandoned–intensive area was significantly greater under aerobic conditions than anaerobic (Fig. 4; 8.8 and 4.6% of TP under aerobic and anaerobic conditions, respectively, and significant at p ≤ 0.05). The large amounts of amorphous and noncrystalline forms of Al content in the Bh horizon along with pH may have played major roles. The pH values of the Bh-horizon soil averaged 6.5, where maximum solubility of many elements, including P, is known to occur. Thus, greater P release under aerobic conditions compared with anaerobic conditions (increase in pH and decrease in Eh) may result in precipitation as calcium phosphates. Though the P released under aerobic conditions from Bh-horizon soil of the active–intensive area was greater compared with that under anaerobic conditions (2.9 and 1.4% of TP, respectively), they were not significantly different, possibly due to overall low release and higher variability.

The net (cumulative) P released during six consecutive 1-h extractions from Bh-horizon soil of the abandoned–intensive area was significantly greater than that of the A horizon (Fig. 5; 67.9 and 24.6 mg P kg⁻¹ from Bh and A horizons, respectively, and significant at p ≤ 0.05). However, in the active–intensive area, P release from A-horizon soil was greater than Bh-horizon soil (A = 59.6 mg P kg⁻¹, Bh = 10.4 mg kg⁻¹). These results suggest a downward movement of manure P over time, as reported by Nair et al. (1998). Thus, while decommissioning dairies could reduce the immediate threat of P enrichment to water bodies, it may not be so in the long term due to the possibility of lateral as well as vertical P movement through the eluted E horizon.

Regression analysis of P released and other selected properties of A- and Bh-horizon soil indicated that double acid–extractable Ca, Mg, Al, and P together predicted 87 and 80% of the variability in P release from soils under aerobic and anaerobic conditions, respectively (Table 3). Under both aerobic and anaerobic conditions, P release was inversely related to double acid–extractable Ca and Al, but directly related to double acid–extractable Mg and P. These observations indicated that acid-extractable Ca and Al would help to reduce P level in the water column, while Mg would increase it. Perhaps Mg-associated P is not as stable as Ca-associated P (despite their co-occurrence), suggesting independent maintenance of equilibrium by each P compound in solution (Pant and Reddy, 2001), and behavior as a mixture of homogenous surfaces for P sorption.

CONCLUSIONS
Amorphous and poorly crystalline Fe generally control P retention and release phenomena in soils and
Table 3. Multiple linear regression analysis of P released from the A- and Bh-horizon soils under aerobic and anaerobic conditions, and selected independent variables.

<table>
<thead>
<tr>
<th>Redox condition</th>
<th>Fitted model equation†</th>
<th>R²‡</th>
<th>SE§</th>
<th>DW¶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic</td>
<td>P release = 8.66 - 0.02(DA-Ca) + 0.24(DA-Mg) - 0.04(DA-A1) + 0.31(DA-P)</td>
<td>87</td>
<td>23.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Anaerobic</td>
<td>P release = 13.85 - 0.01(DA-Ca) + 0.09(DA-Mg) - 0.04(DA-A1) + 0.15(DA-P)</td>
<td>80</td>
<td>12.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

† DA-, double acid-extractable, measured in mg kg⁻¹.
‡ Equivalent to variability explained by the fitted model.
§ Standard error of estimation.
¶ Durbin-Watson statistic (value > 1.4 indicates no autocorrelation in residuals).
# Data from both A and Bh horizons included.

sediments (Pant and Reddy, 2001). However, moderately stable (double acid-extractable) Ca and Al could also influence the net release by re-adsorbing some of the released P. On the other hand, Mg-associated P could contribute to increased P release under both aerobic and anaerobic conditions. Impacted soils not only release P upon flooding, but also tend to saturate the P sorption sites, increasing the equilibrium P concentration. The substantial solubility of P stored in the Bh (19% of TP) and A (8% of TP) horizons suggests that abandoned manure-impacted soils can be problematic to surface and ground waters as far as P enrichment is concerned. Soils from active dairies can also be a potential threat to surface waters because of the high solubility of the stored P (13% of TP) in the A horizon. Such areas may represent less of an immediate threat to ground waters because of the low solubility of P stored in the Bh horizon (4% of TP); however, the release of P from the Bh horizon could increase due to P movement from the surface soils over time. Phosphorus measured in waters collected from in and around STAs and the P storage in different horizons of the STA soils suggest that preestablishing vegetative communities or pretreating manure-impacted soils may help to sequester released P in the early operation phase of the STA.

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