

Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland

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Received 10 April 1998; received in revised form 2 December 1998; accepted 8 December 1998

Abstract

Soils previously used for agriculture are currently being converted to wetlands with the goal that they will function as sinks for nutrients. However, residual fertilizer nutrients, especially phosphorus (P) are rapidly released upon flooding. The objective of this study was to evaluate the efficacy of selected chemical amendments in immobilizing the soluble soil P. Soil used in the study was an organic soil, obtained from a 3-month old constructed wetland created on an agricultural land in Lake Apopka Basin, central Florida. Chemical amendments used were: CaCO₃, (calcite), Ca(OH)₂, CaMg(CO₃)₂ (dolomite), Al₂(SO₄) (alum), FeCl₃ and mixtures of selected amendments. The effective amounts required for each chemical amendment to minimize P release from soil to overlying floodwater were 7–15 g kg⁻¹ for CaCO₃ and Ca(OH)₂, 12 g kg⁻¹ for alum, and 1–2 g kg⁻¹ for FeCl₃. Based on P flux, the order of effectiveness in immobilizing soluble P was as follows: FeCl₃ > alum > Ca(OH)₂ > calcite > dolomite. High rates of chemical amendments are needed to reduce P levels, because of complexation of P binding cations (Ca, Fe and Al) with organic matter. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alum; Flooding; Liming; Phosphorus release; Water quality; Wetland soils

1. Introduction

Phosphorus (P) inputs to aquatic systems are attributed to agricultural runoff, domestic and industrial discharges, and precipitation. Control of point-source discharges by chemical treatment started about 20 years ago, and today it is a well established technology (Balmer and Hultman,

1988). The advantages of chemical amendments over other restoration methods are relative ease of application, wide scope of applicability, and high potential for P inactivation, while disadvantage is the formation of flocculent hydrous oxides which can be potentially resuspended by wave action and currents in shallow lakes (Sanville et al., 1976). Sedimentation on top of existing sediments after applying chemicals may be one of the critical factors in reducing the effectiveness of P entrapment (Cooke et al., 1986).

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The addition of Ca based amendments can result in the formation of a variety of insoluble phosphate compounds. The formation of calcium phosphate compounds is closely related to the concentrations of Mg (Martens and Harris, 1970), carbonate ions (Stumm and Morgan, 1981), organic acids (Sinha, 1971), humic substances (Inskeep and Silvertooth, 1988a), end redox potential (Moore and Reddy, 1994) and pH (Olila and Reddy, 1995). In calcareous sediments, P inactivation is associated with calcium compounds (House, 1990), while in non-calcareous soils it is controlled by the solid phases containing Fe and Al (Hsu, 1975).

The addition of alum and ferric chloride results in decrease of soil pH. Application of Al or Fe salts for P removal results in the precipitation of aluminium hydroxy phosphate ($Al_x[OH]_y[PO_4]_z$) and ferric hydroxy phosphate ($Fe_x[OH]_y[PO_4]_z$). Also, aluminium phosphate and ferric phosphate in discrete forms may be precipitated at lower pH. However, under anaerobic conditions, ferric phosphate compounds dissolve due to the reduction of Fe^{3+} to Fe^{2+} and ortho-phosphate ions are released into the water column. Combined applications of alum with $CaCO_3$ to the soil may have the advantage of controlling pH in the neutral range. It may be essential to apply mixtures of chemicals to soils that have a low pH buffering capacity.

Soils previously used for agriculture are currently being converted to marshes with the hope that these constructed wetlands will function as nutrient sinks. Such systems are created in areas adjacent to sensitive aquatic systems. Flooding previously fertilized agricultural lands results in solubilization of residual fertilizer nutrients such as inorganic P and their release into the overlying water column (D'Angelo and Reddy, 1994). To reduce P flux from soils it may necessary to immobilize soluble P into non-available forms and reduce P flux into floodwater. This may be accomplished by adding chemical amendments containing Ca, Fe, or Al that bind P into insoluble forms. The addition of chemicals to inactivate/precipitate soluble P has long been used in advanced wastewater treatment (Ferguson and McCarty, 1971; Cooke and Kennedy, 1981) be-

cause of their efficiency in P removal and ease of application to wastewater (Balmer and Hultman, 1988). This technology was extended to restore excessively eutrophic lakes (Cooke et al., 1986) and immobilize contaminants in stormwater retention ponds (Babin et al. 1992).

The objectives of this study were to determine: (1) the influence of various chemical amendments on P flux between the soil and the overlying floodwater, and (2) the solubility of P in chemically amended soils and its relation to soil physico-chemical properties.

2. Material and methods

2.1. Soil sampling and characterization

Bulk soil (Typic medisaprists, euic, hyperthermic) was obtained from a 3-month-old constructed wetland under cultivation for the past three decades. The constructed marsh is located on the northwest shore of Lake Apopka (central Florida) at 28°40'N latitude and 81°41'W longitude (Lowe et al., 1989). Crops grown on these soils were vegetables and sod. Bulk soil samples were obtained from the 0 to 15 cm depth, and air-dried to create drained conditions.

Soil pH (1:1 soil:water) was measured with a glass electrode and pH meter. Dissolved P and selected cations were determined by extracting soil with deionized water (1:400, soil:water) for 15 min., followed by filtration through a 0.45 μ m membrane filter. A total of six extractions with distilled water were performed sequentially on each sample. All solution samples were analyzed for dissolved reactive P (DRP) using Standard Methods (APHA, 1992), while Ca, Mg, Al, and Fe in the extracts were determined using atomic absorption spectroscopy.

Total inorganic P and selected metal ions were extracted with 1 M HCl (1:400, soil: 1 M HCl 400) for 3 h, followed by filtration through a 0.45 μ m membrane filter. All extracts were analyzed for P and selected cations as described above. Total P (TP) was determined on soil samples ashed in a furnace at 550°C for 5 h, following the methods described by Anderson (1976). Total P and metal

ions in digested solutions were determined as described above.

2.2. Laboratory incubation

Preliminary studies (Ann, 1995) showed that Lake Apopka marsh soil (created on an agricultural land) is a high potential source of P, and its release to the ambient water can be prevented by treating the soil with selected inorganic chemicals. The amount of chemical amendment added to each of these soil columns was determined on the basis of preliminary studies (Ann, 1995). A known amount of air-dried soil was mixed with selected chemicals at precalculated amounts and placed in a plastic bag. The mixture of soil and specific amendment was transferred into a Plexiglas column (I.D. = 5 cm) stoppered at the bottom and packed to field bulk density of 0.28 g cm^{-3} . The soil was flooded with filtered water from Lake Apopka to obtain a water depth of 10 cm. Each treatment consisted of three replications. The chemical amendments were applied at the following rates (rate is referred as the amount of chemical amendment applied per dry mass of soil):

1. CaCO_3 : (0, 9, 15.3, 40 and 102 g kg^{-1} of soil)
2. Ca(OH)_2 : (0, 6.7, 11.3, 30, and 75 g kg^{-1} of soil)
3. $\text{CaMg(CO}_3)_2$: (0, 14.7, 25.4, 67 and 170 g kg^{-1} of soil)
4. Alum: (0, 3.7, 7.1, 14.5, and 23 g kg^{-1} of soil)
5. FeCl_3 : (0, 1.8, 3.5, 7.1, and 11.5 g kg^{-1} of soil)
6. $\text{CaCO}_3 + \text{Ca(OH)}_2$ (0, $4.5 + 3.34$, $7.6 + 3.8$, $20.2 + 15.1$, and $51 + 38 \text{ g kg}^{-1}$ of soil)
7. $\text{CaCO}_3 + \text{alum}$ (0, $4.5 + 1.9$, $7.6 + 3.8$, $20.2 + 7.3$, and $51 + 11.6 \text{ g kg}^{-1}$ of soil)
8. $\text{CaCO}_3 + \text{FeCl}_3$ (0, $4.5 + 0.92$, $7.6 + 1.8$, $20.2 + 3.5$, and $51 + 5.8 \text{ g kg}^{-1}$ of soil)

On an areal basis (bulk density of soil = 0.28 g cm^{-3} and 20 cm soil depth), 1 g kg^{-1} of amendment is equal to 56 g m^{-2} . The amounts of chemical used in this study were high, as compared to normal agronomic rates or the amounts applied to lakes. Preliminary studies showed that relatively high rates of chemical amendments were needed to reduce mobile P in these organic soils (Ann, 1995). Treatments 6, 7, and 8 were based

on equal proportions of respective chemicals (1:1 ratio on note basis) added at 50% of their individual rates. All soil columns were incubated in the dark at 25°C .

A 50 ml sample was removed from the floodwater once a week for DRP analysis. The amount of water removed was replaced with filtered ($0.45 \mu\text{m}$) marsh water, which resulted in an approximate hydraulic retention time of 4 weeks. This procedure was repeated for a total period of 12 weeks. Filtered ($0.45 \mu\text{m}$) water samples obtained at weekly intervals were analyzed for DRP using Standard Methods (APHA, 1992). Water samples taken every 4 weeks were analyzed for inorganic carbon (IC), TP, Ca, Mg, Fe, Al, Na, K, Mn, Zn, and C1. Electrical conductivity (EC) and pH of the water column were measured once a week. Electrical conductivity was measured using a conductivity meter (YSI Model 31) and inorganic C was analyzed by TOC analyzer (DC-190 ASM, Dohrmann).

At the end of 12 weeks of incubation, soils were extruded under anaerobic conditions. A sub-sample was removed to extract porewater by centrifugation at 6000 rpm for 15 min. The supernatant liquid was filtered ($0.45 \mu\text{m}$) and analyzed for DRP, Cl, and selected cations (Ca, Mg, Fe, Al, Na, K, Mn, and Zn). After porewater removal, the residual soil was sequentially extracted using a modified inorganic P fractionation scheme similar to that of Hieltjes and Lijklema (1980). This modified scheme primarily involved sequential extraction of soil by 1 M KCl (2 h), 0.1 M NaOH (17 h), and 0.5 M HCl (24 h). Phosphorus in all extracts except that of KCl was determined by the ascorbic acid method using an autoanalyzer (Technicon AA II) (APHA, 1992). Phosphorus determination in KCl extracts was slightly modified by heating the sample-reagent mixture to 60°C for 5 min on a hot plate (Folson et al., 1977). The mixture was allowed to cool at room temperature, and the blue color was read at 880 nm using a Shimadzu (W-160) spectrophotometer.

2.3. Mineral equilibria

The computer program SOILCHEM (Sposito and Coves, 1991) was used to predict chemical

Table 1

Selected physico-chemical properties of water and soils used in the study ($n = 3$)

| Parameter | Floodwater (mmol l^{-1}) | Soil (mmol kg^{-1}) | | |
|-----------|-------------------------------------|--------------------------------|---------|-------|
| | | Dissolved | 1 M HCl | Total |
| P | 0.01 | 0.7 | 8.5 | 20 |
| Ca | 0.88 | 8.8 | 954 | 970 |
| Mg | 0.79 | 3.2 | 156 | 159 |
| Fe | 0.001 | 0.2 | 64 | 100 |
| Al | – | – | 33 | 106 |

speciation of P in the liquid phase. Input to the model consisted of the measured concentrations of Al, Ca, Fe, K, Na, Mn, Mg, Zn, P, IC, Cl, and pH. Activity coefficients were calculated using the Davies equation and ionic strength values were calculated by SOILCHEM. When calculating ion activities, precipitation was assumed to not have occurred.

All statistical analysis were performed using the Statistical Analysis System (SAS Institute, 1985). The general linear method (GLM) was used to perform analysis of variance, with calculation of LSD at 0.05 level of significance.

3. Results

3.1. Physico-chemical properties of soils

Selected chemical characteristics of the soil used in the study are shown in Table 1. Total inorganic P as determined by 1 M HCl extraction represented up to 42% of the total P. About 3.5% of the total P (8.4% of the total inorganic P) was in the water extractable fraction. Calcium and Mg were the dominant cations, with water extractable fractions accounting for 0.9 and 2.1% of 1 M HCl extractable Ca and Mg, respectively. Aluminium was not detected in water soluble fractions.

3.2. Dissolved reactive P flux between soil and overlying floodwater

Floodwater dissolved reactive P (DRP) concentrations in unamended soils increased from

150 to $700 \mu\text{g P l}^{-1}$ within 8 weeks of incubation, and decreased to about $550 \mu\text{g P l}^{-1}$ at the end of 12 weeks (Fig. 1). Among the Ca-based amendments, CaCO_3 and Ca(OH)_2 were more effective than dolomite ($\text{CaMg}(\text{CO}_3)_2$) in maintaining low DRP concentrations (Fig. 1). Floodwater DRP concentrations were in a similar range for soils amended with either CaCO_3 or

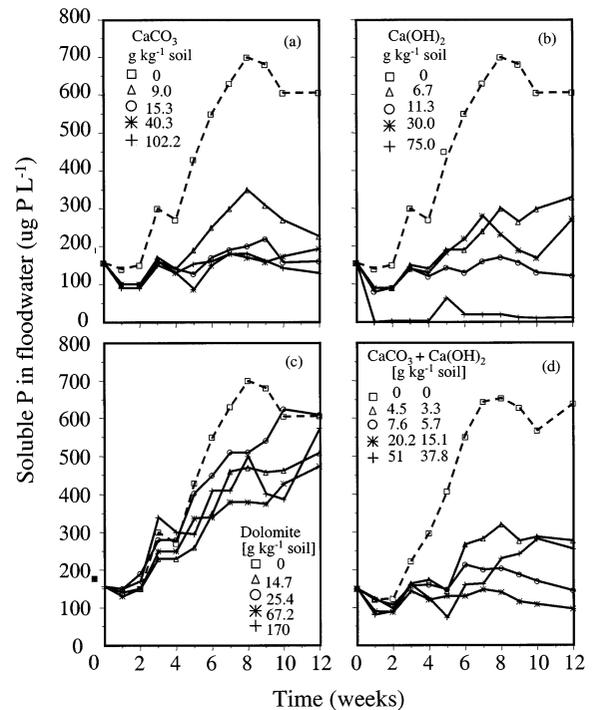


Fig. 1. Effect of chemically amended soils on dissolved reactive P in the floodwater with time of incubation.

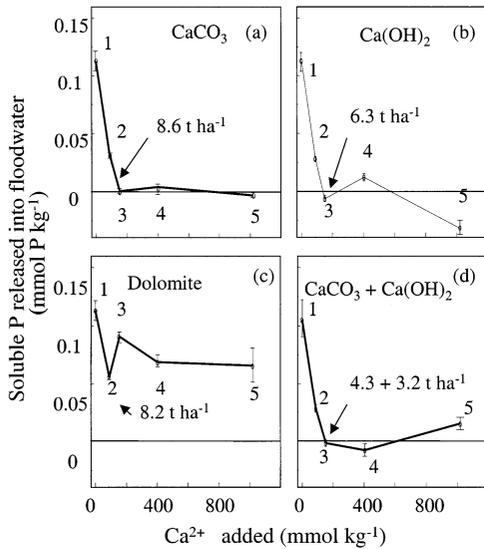


Fig. 2. Effects of Ca materials (CaCO₃, Ca(OH)₂, CaMg(CO₃)₂ and mixture of CaCO₃ and Ca(OH)₂) on immobilizing soluble P in the floodwater.

Ca(OH)₂ or a combination of the two. The low rates of CaCO₃ and Ca(OH)₂ (90 mmol Ca²⁺ kg⁻¹) reduced the floodwater DRP concentrations by up to 30 and 44% of the DRP concentration of the control (unamended soil), respectively ($P < 0.001$). Higher rates of CaCO₃ and Ca(OH)₂ (> 150 mmol Ca²⁺ kg⁻¹) did not improve the reduction of floodwater DRP ($P < 0.01$). However, the highest rate of Ca(OH)₂ treatment (1014 mmol Ca²⁺ kg⁻¹) maintained a low DRP concentration throughout the 12 weeks of incubation. An effective rate of reduction in P flux from the soils treated with Ca-based chemicals was observed at approximately 150 mmol Ca²⁺ kg⁻¹ ($P < 0.001$) (Fig. 2). All rates of dolomite-amended soils released between 0.05 and 0.1 mmol P kg⁻¹ during the 12 weeks of incubation (Fig. 2).

Alum and FeCl₃ treatments were also effective in maintaining low floodwater P concentration (Fig. 3). High rates (> 14.5 g alum or 43.5 mmol Al³⁺ + kg⁻¹) of alum treatment could maintain floodwater DRP concentration of < 100 µg P l⁻¹ ($P < 0.001$) (Fig. 3a), while even the lowest rate of FeCl₃ treatment reduced DRP concentrations to < 50 µg P l⁻¹ throughout

the 12 weeks of the incubation period ($P < 0.001$) (Fig. 3b). Also, mixtures of CaCO₃ with either alum (Fig. 3c) or FeCl₃ (Fig. 3d) showed similar trends in floodwater DRP reduction as did the individual alum and FeCl₃ treatments. Mixtures of CaCO₃ (20.2 g kg⁻¹)/alum (7.3 g kg⁻¹) maintained DRP concentration at less than about 50 g P l⁻¹, ($P < 0.001$), while the mixture of CaCO₃ (4.5 g kg⁻¹)/FeCl₃ (0.9 g kg⁻¹) decreased the concentration to about 100 µg P l⁻¹ ($P < 0.001$) (Fig. 3). However, the CaCO₃/FeCl₃ mixtures were less effective in removing floodwater DRP than FeCl₃ alone, while the CaCO₃/alum mixture was better than alum alone (Figs. 3 and 4).

Water column pH was not significantly different between the control and amended soil treatments, indicating high pH buffering capacity of the soil (Table 2). Soil amended with Ca(OH)₂ increased water pH to as high as 8.1, while the water pH of soils treated with CaCO₃ ranged

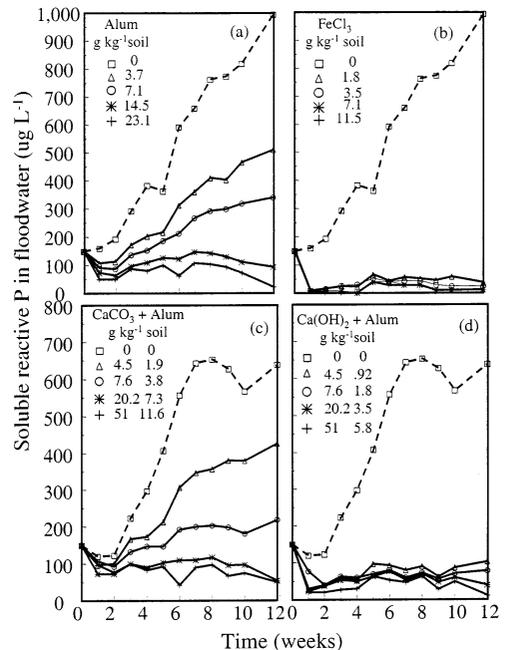


Fig. 3. Effects of chemically amended soils (alum, FeCl₃, and mixtures of CaCO₃ with alum or FeCl₃) on dissolved reactive P in the floodwater with time of the incubation.

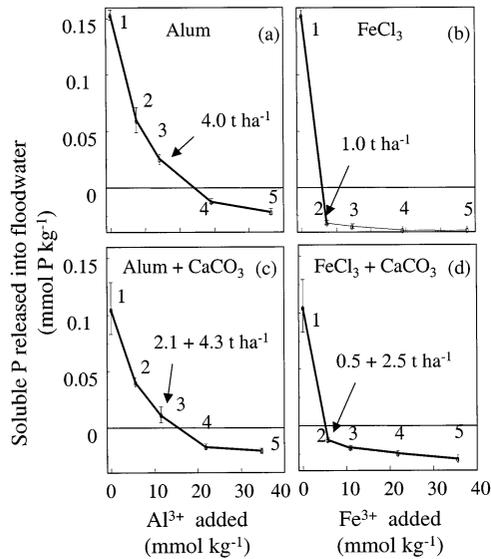


Fig. 4. Effects of alum, FeCl_3 , and the mixtures of CaCO_3 with alum or FeCl_3 on immobilizing water soluble P in the floodwater.

from 7.3 to 7.6 (Table 2). Floodwater pH of the soil treated with alum was near 7, whereas FeCl_3 treatments at the highest rate (7.1 g kg^{-1}) decreased floodwater pH to 5.5 (Table 2). An effective reduction in P flux was observed in soils amended with alum at rates $> 20 \text{ mmol Al}^{3+} \text{ kg}^{-1}$ soil ($P < 0.001$) and FeCl_3 at rates higher $> 5 \text{ mmol Fe}^{3+} \text{ kg}^{-1}$ ($P < 0.001$) respectively (Fig. 4). Similar trends were observed in soils treated with CaCO_3 /alum and CaCO_3 / FeCl_3 com-

Table 2
Influence of chemical amendments on soil and floodwater pH^a

| Chemical amendment | pH | |
|-------------------------------------|---------------|----------------|
| | Floodwater | Soil |
| Control | 7.0 ± 0.3 | 7.2 ± 0.04 |
| CaCO_3 | 7.4 ± 0.4 | 7.9 ± 0.02 |
| Ca(OH)_2 | 7.7 ± 0.5 | 7.9 ± 0.1 |
| $\text{CaMg(CO}_3)_2$ | 7.0 ± 0.3 | nd |
| Alum | 7.0 ± 0.3 | 7.1 ± 1.0 |
| FeCl_3 | 5.9 ± 1.0 | 6.2 ± 1.0 |
| $\text{CaCO}_3 \pm \text{Ca(OH)}_2$ | 7.6 ± 0.5 | N/A |
| $\text{CaCO}_3 \pm \text{Alum}$ | 7.3 ± 0.4 | 7.0 ± 0.2 |
| $\text{CaCO}_3 \pm \text{FeCl}_3$ | 6.9 ± 0.3 | 7.5 ± 0.1 |

^a nd, not determined; $n = 3$.

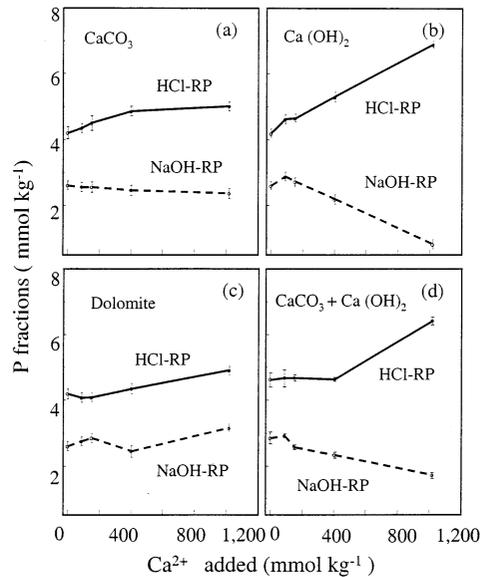


Fig. 5. Effects of Ca-based amendments on inorganic P (NaOH-RP and HCl-RP) of the amended soils. (a) CaCO_3 ; (b) Ca(OH)_2 ; (c) dolomite, and (d) mixture of CaCO_3 with Ca(OH)_2 .

binations, indicating that Al and Fe played a more significant role in the combined treatments than did Ca in controlling P release from soils.

3.3. Phosphorus distribution in amended soils

Soil P fractionation indicated minimal changes in Ca- and Mg-bound P (HCl-RP) and Al and Fe-bound P (NaOH-RP) in soils treated with CaCO_3 and dolomite (Fig. 5). The Ca and Mg bound P fraction increased with increasing amounts of Ca(OH)_2 , applied either alone or in combination with CaCO_3 , while the Al- and Fe-bound P fraction decreased with increasing Ca(OH)_2 application (Fig. 5). Results suggested that transformation of Fe/Al-bound P to Ca/Mg-bound P at a high pH probably occurred during the incubation period. Alum and FeCl_3 applied alone or in combination with CaCO_3 had minimal effect on either Ca and Mg-bound P or Al and Fe-bound P (Fig. 6). The Ca- and Mg-bound P was higher than Al- and Fe-P, regardless of whether soils were amended or not (Figs. 5 and 6).

3.4. Solubility of P compounds in floodwater and soil porewater

Calculated solubility diagrams indicated that floodwater and porewater DRP concentrations in soils amended with lime materials were related to Ca^{2+} activity, and thus possibly controlled by solid phase Ca-P compounds (Fig. 7). Floodwater DRP concentrations in amended and unamended soils were supersaturated with respect to hydroxyapatite, and in some cases to *p*-tricalcium phosphate (TCP) (Fig. 7). In the porewater of all chemically amended soils, DRP was shown to be supersaturated with respect to TCP (Fig. 7). The floodwater DRP of soils amended with the mixtures of CaCO_3 and alum or FeCl_3 also were supersaturated with respect to hydroxyapatite. A solubility diagram based on Fe-P and Al-P compounds showed that floodwater DRP concentrations in soils amended with FeCl_3 and alum were supersaturated with respect to strengite and variscite (Fig. 8).

Ion activity products (IAP) were calculated to determine which minerals would potentially regu-

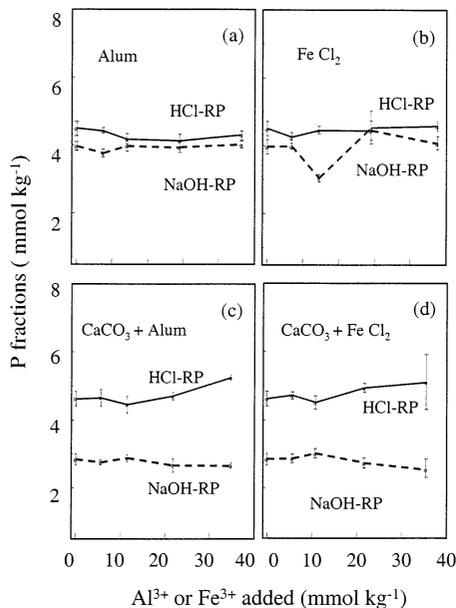


Fig. 6. Effects of chemically amended soils (alum, FeCl_3 , and mixtures of CaCO_3 with alum or FeCl_3) on distribution of soil inorganic P (NaOH-RP and HCl-RP).

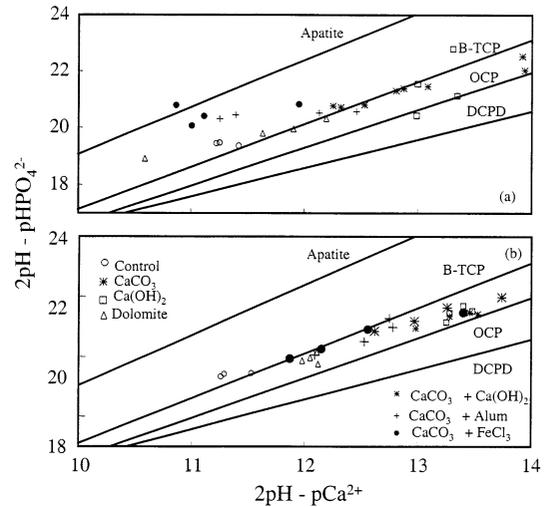


Fig. 7. Solubility diagrams of Ca phosphate compounds and P solubility changes in the (a) floodwater and (b) soil porewater. pTCP: β -tricalcium phosphate, OCP: octacalcium phosphate, pop: dicalcium phosphate.

late P concentrations in the porewater of various chemically amended soils. Mean values of the pIAP (Table 3) showed that DRP in the porewater of unamended and chemically amended soils were supersaturated with respect to hydroxyapatite. Also, TCP was supersaturated in those soils

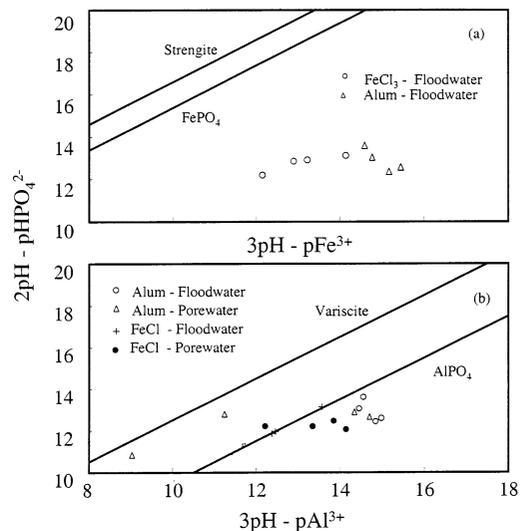


Fig. 8. Solubility diagrams of Al- and Fe-P compounds and P solubility changes in the (a) floodwater and (b) soil porewater.

Table 3

Average pK values of selected phosphate minerals in porewater of chemically amended marsh soils ($n = 3$)^a

| Phosphorus minerals | pK | Control | Chemically amended soils (pIAP \pm SD range) | | | | |
|---|---------------------------|---|--|---|---|--|---|
| | | | CaCO ₃ | Ca(OH) ₂ | Alum | FeCl ₃ | CaCO ₃ /Alum |
| Hydroxyapatite Ca ₁₀ (PO ₄) ₆ (OH) ₂ | 119 | 106 \pm 1.3 (105–107) | 99.8 \pm 0.4 (99–100) | 100 \pm 1.2 (99–100) | 116 \pm 2.6 (107–128) | 114 \pm 7.2 (107–123) | 101 \pm 4.2 (96–103) |
| β -Tricalcium β -Ca ₃ (PO ₄) ₂ | 28.9 | 30 \pm 0.5 (29–31) | 28.4 \pm 0.1 (28–28.4) | 28.5 \pm 0.4 (28–29) | 32.6 \pm 2.6 (30–36) | 31.9 \pm 2.0 (30–35) | 28.6 \pm 1.3 (27–31) |
| Octacalcium | 46.9 | 50.6 \pm 0.5 (50–51) | 49.1 \pm 0.1 (20–21) | 49.4 \pm 0.6 (48.5–50) | 53.9 \pm 3.1 (51–58) | 52.7 \pm 2.4 (50–56) | 49.4 \pm 1.6 (48–60) |
| Dicalcium P Dihydrate CaHPO ₄ ·2H ₂ O | 18.9 | 20.6 \pm 0.1 (20–21) | 20.7 \pm 0.1 (20–21) | 20.8 \pm 0.2 (20–21) | 21.2 \pm 0.5 (20–22) | 20.9 \pm 0.5 (21–22) | 20.7 \pm 0.4 (20–22) |
| Variscite AlPO ₄ | 22.1 19.1 | 22.8 \pm 1.1 22.8 \pm 1.1 (21–24) | 26.3 \pm 0.3 26.3 \pm 0.3 (26–27) | 26.5 \pm 0.3 26.5 \pm 0.3 (28–29) | 21 \pm 1.0 21 \pm 1.0 (20–21) | 20.4 \pm 0.5 20.4 \pm 0.52 (20–21) | 24.2 \pm 1.3 4.2 \pm 1.3 (22–26) |
| Strengite FePO | 26.4 25.9 (24–25.6) | 25 \pm 0.6 25 \pm 0.6 (30.6–32) | 31.5 \pm 0.6 31.5 \pm 0.6 (30–33) | 32.2 \pm 1.0 32.2 \pm 1.0 (23–25) | 24.1 \pm 0.9 24.1 \pm 0.9 | 23.8 \pm 0.6 23.8 \pm 0.6 (23–24) | 29.8 \pm 1.4 29.8 \pm 1.4 (27–31) |
| Wavellite Al ₃ (PO ₄) ₂ (OH) ₃ 5H ₂ O | 73.6 | 78.6 \pm 3 (74–80) | 86.9 \pm 0.7 (78–88) | 87.3 \pm 0.5 (86–88) | 74.1 \pm 2.1 (71–76) | 72.3 \pm 1.2 (71–73) | 81.3 \pm 3.5 (77–87) |
| Whitlockite Ca ₁₈ (Fe,Mg)- H ₂ (PO ₄) ₁₄ | 222 | 233 \pm 3.4 (230–234) | 230 \pm 0.7 (229–231) | 232 \pm 3.4 (227–235) | 248 \pm 14 (233–266) | 242 \pm 12 (231–257) | 230 \pm 7 (222–233) |

^a Values in parenthesis indicate the range of ion activity products.

amended with CaCO₃ and Ca(OH)₂. The calculated pIAP for Al- and Fe-P compounds indicated that alum treated soil was supersaturated with respect to variscite and wavellite, whereas FeCl₃ treated soil was supersaturated with respect to strengite and FePO₄. Soils amended with CaCO₃, Ca(OH)₂, and mixtures of CaCO₃ with alum or FeCl₃ were supersaturated with respect to aragonite and calcite.

Non-apatite Ca-P, such as TCP, OCP, amorphous Al hydroxide, and iron oxide phosphate compounds probably controlled soluble inorganic P in the wafer column and porewater of chemically amended soils. Moore et al. (1991)

predicted that a more soluble mineral phase such as Ca₃(PO₄)₂ and Ca₁₈(Mg,Fe)H₂(PO₄)₁₄ (whitlockite), may be forming instead of apatite in Lake Apopka sediments. In Lake Okeechobee sediments that contained relatively high Al and Fe, P uptake was correlated with Al/Fe oxyhydroxide and organically bound Al (Olila and Reddy 1993).

Results of X-ray diffraction analysis (XRD) of chemically amended soil (Ann, 1995) indicated that smectite, kaolinite, quartz, and weddellite were present in the silt or clay fractions of all soils, but carbonate minerals (calcite) could be found only in the silt fraction of Ca(OH)₂ amended soil.

4. Discussion

Throughout the incubation period, floodwater DRP reduction in CaCO_3 amended soil never surpassed that of Ca(OH)_2 amended soil. Approximately 150 mmol of Ca as CaCO_3 and Ca(OH)_2 4 kg^{-1} soil appeared to be the most efficient amounts for minimum DRP release (Fig. 2). However, the highest rate of Ca(OH)_2 treatment ($1014 \text{ mmol kg}^{-1}$) maintained DRP concentrations at less than $10 \mu\text{g l}^{-1}$ (Fig. 3). These results may be closely related with the increased pH of Ca(OH)_2 amended soil.

Soils amended with Ca(OH)_2 showed increased Ca, Mg, and dissolved inorganic C concentrations in the water column compared to soils treated with CaCO_3 (Ann, 1995). Increased Ca and pH resulted in precipitation of calcite that, in turn, may have induced P sorption. Coprecipitation of P with carbonate has been explained as one of the mechanisms for lowering P concentrations in a marl lake (Otsuki and Wetzel, 1972). Coprecipitation can occur either by simple adsorption (Griffin and Jurinak, 1974; House and Donaldson, 1986) of one compound by another, with the microcomponent adhering to the surface of the host, or by incorporation into particulate carbonate with the rapid growth of the crystals (Otsuki and Wetzel, 1972; Kleiner, 1988).

Calcium phosphate compounds are expected to precipitate in a pH range of 6–8.5. Decreased floodwater DRP concentrations in the water column of all CaCO_3 and Ca(OH)_2 amended soils except with the highest rate of Ca(OH)_2 treatment were attributed to the precipitation of amorphous Ca–P compounds rather than coprecipitation of P with calcite. Calculated solubility diagrams indicated that the floodwater of unamended and chemically amended soils at low application rates were supersaturated with respect to apatite; as rates of CaCO_3 and Ca(OH)_2 addition increased, saturation points moved toward *p*-tricalcium phosphate (TCP) and octacalcium phosphate (OCP). This was attributed to high Ca activity and increased pH. Supersaturation with respect to hydroxyapatite suggests that DRP concentrations in the floodwater were probably controlled by more amorphous Ca–P compounds. This obser-

vation suggests that precipitation of solid phases, especially hydroxyapatite, was inhibited by other components, such as Mg and carbonate ions, and dissolved organic acids (Stumm and Morgan, 1981; Inskeep and Silvertooth, 1988a). Organic ligands inhibit hydroxyapatite precipitation by competing for adsorption sites on the seed crystal, thereby preventing more crystal growth (Inskeep and Silvertooth, 1988a,b). In the natural environment, amorphous P compounds such as dicalcium phosphate (pop) and octacalcium phosphate (OCP) may dominate P compounds and serve as intermediates for the formation of apatite (Berkheiser et al., 1980). The presence of Mg appears to cause the formation of more soluble amorphous Ca-bound P compounds and a magnesium-calcium carbonate rather than formation of crystalline Ca-bound P compounds and calcite/dolomite (Jenkins et al., 1971; Stumm and Morgan, 1981). Increased carbonate concentrations may also cause slower Ca phosphate crystal growth rates by substitution of orthophosphate ions with the carbonate ions in the solid form of Ca phosphate compounds (Jenkins et al., 1971). However, most orthophosphate ions are expected to precipitate with Ca ions before Ca ions are consumed in the formation of calcium carbonate minerals in solution containing low carbonate concentration. The P precipitation with calcium ions is kinetically much faster than calcium carbonate precipitation. Aluminum and Fe salts have long been considered as coagulants for precipitation of P from solution. However, the effectiveness and optimum acidity for P removal have been reported differently. For example, optimum pH for P removal has been reported to be from 5.6 to 7.7 (Hsu, 1975). The DRP concentrations in the water column of alum treatments decreased gradually as the rate of alum additions increased. The FeCl_3 amended soil was more effective for DRP reduction than alum-treated soil. Probably more OH^- was needed to release H^+ from HPO_4^{-2} to provide PO_4^{-3} for the formation of AlPO_4 . However, OH^- also enhances the competition of OH^- with PO_4^{-3} for Al^{3+} (Hsu, 1976).

In conclusion, this laboratory study has shown that all amendments except dolomite were effective in decreasing floodwater DRP concentrations

in Lake Apopka marsh soil. Calcium carbonate, $\text{Ca}(\text{OH})_2$, alum, and FeCl_3 mixed with the soil were effective in controlling labile P in floodwater and porewater. The effective amount required for each chemical amendment to minimize P release from soil to overlying water were 7–15 g kg^{-1} soil for CaCO_3 and $\text{Ca}(\text{OH})_2$, 12 g kg^{-1} soil for alum, and 1–2 g kg^{-1} soil for FeCl_3 . Based on P flux calculations and the floodwater P concentrations throughout the incubation period were the order of effectiveness as follows; $\text{FeCl}_3 > \text{alum} \geq \text{Ca}(\text{OH})_2 > \text{Ca}(\text{CO}_3) > \text{dolomite}$.

Among the chemical amendments $\text{Ca}(\text{OH})_2$ and FeCl_3 appeared to be promising for P inactivation in the soils. Ferric chloride treatments may provide a relatively fast control of DRP in the soil. However, FeCl_3 chloride treatment should be considered carefully because of sensitivity to redox potential change. For the purpose of long-term treatment, it is probably necessary to raise the soil pH to about 8 to induce the formation of more stable Ca-P compounds. However, increased may result in solubilization of organic matter and increased levels of P. Future studies should address the long-term effectiveness of these chemicals in stabilizing mobile P in flooded organic soils.

Acknowledgements

Florida Agricultural Experimental Station Journal Series No. R-06682. Funding for this study was provided in part by the St. Johns River Water Management District, Palatka, Florida. Project officers, Dr M. Coveney, and Dr D. Stites. We thank Drs W.G. Harris and V.D. Nair for their critical reviews of the manuscript.

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