ACCUMULATION AND DOWNWARD TRANSPORT OF PHOSPHORUS IN FLORIDA SOILS AND RELATIONSHIP TO WATER QUALITY*

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ABSTRACT

Accumulation of phosphorus (P) for Florida soils under citrus production may have an impact on groundwater and nearby streams and lakes. Six extracting solutions including Mehlich3, Bray1, double-acid, ammonium bicarbonate-DTPA (ABDTPA), neutral NH_4OAc, and water were used to investigate P accumulation for 44 surface soils. The samples have been collected from old groves in 7 major citrus production counties in Florida. The results indicated P accumulation in most soils investigated. Either Mehlich3, Bray1, or double-acid was a good test to evaluate P accumulation. The average amount of P extracted was 121, 97, and 101 $mg\,kg^{-1}$ soil for Mehlich3, Bray1,

and double-acid, respectively. The high correlation between P and aluminum (Al) removed by these extracts suggested that Al-phosphates were the main forms accumulated in these soils. Vertical distribution of P in soil profile was investigated in three sites (Myakka, Zolfo, and Adamsville) where accumulation was observed in the top soil. The results showed downward movement of P through the soil profile into the saturated zone at a depth of 210 cm for Myakka, 180 cm for Zolfo, and 240 cm for Adamsville. Mehlich3-extractable P for saturated zone soils was 467, 997, and $37 \, mg \, kg^{-1}$ soil, respectively. However, the concentration of P in groundwater was very low at $0.09 \, mg \, L^{-1}$ for Myakka, $1.34 \, mg \, L^{-1}$ for Zolfo, and $0.21 \, mg \, L^{-1}$ for Adamsville. With high rainfall averaging $1400 \, mm \, year^{-1}$, colloidal Al-phosphates formed in the top soil could move down with water through the sandy soil profile and reach the saturated zone. The low P concentration in the groundwater might be related to the low solubility of Al-phosphates in the strong acidic environment observed (pH was 4.38, 4.88, and 4.31 for Myakka, Zolfo, and Adamsville, respectively) for soils in the saturated zone. The relatively high pH values for surface water/sediment systems might explain the high P concentrations detected in some streams, and lakes.

INTRODUCTION

Detection of high phosphorus (P) concentrations for some streams and lakes in Florida has raised public concern of a possible role of agriculture practices as non point sources of pollution. Citrus is a major crop in Florida where current production area covers 857,000 acres. Native soils under citrus production in Florida are generally acidic, light-textured, and P-deficient. Phosphorus along with nitrogen (N) fertilizers are usually applied to sustain high and good quality yield. Smith[1] reported that prior to World War II, citrus fertilizers commonly contained equal amounts of P and N, and bearing groves usually received from 100 to $200 \, kg \, P \, ha^{-1} \, year^{-1}$.

A significant portion of added P is retained by soil constituents in chemical forms that are not readily available to plant roots. Under acidic environments, added P could be sorbed by Al-, iron (Fe)-, and manganese (Mn)-oxides and hydroxides. In laboratory tests, Yuan et al.[2] concluded that application of water-soluble P quickly converted to Al-P forms in three sandy Florida soils. Fiskell and Rowland[3] used sequential extraction and total analysis to show that Al-, and Fe-P were the major forms present in soils of west central Florida.

Soluble P applied to acidic soils is converted with time to more stable forms of Al and Fe minerals (e.g., variscite, and strengite) which are sparingly soluble in soil solution (4).

Many chemical solutions have been proposed to extract potential forms of soil P and its availability to plants. Water probably was the first extractant applied to measure the availability of P and other nutrients in soils. The small amounts of soil P extracted with water and difficulties related to chemical analysis limited its use. Solutions applying aggressive extracting reactions were developed to remove large amounts of P and other nutrients which were related to plant uptake.

Bray and Kurtz (5) suggested a combination of HCl, and NH_4F to remove easily acid soluble P forms, largely Ca-, Al-, and Fe-phosphates. Fluoride ions dissolves Al-, and Fe-phosphates by its complex ion formation with these metal ions in acid solution (6).

Nelson et al. (1953) introduced the double-acid solution (HCl/H_2SO_4) which is more effective than HCl alone as soil P extractant. Sulfate ions can enhance the removal of Al-, and Fe-phosphates due to the formation of soluble Al- and Fe-SO_4 complexes (8), and by replacing phosphate ions adsorbed on colloidal surfaces in soils (9). Anderson (10) in his study on citrus grove sandy soils found that the double-acid solution extracted more soil P than did the Bray1.

Soltanpour and Schwab (11) developed NH_4HCO_3-diethylenetriamine-pentaacetic acid solution (ABDTPA) to extract P, and other nutrients from neutral, and alkaline soils. Similar to the well known $NaHCO_3$-Olsen test (12), ABDTPA extracts soil P with HCO_3 ions. The index values for the ABDTPA extract are as follows: low, 0 to 3 mg P kg^{-1} soil; medium, 4 to 7 mg P kg^{-1} soil; high, 8 to 11 mg P kg^{-1} soil; very high, >11 mg P kg^{-1} soil (13).

In 1984, Mehlich modified his initial soil extracts to develop Mehlich3 solution (14) which is suitable to extract P from acidic and alkaline soils. Mehlich3 solution is a combination of acids (HOAc and HNO_3), NH_4-F and NH_4NO_3, and the chelating agent ethylenediaminetetraacetic acid (EDTA). Hydrogen, fluoride, and acetate are the principle ions used in Mehlich3 to remove mainly Al-, Fe-, and Ca-phosphates.

Initially, neutral NH_4OAc solution was used to measure exchangeable cations in soils (15). Several studies applied this test to determine P (16), and other nutrients (17,18) in Florida soils.

The extracting solution applies certain reactions on soil constituents to release P from the solid to the solution phase. Using various tests that apply different reactions/mechanisms in extracting P may provide information on potential forms of P in addition to its quantities in soils.

Most Florida soils under citrus production have deep sandy profiles with considerable number of macro-pores and high hydraulic conductivity. With precipitation averaging 1400 mm per year, downward movement of soil constituents (dissolved, and colloidal phase) from the surface into subsurface

Table 1. Classification and Some Properties for 44 Surface Soils Investigated

Series	Family	Subgroup	No. of Samples	pH-Water	pH-CaCl$_2$	OM (%)	CEC (Cmol/kg)	EC (S/m)
Adamsville	Uncoated, hyperthermic	Aquic Quartzipsamments	2	6.20–7.14	5.31–6.28	1.00–1.25	4.41–4.31	0.003–0.006
Ankona	Sandy, siliceous, hyperthermic	Arenic Haplaquods	2	4.88–7.31	3.66–6.72	0.35–1.20	3.61–4.36	0.002–0.003
Astatula	Uncoated, hyperthermic	Typic Quartzipsamments	4	7.35–7.71	6.50–6.60	0.65–1.45	4.36–4.51	0.006–0.008
Boca	Loamy, siliceous, hyperthermic	Arenic Ochraqualfs	1	7.33	6.45	0.35	4.58	0.007
Candler	Uncoated, hyperthermic	Typic Quartzipsamments	10	5.05–7.16	4.19–6.28	0.65–1.35	4.05–4.58	0.003–0.007
Chobee	Fine-loamy, siliceous hyperthermic	Typic Argiaquolls	1	8.05	7.3	2.6	4.71	0.021
Holopaw	Loamy, siliceous, hyperthermic	Grossarenic Ochraqualfs	1	6.24	5.68	0.7	4.09	0.013
Immokalee	Sandy, siliceous, hyperthermic	Arenic Haplaquods	1	5.93	5.21	0.75	4.08	0.009
Myakka	Sandy, siliceous, hyperthermic	Aeric Haplaquods	2	6.18–7.38	5.34–6.83	0.85–2.55	4.25–4.70	0.003–0.008

Nettles	Sandy, siliceous, hyperthermic	Alfic Arenic Haplaquods	2	4.78−4.89	3.55−4.07	0.50−1.90	3.51−4.50	0.004−0.016
Riviera	Loamy, siliceous, hyperthermic	Arenic Glossaqualfs	6	5.61−7.74	4.74−6.92	0.80−1.75	4.41−4.71	0.005−0.014
Oldsmar	Sandy, siliceous, hyperthermic	Alfic Arenic Haplaquods	1	5.92	5.39	0.8	4.26	0.015
Pineda	Loamy, siliceous, hyperthermic	Arenic Glossaqualfs	1	4.95	4.42	3.9	4.73	0.037
Pomona	Sandy, siliceous, hyperthermic	Ultic Haploquods	2	5.68−6.03	5.17−5.25	1.05−1.50	4.29−4.66	0.003−0.017
Tavares	Uncoated, hyperthermic	Typic Quartzipsamments	4	6.74−7.58	6.02−6.69	0.85−1.35	4.26−4.52	0.006−0.012
Wabasso	Sandy, siliceous, hyperthermic	Alfic Haplaquods	2	6.24−7.47	5.44−6.56	1.45−2.30	4.58−4.75	0.005−0.008
Zolfo	Sandy, siliceous, hyperthermic	Grossarenic Entic Haplohumods	2	6.29−7.27	5.34−6.56	0.90−1.25	4.29−4.60	0.003−0.007

environments is an active process. Ballard and Fiskell (19) reported that most of the sandy soils of the Southeastern Coastal Plains have a very small retention capacity for water-soluble P against leaching. In a lysimeter study, Neller (20) reported that in four months, 72.4 cm of rainfall leached more than 70% of applied superphosphate P from the surface 20-cm of Leon fine sand.

Examples of colloids transport (in subsurface environment) resulting from natural pedogenic processes are abound in literature (21). Colloidal P forms can move downward from the surface into the subsoil. Flaig et al. (22) concluded that the formation of amorphous Al hydroxides, and Al-P compounds in Florida sandy soils treated with wastewater increased downward movement of P into the subsoil below 200-cm depth.

The objectives of this study were to: (i) compare the ability of six extracting solutions to measure P accumulation in mature citrus grove soils, (ii) study effects of P accumulation in surface soil on downward movement and groundwater quality.

MATERIALS AND METHODS

Surface Soil

Forty four soil samples were collected from the surface 30-cm layer at mature citrus groves throughout Florida. The samples represented major soil series under citrus production in seven counties (Polk, Highland, Hardee, Hendry, Collier, Martin, and St. Lucie). Soil samples were air-dried, mixed, and sieved to pass through 2.0 mm screen. Soil pH was measured in water and 0.01 M $CaCl_2$ extract at 1:2 (w/v) soil:solution ratio. Electric conductivity (EC) was measured only in the water extract. Organic matter (OM) was determined by Walkley–Black procedure (20). Cation exchange capacity (CEC) was determined by Gillman method as described by Rhoades (23). The results of soil properties are presented in Table 1.

Available forms of P in soils were determined in extracts prepared by six different methods. The soil samples were extracted with water 1:2 (w/v) soil:solution ratio. The soil suspension was shaken for 5 minutes then filtering the supernatant through Whatman no. 42 filter paper. The other soil extracts were prepared according to Mehlich3 (14), Bray1 (5), double-acid (0.05 N $HCl + 0.025 N H_2SO_4$) as described by Olsen and Sommers (13), ammonium bicarbonate-diethylenetriaminepentaacetic acid (ABDTPA) (11), and neutral 1.0 N NH_4OAc after Thomas (15). Concentrations of P, Al, Fe, Mn, Ca, and Mg were determined in all soil extracts.

Subsoil and Groundwater

Distribution of P as a function of depth was investigated at three sites of mature citrus groves in Hardee county, Florida. The soil series were Myakka fine sand (Aeric Haplaquods), Zolfo fine sand (Grossarenic Entic Haplohumods), and Adamsville fine sand (Aquic Quartzipsamments) (Table 1). Data obtained from surface soil samples collected at these sites indicated P accumulation.

At each location, a stainless steel auger equipped with long arm was used to collect soil cores at 30-cm intervals along the soil profile. When water-saturated zone was encountered, a soil sample was collected from the saturated zone before termination of sampling. Samples were centrifuged, and filtered to separate groundwater from wet soil collected from the saturated zone. Soil samples were air-dried, mixed, and sieved using 2.0 mm screen. Mehlich3, and water methods were applied to prepare soil extracts. Concentrations of P, Al, Fe, Mn, Ca, and Mg were determined in the two soil extracts and groundwater samples while pH was measured only in water extracts, and groundwater samples.

Concentrations of P, Al, Fe, Mn, Ca, and Mg in all soil extracts, and water samples were determined by Inductively Coupled Plasma Emission Spectroscopy (Perkin Elmer, Plasma 40). SAS programs version 6.11 were employed for the statistical analysis (24).

RESULTS AND DISCUSSIONS

Concentration of Phosphorus in Surface Soils

The pH for the majority of native soils under citrus production in Florida is acidic. Normal practices of lime application and surface irrigation with well water containing high Ca concentration increased pH of most surface soils investigated to slightly acidic and neutral range (Table 1). The high pH (pHw = 8.05, and pHc = 7.30) and Ca concentration for a surface sample (Chobee loamy fine sand) collected from a citrus grove in Hendry county indicated the presence of free $CaCO_3$. This could be attributed to mixing the surface soil with a subsurface layer having high content of $CaCO_3$. On the other hand, unlimed soil sample (Nettles fine sand) collected from St. Lucie county showed a strong acidity (pHw = 4.89, and pHc = 3.55) reflecting the native conditions.

In general, the soil samples had light texture ranging from sandy to loamy fine sand, low OM content (0.35 to 3.9%), CEC (3.51 to 4.75 Cmol kg^{-1}), and EC (0.002 to 0.037 S m^{-1}) (Table 1).

Apart from adsorbed forms, P is associated mainly with Ca, and Mg in neutral, and alkaline soils, while Al-, Fe-, and Mn-phosphates are predominant in

Table 2. Range and Average of P, Ca, Mg, Al, Fe, and Mn Amounts (mg/kg Soil) Extracted with 6 Solutions for 44 Surface Soils Investigated

	MEHLICH 3						BRAY 1					
	P	Ca	Mg	Al	Fe	Mn	P	Ca	Mg	Al	Fe	Mn
Minimum	4.50	53.65	7.30	41.25	30.15	0.25	1.85	0.10	0.10	24.45	19.70	0.10
Maximum	445.20	34123.00	272.10	1353.75	342.30	99.70	410.70	1916.60	272.05	3088.90	294.75	50.85
Average	121.20	1574.44	101.15	436.53	156.88	32.32	96.94	126.90	79.91	973.66	117.59	17.99
	ABDTPA						DOUBLE-ACID					
Minimum	2.19	26.20	2.97	1.49	16.10	0.09	1.10	34.82	4.05	14.05	0.18	0.15
Maximum	78.32	359.41	50.38	85.93	186.52	14.76	588.02	7948.80	589.45	748.03	132.13	37.45
Average	29.75	254.58	26.94	13.95	58.24	4.85	100.62	1165.03	128.40	153.06	23.99	15.02
	NH$_4$OAc						WATER					
Minimum	0.64	26.44	3.84	0.36	0.12	0.08	0.72	0.72	0.21	0.56	0.37	0.00
Maximum	11.04	3464.24	101.60	9.84	1.68	5.08	7.92	121.76	22.12	103.63	27.67	0.75
Average	4.27	553.14	46.12	2.40	0.37	1.07	2.91	20.64	5.23	19.34	6.03	0.19

acidic environments (4). The amount of associated elements (Al, Fe, Mn, Ca, and Mg) removed along with P by an extracting solution may provide information on potential forms of P present in soils.

The chemical composition of water extract may approach a situation similar to that in the soil solution under field conditions. The data (Table 2) show that P concentrations in the water extract ranging between 0.72 and 7.92 $mg\,kg^{-1}$ soil, with an average of 2.91 $mg\,kg^{-1}$ soil. In this study, the efficiency of the other solutions in extracting soil P was measured by comparing it with the water extract.

The efficiency of the five solutions in extracting soil P followed the decreasing order: Mehlich3, double-acid, Bray1, ABDTPA, and NH_4OAc. These solutions removed an average of 42-, 35-, 33-, 10-, and 1.5-fold greater P than that removed by water, respectively. The data indicated the high effectiveness of $H^+\&F^-$ (Mehlich3, and Bray1), and $H^+\&SO_4^-$ ions combination (double-acid) in removing accumulated soil P.

Highly significant correlation was observed between P extracted with different solutions, and between each individual solution and water (Table 3). The high correlation suggests that water and other solutions are removing P (with varying levels of efficiency) from the same potential forms in soils.

In general, the statistical correlation (data are not given in this report) indicated that pH, OM, CEC, and EC had no effects on the amount of P extracted with different solutions. It appeared that the amount of P extracted was mainly dependent on the principle ions used in solution (e.g., H^+, F^-, SO_4^-, HCO_3^-, and OAc^-) to remove potential forms of P in soils.

Water Extract

The concentration of elements in water extract may represent the chemical composition in soil solution under field conditions (13). The amount of P

Table 3. Simple Correlation Between P Extracted with 6 Solutions for 44 Surface Soils Investigated

	MEHLICH3	BRAY1	Double-acid	ABDTPA	NH_4OAc
BRAY1	0.983**				
Double-acid	0.908**	0.867**			
ABDTPA	0.708**	0.686**	0.513**		
NH_4OAc	0.590**	0.594**	0.501**	0.636**	
Water	0.605**	0.611**	0.401**	0.705**	0.582**

** indicates 1% significant level.

extracted with water was generally small with an average of $2.91 \, \mathrm{mg \, kg^{-1}}$ soil. The results obtained for elements usually associated with soil P (Table 2) show that the average concentrations were 20.6, 5.23, 19.3, 6.03, and $0.19 \, \mathrm{mg \, kg^{-1}}$ soil for Al, Fe, Mn, Ca, and Mg, respectively.

With respect to the relationship between P, and associated elements in the water extract, the data (Table 4) show a significant simple correlation between P and Al, whereas no relation was detected for other associated elements. Multiple regression including Al and Fe as the best two independent parameters accounted for only 19% of variations in the value of extractable P. These results indicated that the water extract was not a suitable index to determining accumulated P forms for the soils investigated.

Mehlich3 Extract

The data in Table 2 show considerable amounts of P extracted with this solution ranging between 4.50, and $445 \, \mathrm{mg \, kg^{-1}}$ soil, with an average of $121 \, \mathrm{mg \, kg^{-1}}$ soil. The combination $H^+ \& F^-$ are the principal ions used in Mehlich3 solution to remove various forms of soil P. The solution also contains $H^+ \& OAc^-$ ions combination which are not as vigorous in removing P forms. However, $H^+ \& OAc^-$ ions have the ability to dissolve Ca-minerals in soils such as calcite, and dolomite (23). As mentioned above, Chobee loamy fine sand was the only soil sample investigated that contained free $CaCO_3$. Accordingly, the concentration of Mehlich3-extractable Ca was $34,123 \, \mathrm{mg \, kg^{-1}}$ soil.

Except for Al, Mehlich3 solution removed larger amount of P and associated elements than other extracts. It removed an average of 42-fold P, 76-fold Ca, 19-fold Mg, 23-fold Al, 26-fold Fe, and 170-fold Mn greater than that extracted with water.

Simple and multiple correlations relating extractable P to Al, Fe, and Mn are given in Table 4. Highly significant simple correlation with Al (r = 0.81**) and Fe (r = 0.63**) suggested that P extracted with Mehlich3 were derived mainly from Al-, and Fe-phosphates. Including Al and Fe as independent parameter in a multiple regression equation could predict 73% of variations in the value of extractable P. Similarly, McLaughlin et al. (25) used the high correlation between P and Al extracted with acid ammonium oxalate solution to conclude that sorption of P occurred on amorphous Al-hydroxides in soils of pH less than 7.

BRAY1 EXTRACT

The high concentrations of P extracted with Bray1 solution indicated the efficiency of $H^+ \& F^-$ ions combination in removing the element. Concentrations

Table 4. Simple and Multiple Correlations Relating P to Al, Fe, and Mn in Six Extracting Solutions for 44 Surface Soils Investigated

Soil Extract	Simple Correlation (R)			Multiple Correlation	
	Al vs. P	Fe vs. P	Mn vs. P	Regression Equation	R2
Mehlich 3	0.813**	0.631**	0.281	P = −41.7 + 0.23Al + 0.41Fe	0.731**
Bray 1	0.681**	0.361**	0.277	P = 9.67 + 0.08Al + 0.65Mn	0.475**
ABDTPA	0.254	0.481**	0.446**	P = 4.90 + 0.22Fe + 2.53Mn	0.375**
DOUBLE-ACID	0.846**	0.303*	0.382**	P = −21.03 + 0.68Al + 0.71Fe	0.744**
NH4OAc	0.213	−0.127	0.064	P = 4.05 + 0.43Al − 2.16Fe	0.081
WATER	0.296*	0.179	0.168	P = 2.78 + 0.11Al − 0.33Fe	0.185*

* and ** indicate 5% and 1% significant level, respectively.

ranging from 1.85 to 411 mg P kg^{-1} soil, with an average of 96.9 mg P kg^{-1} soil were found in the 44 soils investigated. Bray1 solution extracted 33-fold P, 6-fold Ca, 15-fold Mg, 50-fold Al, 20-fold Fe, and 95-fold Mn greater than those extracted with water. The solution extracted substantial amounts of Al. It removed 974 mg Al kg^{-1} soil, more than double the amount of Al removed by Mehlich3 (437 mg Al kg^{-1} soil). Under acidic conditions, the ability of fluoride ions to complex Al ions is dependent on its concentration in solution (4,6). Fluoride concentration in Bray1 solution (0.03 M) is twice as much as that in Mehlich3 solution (0.015 M).

The statistical data given in Table 4 show highly significant correlation between extractable P, and either Al or Fe while no relation was observed for Ca, Mg, and Mn. The data for Ca, and Mg are not given in Table 4. Similar to Mehlich3, these results implied that P was removed mainly from Al-, and Fe-phosphates. A multiple regression equation including Al and Fe as independent parameters could predict 48% of variations in P values.

Double-Acid Extract

The double-acid solution extracted considerable amounts of P which were comparable to those removed by Mehlich3 and Bray1. Phosphorus extracted with the double-acid solution ranged between 1.10 and 588 mg kg^{-1} soil, with an average of 101 mg kg^{-1} soil. These results suggest that, under acidic conditions, SO$_4$ ions (H$^+$ & SO$_4^-$) are as efficient as F ions (H$^+$ & F$^-$) in removing soil P. Two mechanisms could be involved in P extraction with SO$_4$ ions. The first mechanism involved dissolution of P minerals (e.g., variscite and strengite). The role of SO$_4$ in increasing minerals dissolution has been reported by other investigators. Bloom and Erich (8) and Ridley et al. (26) concluded that SO$_4$ increased the dissolution of gibbsite due to formation of soluble Al-Sulfate complexes. Elrashidi et al. (27) reported that SO$_4$ increased the dissolution of Mn minerals due to formation of soluble Mn-Sulfate complexes.

The second mechanism involved replacement of phosphate on colloidal surfaces by SO$_4$ in solution. Many scientists reported the ability of SO$_4$ in removing phosphate adsorbed on colloidal surfaces in soils [e.g., Hingston (28), Bolan et al. (29)].

The double-acid solution extracted 35-fold P, 56-fold Ca, 25-fold Mg, 8-fold Al, 4-fold Fe, and 79-fold Mn greater than that extracted with water. The data (Table 4) show a significant correlation between P and either Al, Fe, or Mn suggesting that P was derived mainly from Al-, Fe-, and Mn-phosphates. Using Al, and Fe as independent factors in a multiple regression equation enabled the prediction of 74% of variations in P values.

ABDTPA Extract

Bicarbonate are the principal ions used in ABDTPA solution to remove soil P forms. In general, ABDTPA dissolved much lesser P than extractants using $H^+ \& F^-$ ions (Mehlich3, and Bray1) or $H^+ \& SO_4^{2-}$ ions (double-acid). Soltanpour and Schwab (11) developed this solution to extract P and other nutrients for neutral and alkaline soils. Since its introduction, however, the extractant has been used to measure available P and macro-, and micro-nutrients for both alkaline, and acidic soils (13).

In this study, ABDTPA solution extracted P concentrations ranging from 2.19 to 78.3 mg kg^{-1} soil, with an average of 21.4 mg kg^{-1} soil. Similar results were reported by Alva (18) for Florida citrus soils where ABDTPA-extractable P varied between 5.0, and 84.9 mg kg^{-1} were determined.

The solution extracted 10-fold P, 12-fold Ca, 5-fold Mg, 10-fold Fe, and 26-fold Mn greater than those extracted with water. On the other hand, ABDTPA removed only 72% of the amount of Al found in the water extract. These results showed the limited ability of ABDTPA to remove Al-phosphates which are potential sources of available P in these soils.

With respect to the relationship between P and associated elements removed by ABDTPA, significant correlation was detected for Fe and Mn whereas no relation was found for Al, Ca, or Mg. The absence of any relation between P and Al could be due to the limited ability of ABDTPA to remove Al-phosphates. Including Fe and Mn in multiple regression equation, could detect 38% of variations in P values.

Neutral NH$_4$OAc Extract

Neutral ammonium acetate removed somewhat higher amounts of P than water. The extractable P ranged between 0.64, and 11.0 mg kg^{-1} soil, with an average of 4.27 mg kg^{-1} soil. But, the NH$_4$OAc ability to extract soil Ca, and Mg was much greater than that of the water extract. The average Ca concentrations were 553, and 20.6 mg kg^{-1} soil for NH$_4$OAc and water, respectively while the corresponding values for Mg were 46.1, and 5.2 mg kg^{-1} soil. It appeared that both NH_4^+, and OAc^- ions contributed to Ca, and Mg removal. Ammonium replaced Ca, and Mg on colloidal surfaces while OAc^- could dissolve Ca-, and Mg-minerals in soils.

On the other hand, NH$_4$OAc removed much lower amounts of Al and Fe than water. The average concentrations of Al, and Fe removed by water were 8, and 16 fold greater than that removed by NH$_4$OAc. The low pH values in the water extract for most soils investigated (Table 1) might explain these results.

The small amounts of P removed and the absence of any relation with associated elements might indicate that the neutral NH_4OAc was not a suitable index to determining P accumulation for these soils.

Distribution of Phosphorus in Soil Profile

The data on Mehlich3-extractable P as a function of depth for Myakka, Zolfo, and Adamsville soil profiles are shown in Fig. 1. Phosphorus appeared to accumulate in the surface 30-cm layer for Myakka soil where a concentration of 386 mg/kg was determined. The element concentration decreased sharply at 30–90 cm segment then increased again with depth where a concentration of up to 478 $mg\,kg^{-1}$ was detected in the soil between 120-cm depth and the saturated zone at 210-cm depth.
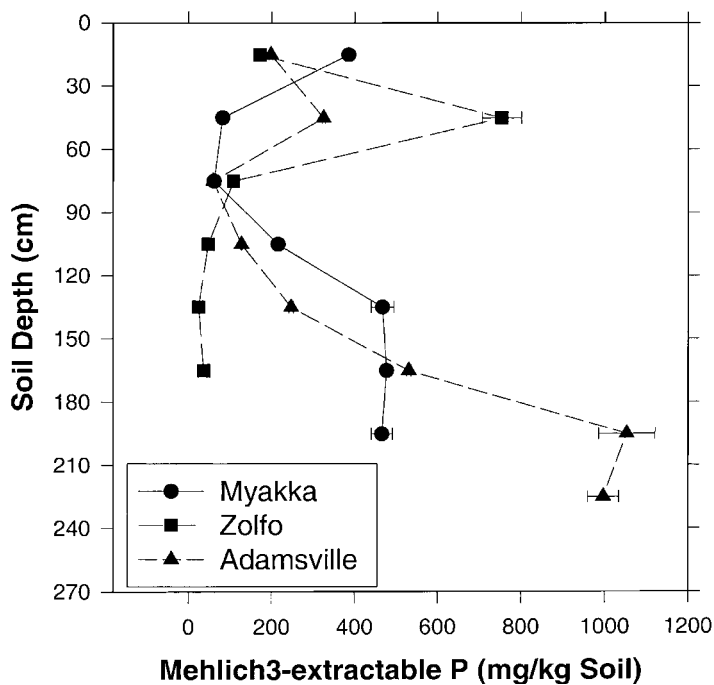
Figure 1. Mehlich3-extractable P as a function of depth for Myakka, Zolfo, and Adamsville soils. Error bars representing one standard deviation are shown when they exceed the size of the symbol.

For Zolfo soil, P concentration increased from $172\,mg\,kg^{-1}$ in the surface 30-cm layer to $754\,mg\,kg^{-1}$ in the soil at $30-60\,cm$ depth. The element concentration decreased sharply to $109\,mg\,kg^{-1}$ in $60-90\,cm$ segment, then decreased gradually with depth until reaching a concentration of $37\,mg\,kg^{-1}$ in the saturated zone at 180-cm depth.

For Adamsville soil, P accumulation was observed in the surface where it varied from 198 to $325\,mg\,kg^{-1}$ in the top 60-cm layer. The element concentration decreased to its lowest value of $59\,mg\,kg^{-1}$ in $60-90\,cm$ segment. Then, P concentration increased sharply with depth until reaching about $1000\,mg\,kg^{-1}$ in the saturated zone at 240-cm depth.

These data provide a clear evidence of downward transport of P through the soil profile. Neller (30) reported that in 4 months, $72.4\,cm$ of rainfall leached more than 70% of applied superphosphate-P $(280\,kg\,acre^{-1})$ from the surface 20 cm of Leon fine sand (Aeric Haplaquods).

The data on Al concentration at various depths for Myakka, Zolfo, and Adamsville soil profiles are illustrated in Fig. 2. The vertical distribution of Al through the profile of each soil followed similar pattern to that observed for P. In their study on Florida sandy soils, Zhang et al. (31) found that the distribution patterns of various forms of P along the soil profile were somewhat similar to the distribution of Al and Fe.

Significant correlations between Mehlich3-extractable P and Al were obtained for soil samples collected at various depths for Myakka (r = 0.81), Zolfo (r = 0.90), and Adamsville (r = 0.97). Using Al and soil pH as independent parameters in a multiple regression equation contributed to 92, 88, and 94% of variations in P concentrations for Myakka, Zolfo, and Adamsville soil, respectively.

These data indicated a close relationship between P and Al forms moving down through the soil profile. The pH of subsurface soil samples was generally below 5.0 for the three soils (Fig. 3). The solubility of common Al-phosphate minerals (e.g., variscite) are extremely low in acidic soils at pH < 5.0 (4). It is improbable that the downward transport of P through the soil was in solution phase. It is likely to occur mainly as Al-phosphates in colloidal phase.

It is well established that the mobility of soil colloids (such as Al, Fe, Si, and organic C) plays a major role in soil formation and pedogenic processes (21). Understanding colloidal transport in the subsurface environment has attracted lot of attention because of the possible role of colloids in enhancing transport of contaminants to groundwater (32,33). In this study, it is possible that Al-phosphates are moving down through the soil either as a discrete phase or as a precipitate on surfaces of colloidal clay particles.

In field experiments, Burgoa et al. (34) studied effects of cattle manure application on P distribution in sandy soils of Southern Florida. They found P accumulation in the top 20 cm was as much as 200 times larger than determined
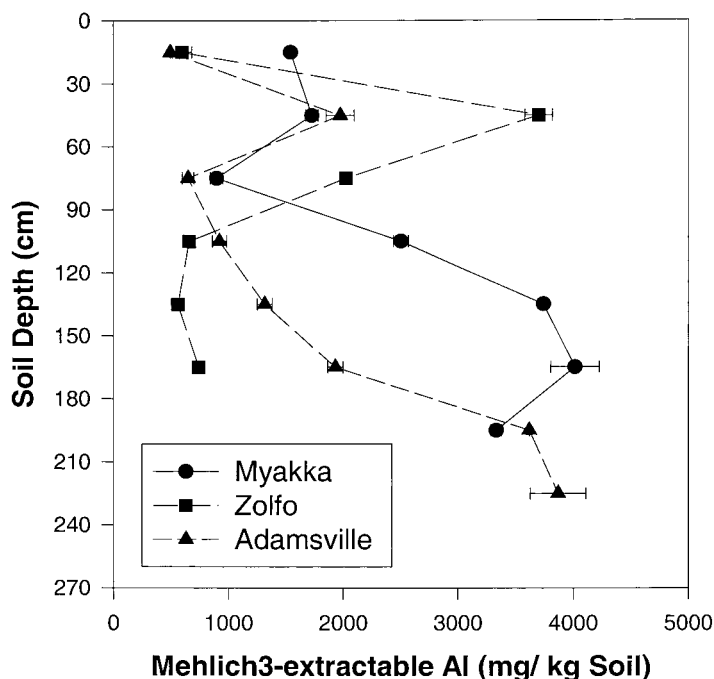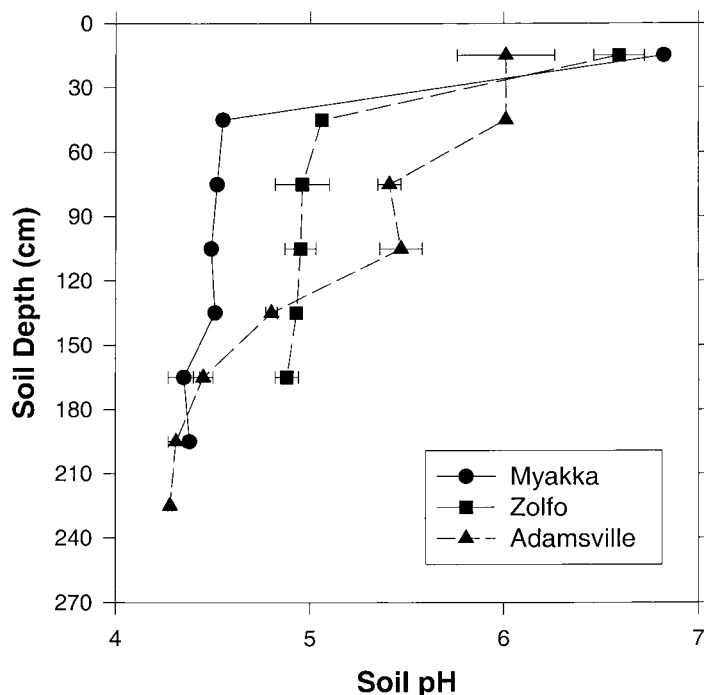
Figure 2. Mehlich3-extractable Al as a function of depth for Myakka, Zolfo, and Adamsville soils. Error bars representing one standard deviation are shown when they exceed the size of the symbol.

in the native soil, and high P concentrations as deep as 1.2 and 2.0 m in the soil profile. Burgoa et al. (34) concluded that P was possibly accumulated in a precipitated form because soils had very small P sorption capacity.

Water-extractable P for Myakka, Zolfo, and Adamsville soils as a function of depth is shown in Fig. 4. It was generally low ranging from 0.12 to 2.14 mg kg^{-1} for Myakka, 1.11 to 1.83 mg kg^{-1} for Zolfo, and 0.2 to 3.18 mg kg^{-1} for Adamsville. Statistical analysis indicated the absence of any significant correlation between water-, and Mehlich3-extractable P.

The data on Mehlich3-extractable P for soil samples collected from the saturated zone (at a depth of 210 cm for Myakka, 180 cm for Zolfo, and 240 cm for Adamsville) show concentrations of 467, 997, and 37 mg P kg^{-1}, respectively (Fig. 1). However, the water-extractable P determined for these soil samples, and the concentration of P in groundwater was relatively low. The water-extractable P was 0.12, 1.35, and 0.20 mg kg^{-1} for Myakka, Zolfo, and Adamsville, respectively. Meanwhile, the concentration of P in groundwater was
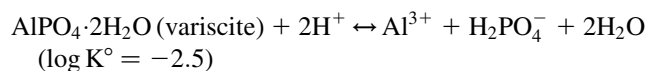
Figure 3. Soil pH (water) as a function of depth for Myakka, Zolfo, and Adamsville soils. Error bars representing one standard deviation are shown when they exceed the size of the symbol.

$0.09 \, mg \, L^{-1}$ for Myakka, $1.34 \, mg \, L^{-1}$ for Zolfo, and $0.21 \, mg \, L^{-1}$ for Adamsville.

These P concentrations might reflect the solubility of Al-phosphates in acidic environments. Lindsay (4) reported that variscite ($AlPO_4$-$2H_2O$) is the most stable Al-phosphate mineral in acid soils and can control P concentration in soil solution according to the equilibrium reaction:

$$AlPO_4 \cdot 2H_2O \, (\text{variscite}) + 2H^+ \leftrightarrow Al^{3+} + H_2PO_4^- + 2H_2O$$
$$(\log K^\circ = -2.5)$$

where K° = equilibrium constant.

Sodek et al. (35) reported the presence of substantial amounts of kaolinite and quartz in the soil profile of Adamsville, Myakka, and Zolfo soil series. For the three sites investigated, if Al^{3+} concentration in the aquifer was in equilibrium with kaolinite/quartz system, variscite would support 0.44, 1.38, and 0.35 mg
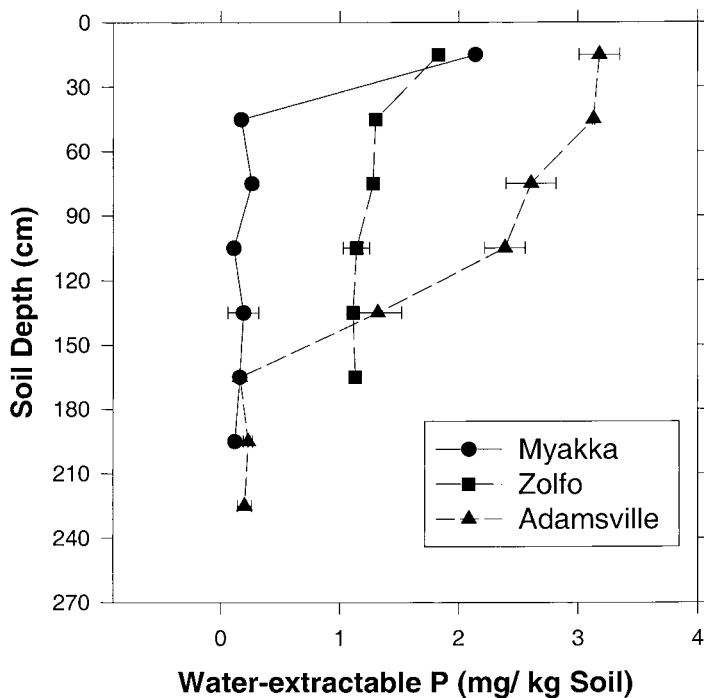
Figure 4. Water-extractable P as a function of depth for Myakka, Zolfo, and Adamsville soils. Error bars representing one standard deviation are shown when they exceed the size of the symbol.

PL^{-1} (activity) in the groundwater for Myakka, Zolfo, and Adamsville, respectively (4). However, the respective P activities would be 0.02, 0.06, and 0.02 mg P/L in the groundwater if Al^{3+} concentration was in equilibrium with gibbsite $[Al(OH)_3]$. At the ionic strength observed for groundwater at these sites, calculated P concentrations would be about two folds of activities.

CONCLUSIONS

The data obtained on extractable forms of P indicated an accumulation in most surface soil samples collected from old citrus groves. Either Mehlich3, Bray1, or double-acid extracting solution can be a good index to evaluate P accumulation in these soils. Further, the high correlation observed between P and Al concentrations in Mehlich3, and other extractants suggest the formation of Al-phosphates in soils. The distribution of P in profiles of selected soils indicate a

considerable transport of P from the surface horizon through the soil column into the saturated zone.

With high rainfall, sparingly soluble Al-phosphates formed in the surface soil could move down as colloidal particles through the sandy soil column and reach the saturated zone. Similarly, Al-phosphates could reach surface water bodies through subsurface flow in addition to surface water runoff.

The low P concentration in water extract for soil samples collected from the saturated zone, and in the adjacent groundwater might be related to the low solubility of Al-phosphates. The solubility of Al-phosphate mineral such as variscite is dependent on pH, and Al^{3+} concentration. Changes in the soil pH and/or Al^{3+} concentration in the saturated zone can affect P concentrations in groundwater. For example, raising pH in the saturated zone by one unit at a constant Al^{3+} concentration would increase P concentration in groundwater by 10-fold.

The relatively high pH values for surface water/sediment systems might explain the presence of high P concentrations in some streams and lakes in Florida. However, verification of such assumption needs further investigation.

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