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Phosphorus retention in drainage soils of commercial greenhouses^{1,2}

José A. Dumas³, Joaquín A. Chong⁴, Magaly Cintrón⁵ and Luis Reinaldo Santiago⁶

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ABSTRACT

Five commercial greenhouses in the central mountainous zone of Puerto Rico were studied in order to identify changes in soil factors that affect P retention. Soils were collected both within and outside drainages at a 0- to 15-cm depth. Soil physicochemical properties varied in samples taken both within and outside drainages. The high Fe and Al content in the soils of this study suggested a high phosphorus retention capacity. Laboratory estimates of P retention parameters indicated differences in P sorption capacity among soils. Phosphorus retention parameters were highly correlated with citrate dithionite extractable Fe. The equilibrium P concentration was also correlated with citrate dithionate Al in soils outside drainages. This finding was due to the higher soil organic matter counterbalancing the soil P retention capability of Al, all of which indicates the importance of clearing all drainages of organic residues in order to avoid excessive movement of P outside the greenhouse premises.

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³Chemist, Department of Crops and Agroenvironmental Sciences, Agricultural Experiment Station, University of Puerto Rico, 1193 Calle Guayacán, Jardín Botánico Sur, San Juan, PR 00926-1118.; E-mail: josea.dumas@upr.edu

⁴Plant Physiologist, Assistant Researcher, Department of Crops and Agroenvironmental Sciences, Agricultural Experiment Station, Río Piedras, P.R. E-mail: joaquin. chong@upr.edu

⁵Assistant Chemist, Department of Crops and Agroenvironmental Sciences, Agricultural Experiment Station, Río Piedras, PR. E-mail: magaly.cintron@upr.edu

⁶Horticulturist, Associate Researcher. Department of Crops and Agroenvironmental Sciences, Agricultural Experiment Station, Río Piedras, PR. E-mail: luis.santiago@upr.edu

Key words: phosphorus sorption, organic matter, iron, aluminum

RESUMEN

Retención de fósforo en suelos de drenaies en invernaderos comerciales

Se estudiaron cinco invernaderos comerciales en la zona montañosa interior de Puerto Rico para identificar los cambios en las propiedades del suelo que afectan la retención de fósforo. Las muestras de suelo se tomaron a una profundidad de 0 a 15 cm dentro y fuera de los drenaies de los invernaderos. Las propiedades físico-químicas de los suelos dentro y fuera de los drenaies fueron diversas. El alto contenido de Fe y Al en los suelos de este estudio sugiere una alta capacidad de retención de fósforo. Los parámetros de retención de P estimados en el laboratorio indicaron diferencias en la capacidad de absorción de P entre los suelos. Los parámetros de retención de P se correlacionaron altamente con el Fe extraíble con ditionito-citrato. La concentración de P en equilibrio también se correlacionó con el Al extraíble con ditionito-citrato en los suelos fuera de los drenajes. Este hallazgo se debió a que el alto contenido de materia orgánica del suelo en los drenaies tuvo el efecto de contrarrestar la capacidad de retención de P que tiene el AI, lo cual indica la importancia de limpiar los drenaies de los residuos orgánicos para evitar el movimiento excesivo de P fuera del área de los invernaderos.

Palabras clave: adsorción de fósforo, materia orgánica, hierro, aluminio

INTRODUCTION

Fertilizers are widely used in ornamental plant production because the growing media do not provide sufficient nutrients for proper plant growth and development. Most fertilizer programs recommend 1.8 kg/m³ of superphosphate to soil-based substrates, and 2.7 kg/m³ of the same material to soil-less substrates (Nelson, 1985). Higher rates are required in soil-less substrate because phosphorus is not extensively fixed in these systems and is readily leached out. The frequency of application can be monthly, weekly and even daily, depending on the crop. The high rates of fertilizer used may increase the potential movement of nutrients outside greenhouse premises, all of which may impair water resources nearby. For years it has been reported that applications of fertilizers as well as of animal manure in agriculture have caused a widespread increase of nitrogen and phosphorus concentration in streams across the United States (USGS, 1999).

The major impact of phosphorus and other nutrients on surface waters is the stimulation of algae growth, which could result in eutrophication (USGS, 1999; Wetzel, 1983). It has long been accepted that phosphorus is the most important nutrient for primary productivity in freshwater bodies (Schindler, 1977). Excessive nutrient applications could lead to phosphorus movement by runoff water during and after irrigation. Phosphorus can reach surface waters through greenhouse drainages as P dissolves in runoff water and attaches to soil particles from soil erosion. Nutrient movement through runoff beyond the greenhouse premises depends on many factors, including the irrigation regime, physical and geochemical soil properties, and nutrient uptake by microorganisms and plants (Bruland and Richardson, 2004; Lyons et al., 1998). Factors such as climate, pH, ionic strength, soil redox potential and water depth (Young and Ross, 2001; Lyons et al., 1998; He et al., 1997; Young et al., 2001; Lathwell, 1979) influence the movement of nutrients with runoff (Pote et al., 1999).

Phosphorus retention by soils is controlled by mineral, organic and biological factors (Bridgham et al., 2001). In soils, amorphous and crystalline iron (Fe) and aluminum (Al) hydroxyl oxides have great influence on P retention/release processes (Lyons et al., 1998; Giesler et al., 2005; Bruland and Richardson, 2004). Other important factors in P retention are organic and inorganic carbon content (Bruland and Richardson, 2004). In organic humic soils, ligand competition among organic dissolved anions affects the soil P retention (Pr) capacity (Geisler et al., 2005; Delgado et al., 2002).

Phosphorus retention by soils has been successfully evaluated by using the equilibrium P concentration (EPC_o) (Guertal et al., 1991). The EPC, is the solution concentration of P at which zero fixation occurs (P is neither released nor retained in the soil). This concentration is calculated from P adsorption isotherms. When P concentration in soil water drops below the EPC_o the soil is no longer a sink of P but rather a source. This variable has been suggested as a way to measure mobility of P from soils to flood water (Cooper and Gilliam, 1987). Another way to measure the potential for mobility of P is with the traditional P tests such as Bray 1, Bray 2, Mehlich 3 and Olsen (Young and Ross, 2001: Daverede et al., 2003). There is a lack of information about P and dynamics in drainage soils of commercial greenhouses in the tropics, and about how cultural practices could affect P retention in the soils. The EPC, and the traditional P test could help provide information on P dynamics in greenhouse drainage soils.

The specific objectives of this study were i) to evaluate P status and the capacity of P retention in soils in greenhouse drainages; and ii) to determine the relationship between phosphate release and soil physicochemical characteristics that could be affected by growers' cultural practices, characteristics such as extractable P, the equilibrium P concentration (EPC_o), crystalline and amorphous Fe and Al, soil organic matter, pH, and electrical conductivity.

MATERIALS AND METHODS

Study Sites. The study was carried out in five greenhouses in the central region of Puerto Rico, where the topography is predominantly hilly with tilled plains. The altitude is approximately 1,100 m, with a mean annual rainfall of 5.080 mm. Soil samples were collected 8 November 2007. Table 1 shows the greenhouses' dimensions, predominant soil series and general types of ornamental plants grown during sampling. Greenhouse water irrigation of the study site comes from the Caguas-Juncos Valley Aquifer, except that for greenhouse 1, which receives water from the Cavey Valley Aquifer. Both aquifers are predominantly sand and gravel inter-layered with clay and silt (Molina, 1997) The irrigation water of each greenhouse was collected in order to assess its quality. The pH, electrical conductivity (EC), alkalinity and P of the irrigation water were measured by using U.S. EPA methods 150.1, 120.1, 310.1, and 365.1, respectively (USEPA, 1983). Irrigation water of all greenhouses, except that of greenhouse 1, had an average pH of 7.21, EC of 479 µS/cm and alkalinity of 193 mg CaCO, /L. The water of greenhouse 1 had a pH of 7.06 and 5.50 after acidification by the grower: EC of 246 uS/cm; and alkalinity of 96 mg CaCO./L. The average dissolved P value in the collected waters was 0.027 mg/L.

Soil Sampling. Three soil samples composed of 20 soil cores were collected at random with an auger sampler in three areas along the drainage (GD) and in three areas outside the drainage (OD) of each greenhouse. The three areas along the drainages were separated by 1 to 2 m. The soil cores were taken from the top 15 cm, and were placed in sealable plastic bags.

Phosphorus Sorption. Soil samples were air-dried, ground and passed through a 2-mm mesh sieve. Soils were sterilized by fumigation with chloroform (Bridgham et al., 2001). Fifteen grams of soil was weighed in a beaker and 30 mL of chloroform was measured in another beaker. Both beakers were placed inside a desiccator. The air was purged out by vacuum until the chloroform began to boil. It was boiled for one minute to assure that the soil was kept under a chloroform atmosphere. The chloroform atmosphere was maintained for at least four days.

Phosphate adsorption isotherms were determined as described by Lyons et al. (1998) except for slight modifications. For each sample, 1.0 g of air-dried sterile soils was placed in a 50-mL plastic sterile vial, and 15 mL of a P standard solution was added. The P standard solutions were 0, 3, 5 or 7 mg P/L. The vials were capped and placed on a top to end shaker for 24 h in the dark at room temperature. The samples were centrifuged at 1000 rpm for 2 min, and filtered (0.20 µm nylon

Location (Municipality)	Greenhouse number	$\begin{array}{c} Greenhouse \\ Area \left(m^2 \right) \end{array}$	Soil Series	Soil classification	Type of irrigation	Years in operation	Ornamental plants
Cayey	1	892	Caguabo	Loamy, mixed, active, isohyperthermic, shallow Typic Eutrudepts	Sprinkler	12	Annual plants
Aibonito	2	139	Daguey	Very-fine, kaolinitic, isohyperthermic Inceptic Hapludox	Sprinkler	15	Annual plants
Aibonito	3	327	Río Piedras clay	Fine, kaolinitic, isohyperyhermic Typic Hapludults	Hose	24	Poinsettia (Euphorbia pulcherrima)
Aibonito	4	186	Montegrande clay	Very-fine, mixed, superactive, isohyperthermic Chromic Hapluderts	Hose	3	Poinsettia (Euphorbia pulcherrima)
Aibonito	5	486	Río Arriba clay	Fine, mixed, subactive, isohyperthermic Vertic Paleudults	Sprinkler	20	Annual plants

 TABLE 1.—Description of greenhouses, predominant soil series, soil classification and type of ornamental plants.

filter). The filtrates were analyzed for soluble P by using an HPLC chromatographic system.

The HPLC chromatographic system consisted of a Waters 600 HPLC pump together with a Waters IC-Pak A HR analytical column. Phosphorus was detected with a Waters 341 conductivity detector. The mobile phase was prepared as follows: The concentrate solution A was prepared by dissolving 16 g of sodium gluconate, 18 g of boric acid and 25 g of sodium tetraborate in a 25:75 v/v mixture of glycerol:water to 1 L. The working mobile phase was 20 mL of the concentrate solution A, 20 mL of n-propanol, 120 mL of acetonitrile and water up to one liter. This mobile phase was filtered (0.45 µm nylon filter) before use. Its conductivity was of about 270 µS/cm (% Full Scale). The flow rate was 1 mL/min. The detector was operated at a base range of 200 µS/cm.

The adsorption isotherm was obtained by plotting the net amount of added P retained by soil at equilibrium (S_r) vs. the solution P concentration (C_e) measured after a 24-h equilibration. The general formula of the above mentioned graph at low equilibrium concentrations is usually linear (Rao and Davidson, 1979) and fits the following equation (Pant and Reddy, 2001):

$$S_r = K_d \times C_e - S_o$$

The slope of the isotherm curve is the distribution coefficient (K_d) and the intercept in the y-axis is the natural P concentration (S_0) in the soil at the point where no net adsorption nor desorption occurs. When S_r is zero (the point where no net adsorption or desorption of P occurs) the EPC₀ can be calculated by reducing the linear equation to:

$$C_e = EPC_o = \frac{S_o}{K_o}$$

where the intercept of the isotherm on the x-axis is equal to EPC_o.

Soil analysis. The amorphous Fe and Al (Fe_H and Al_H) were measured by extraction with hydroxylamine hydrochloride (Ross et al., 1985). The crystalline forms of Fe and Al (Fe_D and Al_D) were extracted by the citrate dithionite method (Holmgren, 1967). Soil organic matter (SOM) was determined by the Walkley and Black method (Nelson and Sommers, 1996). Soil pH and conductivity were determined by using 1:2 soil-water ratio. Available P (AP) was determined by the Bray 1 or Olsen methods (Olsen and Summers, 1982) depending on the soil pH.

Analysis of variance (ANOVA) and principal component analysis were performed using XLSTAT-Pro 7.0 statistical software (Addinsoft, 2003). Pearson's procedure was used to correlate the data with a significance of each test to $p \le 0.05$ (pH, EC, P retention, EPC_0 , Fe_D , Al_D , Fe_H , Al_H , and SOM).

RESULTS AND DISCUSSION

The pH of irrigation water is an important issue for ornamental plant growers because ornamental peat base-grown plants usually require a pH range of 5.6 to 5.8 (Nelson, 1985) to promote adequate nutrient availability to the plants. The pH of all irrigation waters of this study was above 7.06, except for that in greenhouse 1, which was adjusted to 5.5. When the irrigation water has a pH greater than 5.8, these growers increase the amount of fertilizer used in order to compensate for nutrient deficiencies induced by the high pH. Nutrient deficiencies occur because irrigation water with high pH also has a high content of calcium and magnesium. Nutrients applied in excess can migrate outside of greenhouse premises through drainages, all of which may affect physicochemical properties of soil in drainages.

The pH values found in greenhouse drainage (GD) soils and outside drainage (OD) soils were significantly different (Table 2). The pH values in GD soils of greenhouses 1, 4 and 5 were significantly lower than those in OD soils. However, the pH values in GD soils of greenhouses 2 and 3 were significantly higher than those in OD soils. This pattern could be due to the predominant clay in the soils. Table 1 shows that the soils in the greenhouse areas of this study are from different soil classifications and have different capacity to absorb or provide protons. Caguabo and Montegrande clay are mixed clay mineral soils with high CEC. Río Arriba clay has mixed

Greenhouse Id.	pHw	Electrical conductivity µS/cm	${\mathop{\rm SOM}_{\%}}$	${ m Fe}_{ m D} { m Mg/g}$	Fe _H Mg/g	${ m Al}_{ m D} { m Mg/g}$	$egin{array}{c} { m Al}_{ m H} \ { m Mg/g} \end{array}$
1 GD^1	$6.55 \ b^2$	158 a	3.26 a	24.61 a	9.46 a	2.62 a	2.34 a
1 OD	7.47 a	$114 \mathrm{b}$	0.95 b	18.94 b	7.57 a	2.66 a	2.45 a
2 GD	7.24 a	279 a	5.50 a	26.47 a	$13.58 \mathrm{b}$	3.80 a	3.40 a
2 OD	$5.51 \mathrm{b}$	69 b	$2.42 \mathrm{b}$	27.07 a	28.51 a	$2.82 \mathrm{b}$	3.70 a
3 GD	5.67 a	111 a	1.73 a	31.97 a	10.39 a	3.31 a	2.83 a
3 OD	4.95 b	95 b	0.56 b	26.03 b	7.16 a	3.29 a	2.32 a
4 GD	$4.48 \mathrm{b}$	49 a	1.10 a	58.38 a	10.52 a	5.00 a	3.08 a
4 OD	5.26 a	77 a	1.99 a	29.90 b	6.49 a	3.66 b	3.32 a
5 GD 5 OD	6.47 b 7.69 a	252 a 183 b	4.23 a 1.08 b	26.41 a 18.27 b	10.85 a 10.21 a	3.47 a 2.58 b	4.78 a 3.49 b

TABLE 2.—Chemical and physical characteristics of soils from five ornamental greenhouses.

¹GD = greenhouse drainage channel; OD = outside drainage channel of greenhouse. ²Values among soils for each greenhouse followed by the same letter within a column

are not significantly different, using Fisher ANOVA on rank test.

clay content with low CEC activity (subactive). Daguey and Río Piedras are kaolinitic soils that have low CEC and would be in a subactive class by definition (Seybold et al., 2005). It is known that soils with high content of kaolinite, such as those in greenhouses 2 and 3, have little capacity to absorb or produce protons (Weaver et al., 2004). These soils are greatly affected by grower practices. Meanwhile, the pH in soils with mixed mineralogy is affected according to the proportions of the types of soil clays (Weaver et al., 2004). The interplay between soil clay type and grower practices could explain differences in soil pH values between GD and OD in this study (Tables 1 and 2).

The soil electrical conductivity (EC) values were significantly higher in GD soils than in the OD soils, except in greenhouse 4. Greenhouse 4 was new in operation and the effect of the greenhouse's runoff in soil EC was probably slight (Tables 1 and 2). The ECs were 39, 304, 17 and 38% higher for GD than for OD in greenhouses 1, 2, 3 and 5, respectively. The EC is directly affected by soil type and nutrients such as N and K, and is influenced by the soil texture, CEC and humic matter (Heiniger et al., 2003). Soil EC is primarily associated with exchangeable cations in the soil solution: therefore, any change in nutrient loads directly affects the soil exchangeable surfaces. In other words, changes in soluble salts, thus in EC, can greatly affect soil nutrient dynamics and can change the physicochemical (mineral and organic available sorption surfaces) and biological soil characteristics. When samples collected in the greenhouses were grouped by sampling sites (GD and OD), an exponential relationship between pH and EC could better fit for the GD group ($R_2 = 0.88$) than for the OD ($R_2 = 0.59$) group (Figure 1). These findings suggested that there were changes in soil properties within greenhouses' drainages, changes which could affect the movement of nutrients.

Soil organic matter (SOM) is an important soil component related to movement of nutrients. The SOM at GD varied from 1.10 to 5.50% whereas in OD soils SOM varied from 0.56 to 2.42%. The SOM at the GD sites was 2.3 to 3.9 times greater than that at OD sites, except for greenhouse 4, which was new in operation (Table 2). The higher content of SOM in GD soils was probably the result of gradual movement of plant debris, substrate and soluble organic matter with greenhouse runoff. The SOM contains numerous functional groups that are Bronsted and Lewis acids. These functional groups in the SOM may have caused P-binding site blockage at the mineral surfaces, all of which could enhance P mobility (Moore et al., 1998). Therefore, from the above-mentioned data we can denote the importance of maintaining



 $F_{\rm IGURE}$ 1. Relationship between electrical conductivity and pH values for greenhouse drainage (GD) soils and outside drainage (OD) soils from five commercial greenhouses in Puerto Rico.

greenhouse drainages clear of organic matter debris in order to avoid enhanced P movement with greenhouse runoff.

Iron and aluminum oxide minerals are important soil components for P retention. All GD soils had significantly more iron oxides (Fe_D) than OD soils, except for those in greenhouse 2 (Table 2). The Fe_H was not significantly different between GD and OD soils, except in greenhouse 2, where it was greater in OD soils. The data indicates that crystalline iron is the predominant form in most soils, except for 2-OD, where Fe in the amorphous and poorly crystalline forms predominates. The Al_D in GD was significantly higher than in OD at greenhouses 2, 4 and 5, whereas only in greenhouse $5 Al_H$ in GD was significantly higher than that of OD. The points of zero charge of iron and aluminum oxides were 6.7 and 9.1, respectively. The pH values of all the soils in this study were well below 9.1; thus Al is a main factor in P retention, but for those soils with pH higher than 6.7, the net negatively charged surfaces of iron oxides could play a predominant role in increasing P mobility.

The available phosphorus (AP) is an indicator of phosphorus in the soil solution and phosphate movement with water overlay (Moore et al., 1998). The AP (Table 3) values in GD were greater than those in OD soils for greenhouses 1 through 3 because of the higher concentration of P accumulated at GD which was due to standard greenhouse operations. The AP in GD and OD soils in greenhouse 4 were similar because this greenhouse was new in operation. In greenhouse 5, similar AP between GD and OD soils was probably due to interaction effects of SOM with Al, effects which inhibit aluminum oxide crystallization. The resulting poorly crystalline aluminum oxides (Al_H) had high P adsorption capacity (Borggaard et al., 1990) that decreases phosphorus concentration in soil solution.

The P adsorption capacity for GD and OD soils was estimated in the laboratory by using isotherms. The linear adsorption coefficients were not significantly different between GD and OD, except in greenhouse 5 (Table 3). The EPC₀ values were similar between GD and OD, except in greenhouse 2. This result suggests that the grower's cultural practices, such as fertigation rates, irrigation patterns, and drainage clearances of organic matter debris, have influenced P sorption capacity of the soils in greenhouse 2 even though the linear adsorption coefficients (K_d) were similar between GD and OD soils (Table 3). This finding is explainable by the amount of amorphous and poorly crystalline forms of iron, which was significantly higher in 2-OD. The higher EPC₀ of GD soil in greenhouse 2 is because of the effect of pH (7.24) and the partial blockage of mineral surfaces by the SOM. The native sorbed P (S_0) in soils could be

Greenhouse	AP (Bray I)	\mathbf{K}_{d}	$\mathrm{EPC}_{\mathrm{o}}$	\mathbf{S}_{0}^{1}
Id.	µg/g	L/kg	mg/L	Mg/kg
$\begin{array}{c} 1 \ \mathrm{GD}^2 \\ 1 \ \mathrm{OD} \end{array}$	26 a³ 3 b	18.9 a 18.9 a	0.15 a 0.16 a	-2.8 a -4.3 a
2 GD	99 a	22.0 a	0.50 a	-11.0 a
2 OD	6 b	23.5 a	$0.04 \mathrm{b}$	-1.3 b
3 GD	42 a	23.4 a	0.08 a	-1.9 a
3 OD	4 b	25.0 a	0.003 a	-0.1 a
4 GD	2 a	0.04 a	0.001 a	0.0 a
4 OD	4 a	0.04 a	0.001 a	0.0 a
5 GD 5 OD	31 a 33 a	19.4 a 16.9 b	0.22 a 0.24 a	-4.2 a -4.0 a

TABLE 3.—Phosphorus adsorption characteristics of soils from five ornamental greenhouses.

¹native adsorbed P (negative sign represents the water desorbable P).

 2 GD = greenhouse drainage channel, OD = outside drainage channel of greenhouse.

³Values among soils for each greenhouse followed by the same letter within a column are not significantly different, using Fisher ANOVA on rank test. an indicator of P load with the greenhouse's runoff. The highest S_0 was in greenhouse 2 GD, the same greenhouse that had higher AP and EPC₀. It is important to mention at this point that contrary to other growers of this study, the grower of greenhouse 2 had poor drainage cleanup practices. This finding indicates that the cultural practices used in greenhouse 2 affected P soil sorption characteristics.

Available P was positively correlated with pH, and EC at both GD and OD soils, and with SOM at GD soils, whereas it was negatively correlated with Fe_p at GD and OD soils (Table 4). The lack of correlation between AP and SOM at OD was due to the fact that most OD soils have similar and low content of both AP and SOM (Tables 2 and 4). This finding indicates that SOM accumulation at GD sites increases AP at GD (Table 4) and may increase the potential environmental impact of P. The EPC s were highly influenced by SOM, amorphous and poorly crystalline forms of Fe and Al, and by the electrical conductivity of the soils (Table 4). The EPC_o was positively correlated with pH, EC and AP in GD and OD soils, and with SOM in GD soils; EPC, was negatively correlated with Fe_p and Al_p in GD and OD soils. Results from this study have shown that both the EPC, and the traditional Bray 1 test are useful tools for evaluating the potential movement of phosphorus in greenhouse drainages. Highly significant correlations were found in EPC, and AP with soil pH, all of which suggests that acidifying irrigation water prior to fertilization could reduce P mobility in drainages (Table 4).

The results indicate that generally GD soils have higher content of SOM than OD soils (Tables 2 and 3). Other soil parameters, such as pH, EC, Fe and Al oxides, have great importance in the dynam-

	A	Р	EPC_{o}		
Parameter ¹	GD	OD	GD	OD	
pHw	0.772^{*2}	0.587^{*}	0.822*	0.837*	
EC SOM AP	0.712^{*} 0.767^{*}	0.822* NS	0.837^{*} 0.901^{*} 0.890^{*}	0.754* NS 0.707*	
Fe _H	NS	NS	NS	NS	
Al_{H}	NS	\mathbf{NS}	NS	NS	
Fe_{D} Al_{D}	-0.571^{*} NS ³	-0.547* NS	-0.586* NS	-0.807* -0.682*	

TABLE 4.—Correlation coefficients between equilibrium P sorption parameters (AP and EPC_{o}) and selected physicochemical parameters of the greenhouse soils.

 $^1\!\mathrm{EC}$ - electrical conductivity (µS/cm); SOM-soil organic matter (%); AP-extractable P-Bray 1; X_H- hydroxylamine hydrochloride extractable (mg/g); X_D- citrate dithionite extractable.

^{2*}Significant at the 0.05 probability level.

 ^{3}NS denotes non significant at P < 0.05.

ics of phosphorus. Phosphorus retention in those soils increased with iron and aluminum oxides (Fe_D and Al_D) (Table 4). Higher SOM has increased the P availability at GD; however, this relationship was not observed in OD, probably because of the similar low SOM in OD soils. Among the greenhouses in this study, parameters such as EPC₀ and AP indicate that the soils in greenhouses 3 and 4 had the lower potential for P mobility as compared to that of the other soils in this study, with the greater P mobility in greenhouse 2. This research has also demonstrated that growers' practices could change soil characteristics affecting P retention capacity.

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