

Phosphorus fixation and its relationship with soils chemical properties of the coffee zone of Huila, Colombia

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ABSTRACT

Adsorption is one of the critical processes in phosphorus (P) availability in plants. In the coffee crop (*Coffea arabica*), the highest dose of P is supplied in the vegetative phase, so its management is fundamental to guarantee the optimum growth of plants. The aim of this work was to determine the P fixation capacity and its relationship with the soil chemical properties of the Huila coffee zone, Colombian department, with the largest area planted with coffee. The adsorption isotherms were obtained by equilibrating the soil with 30mL of KH_2PO_4 solution dissolved in a 0.01M $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, containing concentrations of P between 50 and 4.200 mg kg^{-1} . The P adsorption was measured for 60 soil samples collected from the five main cartographic units of the department: Campoalegre, El Recreo, La Cristalina, Saladoblanco, and San Simón. The data fitted to the linear and nonlinear Langmuir model forms. It was found that the soils of the region have a variable P fixation capacity, with values of q (adsorption at 0.2 mg L^{-1} in solution) between 8 and 1330 mg kg^{-1} and b (maximum adsorption capacity) from 117 to 3916 mg kg^{-1} , without finding an association with the evaluated soil units. A correlation of q and b was found between Al^{3+} , Al^{3+} saturation, pH, Ca^{2+} and Mg^{2+} , and base saturation.

Key words: Langmuir isotherms; phosphorus adsorption; soil acidity; soil cartographic unit.

1 INTRODUCTION

Phosphorus (P) is essential for plant growth by controlling primary physiological processes such as water and nutrient uptake and carbon metabolism (Bang et al., 2021). Due to its determining function in the adequate growth of the roots, which suffer morphological, physiological, and metabolic alterations in response to the deficiency of this nutrient, the growth of the aerial part of the plants is affected and, therefore, crop yields (Taiz et al., 2015). In this way, phosphorus constitutes one of the nutrients of most significant interest within crop fertilization plans.

For coffee crops in Colombia, the application of P (60-80 kg ha^{-1}) is recommended during the seedling and field establishment stages. The preceding is a consequence of the poor development of the root system, which prevents increasing the exploration capacity of the roots for the uptake of P (Sadeghian; Ospina, 2021).

P is a nutrient with low mobility in the soil, and it is estimated that around 90% of the element fixed in the soil is not available to plants (Maathuis, 2009; Havlin et al., 2017). For this reason, during the initial stages of crops, sources of phosphorus fertilizers are applied more frequently.

P is applied to the soil through fertilizers that dissolve to produce phosphate ions (H_2PO_4^- , HPO_4^{2-}), which can react with various soil components, thus being converted to less soluble forms. This phenomenon is known as P fixation or retention and largely determines the dynamics of the element in the soil and, consequently, its availability to plants (Zhao; Li; Yang, 2021; Havlin et al., 2017; Mahdi et al., 2012; Richardson et al., 2009).

This fixation occurs when the solid phase adsorbs the P from the soil solution, and there are two ways in which it can happen: one physical and one chemical. When negatively charged phosphate ions are adsorbed on the surface of soil particles by forces of electrostatic attraction, the process is physical, whereas when adsorption occurs with particles of variable charge, such as iron and aluminum oxides and hydroxides and secondary P minerals are formed (precipitation), the process is chemical (Zhao; Li; Yang, 2021).

One of the ways to describe the P fixation process is by applying adsorption isotherms, mainly through the LANGMUIR and FREUNDLICH equations (Alleoni; Mello; Rocha, 2009), classified as high-affinity adsorption equations (Yusran, 2010). Through these, the P adsorbed at 0.2 mg L^{-1} in the equilibrium solution (q) can be estimated, a concentration in the soil solution considered adequate for plant growth (Pierzynski; Madoweel; Thomas, 2005). Additionally, the Langmuir equation allows for estimating the maximum P adsorption capacity (b) and the binding energy between phosphate ions and the surface of the soil particles (K) (Singh, 2016; Nair; Reddy, 2013). These three parameters have been related to soil properties and have made it possible to identify the characteristics that may be responsible for P fixation and its dynamics in soils from countries such as Cameroon (Mbene et al., 2017), Colombia (González-Osorio et al., 2020; Díaz-Poveda; Sadeghian, 2017), Kenya (Muindi et al., 2015), Ethiopia (Hadgu et al., 2014) and Iran (Moazed et al., 2010), among others.

For Colombia, specifically in soils derived from volcanic ash in the coffee region, a high P fixation capacity has been found and, in turn, a difference in the degree of affinity for

the element (Díaz-Poveda; Sadeghian, 2017; Bravo; Gomez, 1974). This behavior can affect P fertilizer applications because part or all of the element can be fixed.

Among the country's coffee departments, Huila is the first producer, having a share of 18% in national production, and is the first in arable areas. The department is located in the denominated South and Center coffee regions between 1,200 and 2,000 m.a.s.l. with a medium temperature of 18.9 °C and an annual precipitation between 1,600 and 1,800 mm distributed bimodally for most of the department. An average density of 5,289 trees per hectare and an average age of 5.41 years stand out. The department's coffee growing is mostly in free sun exposure and with varieties resistant to rust (*Hemileia vastatrix*) (Centro Nacional de Investigaciones de Café - Cenicafé, 2019; Federación Nacional de Cafeteros de Colombia - FNC, 1985; Instituto Geográfico Agustín Codazzi - IGAC, 2017). Considering the importance of the soils of this region and the relevance that P has in the nutrition of the coffee crop, especially for the significant quantities applied in seedling and field establishment stages, this work was carried out to evaluate the fixation of P in soils of the department of Huila and its relationship with the soil chemical properties. These results can help to understand P availability according to some soil characteristics and how to make correct fertilizer applications in relation to soil type.

2 MATERIAL AND METHODS

2.1 Area of study, soil sampling, and taxonomic classification

The samplings were carried out in five of the cartographic units more representative of the Huila department in coffee lots. A composite sample of 1kg of soil was taken in the layer from 0 to 20 cm for each selected lot. The plantations corresponded to the Colombia, Castillo®, and Caturra varieties, with densities of over 4,000 plants ha⁻¹ and an age greater than 1.5 years. The soil units and the number of samples were defined based on the area cultivated in coffee through the ArcGis 10.2 (2013) software; specifically, stratified sampling was made by land unit area according to the association. These were: La Cristalina (LC) with 5 samples, Saladoblanco (SB) with 6, San Simón (SS) with 14, Campoalegre (CA) with 16 and El Recreo (ER) with 19, for a total of 60 samples (Figure 1). Table 1 indicates the soil unit's taxonomic categories and relevant information (FNC, 1985). It is important to highlight that the FNC, in its soil surveys, defined criteria to establish the type of soil unit, among them the association, defined as two or more typologies that occupy more than 30% of the delimited area and are easily separable in scaled surveys a little more detailed (Lince-Salazar; Sadeghian, 2021).

2.2 Soil chemical analysis

The samples were dried in an oven at 40 °C and passed through a 2-mm sieve. The following chemical properties were analyzed: pH (potentiometric method–soil: deionized water ratio 1:1 w/w), organic matter (OM) (Walkley–Black method), exchangeable calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) (extraction with ammonium acetate 1N pH 7.0), exchangeable aluminum (Al) (extraction with 1N KCl), phosphorus (Bray II method), cation exchange capacity (CEC) (extraction with 1N pH 7.0 ammonium acetate), sulfur (S) (extraction with monocalcium phosphate), iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) (extraction with 0.01M EDTA and 1M ammonium acetate) and boron (B) (extraction with monocalcium phosphate). Additionally, aluminum saturation and base saturation percentages were calculated.

2.3 Phosphorus adsorption isotherms

The P adsorption capacity was measured through the method proposed by Fox and Kamprath (1970). By triplicate, 3.0 g of dried soil were transferred to 50 mL propylene conic tubes, and 30 mL of a KH₂PO₄ solution dissolved in 0.01M CaCl₂·2H₂O with the following concentrations: 50, 100, 200, 400 y 800 mg P kg⁻¹ of soil were added. According to the phosphorus's retention capacity, applications with concentrations up to 4,200 mg kg⁻¹ of soil were continued for some soils. The tubes were shaken for 24 h and centrifuged at 4,000 rpm for 10, after which the samples were filtered using 0.45µm filter paper; finally, the concentration of P was quantified using the molybdenum blue method. The amount of P adsorbed was calculated as the difference between the initial concentration of the added solution and the final concentration obtained in the equilibrium solution.

For each soil, the adsorbed P was expressed as a function of its concentration in the equilibrium solution. The Langmuir equations in their nonlinear and linear forms were used to fit the data according to Equations 1 and 2:

nonlinear Langmuir

$$\frac{x}{m} = \frac{K C b}{(1 + K C)} \quad (1)$$

linear Langmuir

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b} \quad (2)$$

Where:

x/m = adsorbed P concentration, mg kg⁻¹ of soil

K = constant related with the binding energy between phosphate ions and soil particles surface, mg L⁻¹

C = solution P concentration, mg L⁻¹

b = P maximum adsorption, mg kg⁻¹ of soil

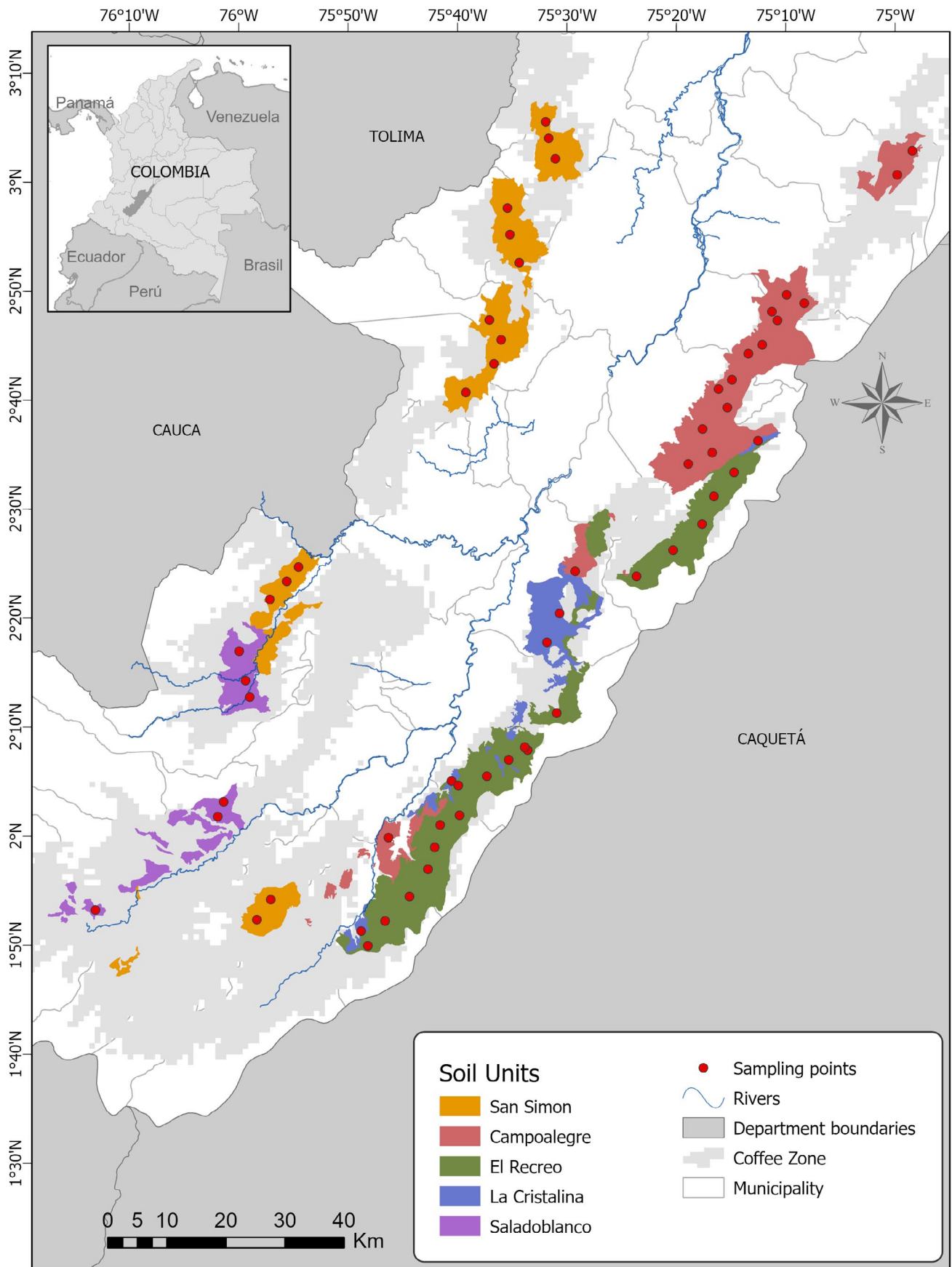


Figure 1: Location and sample distribution map by soil unit in Huila's department, Colombia.

Table 1: Taxonomic categories, geological formation, parental material, and unit area of Huila's department's more representative cartographic soil units.

Soil unit	Taxonomic classification	Geological formation	Parental material	Unit area, ha	Samples
La Cristalina	Typic Dystrudepts 45%, Paralithic Dystrudepts 30%, and others (Typic Tropaquepts and Typic Hapludalfs) 25%.	Sedimentary	Colluvia, biotite gneiss, andesites	15,052	5
Saladoblanco	Lithic Udorthents 50%, Typic Dystrudepts 30%, and others (Typic Tropudalfs, Lithic Dystrudepts, and Typic Hapludands) 20%.	Igneous	Volcanic tuff	18,214	6
San Simón	Typic Udorthents 40%, Typic Dystrudepts 30%, and others (Paralithic Udorthents, Paralithic Dystrudepts, Andic Dystrudepts, and Lithic Udorthents) 30%.	Igneous	Biotite granite	44,698	14
Campoalegre	Typic Dystrudepts 40%, Typic Udorthents 30%, and others (Entic Dystrudepts, Paralithic Udorthents, and Paralithic Dystrudepts) 30%.	Igneous	Muscovitic granite	49,867	16
El Recreo	Typic Eutrocept 40%, Paralithic Eutrocepts 35%, and others (Typic Udorthents and Paralithic Udorthents) 25%.	Metamorphic	Marly gneiss	57,071	19

The P adsorption at a 0.2 mg L⁻¹ concentration in the equilibrium solution was calculated based on previous equations. Afterward, each soil was classified according to its maximum fixation value (b), in concordance with the ranges set by Juo and Fox (1977): less than 10 mg kg⁻¹ very low, between 10 and 100 mg kg⁻¹ low, between 101 and 500 mg kg⁻¹ medium, between 501 and 1,000 mg kg⁻¹ high and, greater than 1,000 mg kg⁻¹ very high.

2.4 Statistical analysis

To evaluate the fit of the adsorption isotherms described in Equations 1 and 2, the following selection criteria were determined: adjusted determination coefficient (adjR²), root mean square error (RSME), and the Bayesian information criteria (BIC), as a relative quality measure of the models. Low values of the RMSE and BIC indices denote a better fit; the first take into account the minimum error distribution between the experimental and predicted values (Khandelwal et al., 2020; Vishali; Mullai, 2016) and the second measures the precision and complexity of the model (Neath; Cavanaugh, 2012). On the other hand, high values of adjR² show the ability of the independent variables to explain the dependent variable.

The adsorption isotherms parameters obtained by the selected model were evaluated by analyzing generalized linear models (GLM) at 5%, with an inverse Gauss response function. The differences between soil units were measured by comparing means by least squares according to a 5% paired t-test. The equation coefficients that better fit the adsorption isotherms were used to determine the Spearman correlation coefficient. The values of adsorption parameters of P at 0.2mg L⁻¹ (q) and the P maximum adsorption capacity (b) were related to soil properties. The statistical analysis of the data was carried out with the programs SigmaPlot 10.0 (2006), Statgraphics Centurion XV 15.2.14 (2007), and RStudio 1.4.1106 (2009-2021).

3 RESULTS

3.1 Chemical properties of the soils

The summary of the chemical properties of the samples per soil unit is presented in Table 2. According to the parameters defined for coffee in Colombia, the soil units were characterized by having a classification that covers all ranges: low, medium, and high content of elements and pH values (Sadeghian, 2013). For the case of Ca and Mg, the high values can be related to pH adjustment by applying dolomite (CaMg(CaCO₃)₂). On the other hand, the OM content presents a difference by soil unit; Campoalegre, La Cristalina, and Saladoblanco were low (< 8%), in comparison with El Recreo and San Simon, which presented a sample for each one with high contents (> 16%). This can be appreciated in this property's standard deviation values (SD).

3.2 Phosphorus adsorption isotherms

The P adsorption isotherms for each soil unit are presented in Figure 2. The concentration of P adsorbed and in equilibrium increased with the increasing levels of P applied, finding that at specific concentrations of P in equilibrium tends to stabilize so that the soil exhausts its retention capacity.

Variations in the adsorption of P were recorded, both between soil units and soil samples belonging to the same unit. Some of the samples collected in the cartographic units of San Simón and Saladoblanco present the highest values, which required the application of high doses, between 4,000 mg kg⁻¹ and 4,200 mg kg⁻¹, respectively, while most of the samples from El Recreo and Campoalegre units the lowest values were found it. The Langmuir parameters in their linear and nonlinear forms for each analyzed sample are presented in Table 3.

Table 2: Chemical properties of soils according to soil unit from the department of Huila. The data correspond to mean \pm SD (median).

Property	Soil unit				
	La Cristalina (n=5)	Saladoblanco (n=6)	San Simón (n=14)	Campoalegre (n=16)	El Recreo (n=19)
pH	4.68 \pm 0.71 (4.39)	4.89 \pm 0.35 (4.86)	4.90 \pm 0.49 (4.85)	5.53 \pm 0.55 (5.48)	5.01 \pm 0.50 (5.00)
MO, %	4.44 \pm 0.38 (4.60)	6.31 \pm 1.89 (6.40)	5.70 \pm 4.55 (4.28)	3.52 \pm 1.30 (3.17)	6.61 \pm 3.20 (6.90)
K, cmol _c kg ⁻¹	0.40 \pm 0.29 (0.30)	0.49 \pm 0.28 (0.43)	0.40 \pm 0.24 (0.37)	0.37 \pm 0.16 (0.33)	0.41 \pm 0.29 (0.32)
Ca, cmol _c kg ⁻¹	4.05 \pm 3.69 (3.16)	3.47 \pm 1.87 (2.79)	4.38 \pm 4.06 (3.75)	7.01 \pm 3.79 (6.81)	5.14 \pm 4.90 (3.79)
Mg, cmol _c kg ⁻¹	1.57 \pm 1.08 (2.08)	1.54 \pm 0.84 (1.34)	1.55 \pm 1.26 (1.23)	2.15 \pm 2.04 (1.38)	1.32 \pm 1.08 (0.81)
Na, cmol _c kg ⁻¹	0.04 \pm 0.04 (0.02)	0.08 \pm 0.03 (0.09)	0.13 \pm 0.03 (0.14)	0.12 \pm 0.07 (0.14)	0.04 \pm 0.03 (0.03)
Al, cmol _c kg ⁻¹	1.12 \pm 1.07 (1.20)	1.07 \pm 1.30 (0.68)	1.74 \pm 1.88 (0.93)	0.31 \pm 0.45 (0.08)	0.99 \pm 1.25 (0.31)
CEC, cmol _c kg ⁻¹	15.80 \pm 7.98 (11.00)	23.91 \pm 12.28 (18.50)	18.72 \pm 11.27 (14.00)	17.15 \pm 5.10 (17.24)	17.73 \pm 4.64 (17.00)
P, mg kg ⁻¹	21.57 \pm 17.12 (24.00)	11.90 \pm 12.45 (7.56)	20.16 \pm 17.50 (14.31)	23.94 \pm 32.16 (14.75)	14.77 \pm 17.02 (6.95)
Fe, mg kg ⁻¹	633.99 \pm 199.84 (643.00)	508.64 \pm 235.77 (489.00)	269.84 \pm 153.44 (255.29)	244.69 \pm 155.93 (225.36)	443.90 \pm 221.75 (359.00)
Mn, mg kg ⁻¹	49.33 \pm 22.90 (51.00)	26.62 \pm 19.51 (20.51)	20.42 \pm 20.70 (16.67)	17.17 \pm 17.78 (11.23)	33.35 \pm 29.69 (19.00)
Zn, mg kg ⁻¹	4.68 \pm 2.99 (4.10)	4.29 \pm 2.66 (3.35)	2.54 \pm 1.73 (2.17)	2.27 \pm 1.81 (1.09)	5.28 \pm 4.99 (3.16)
Cu, mg kg ⁻¹	5.50 \pm 5.24 (4.38)	2.91 \pm 2.59 (1.44)	3.10 \pm 2.32 (2.22)	2.09 \pm 1.42 (1.57)	3.68 \pm 2.89 (3.20)
B, mg kg ⁻¹	0.32 \pm 0.25 (0.40)	0.29 \pm 0.17 (0.27)	0.21 \pm 0.11 (0.19)	0.29 \pm 0.19 (0.20)	0.45 \pm 0.23 (0.40)
S, mg kg ⁻¹	10.60 \pm 3.28 (11.00)	12.08 \pm 6.16 (10.23)	4.15 \pm 1.79 (3.79)	5.89 \pm 2.44 (5.09)	8.38 \pm 2.97 (8.58)
AlSat*, %	23.94 \pm 21.95 (29.10)	17.39 \pm 17.87 (10.66)	26.40 \pm 27.80 (14.18)	5.87 \pm 10.23 (0.61)	21.78 \pm 29.19 (7.32)
BaseSat**, %	37.68 \pm 24.79 (24.85)	26.07 \pm 15.66 (21.93)	48.89 \pm 34.08 (36.68)	55.58 \pm 24.97 (49.75)	37.23 \pm 23.09 (40.14)

*AlSat: aluminum saturation.

**BaseSat: base saturation.

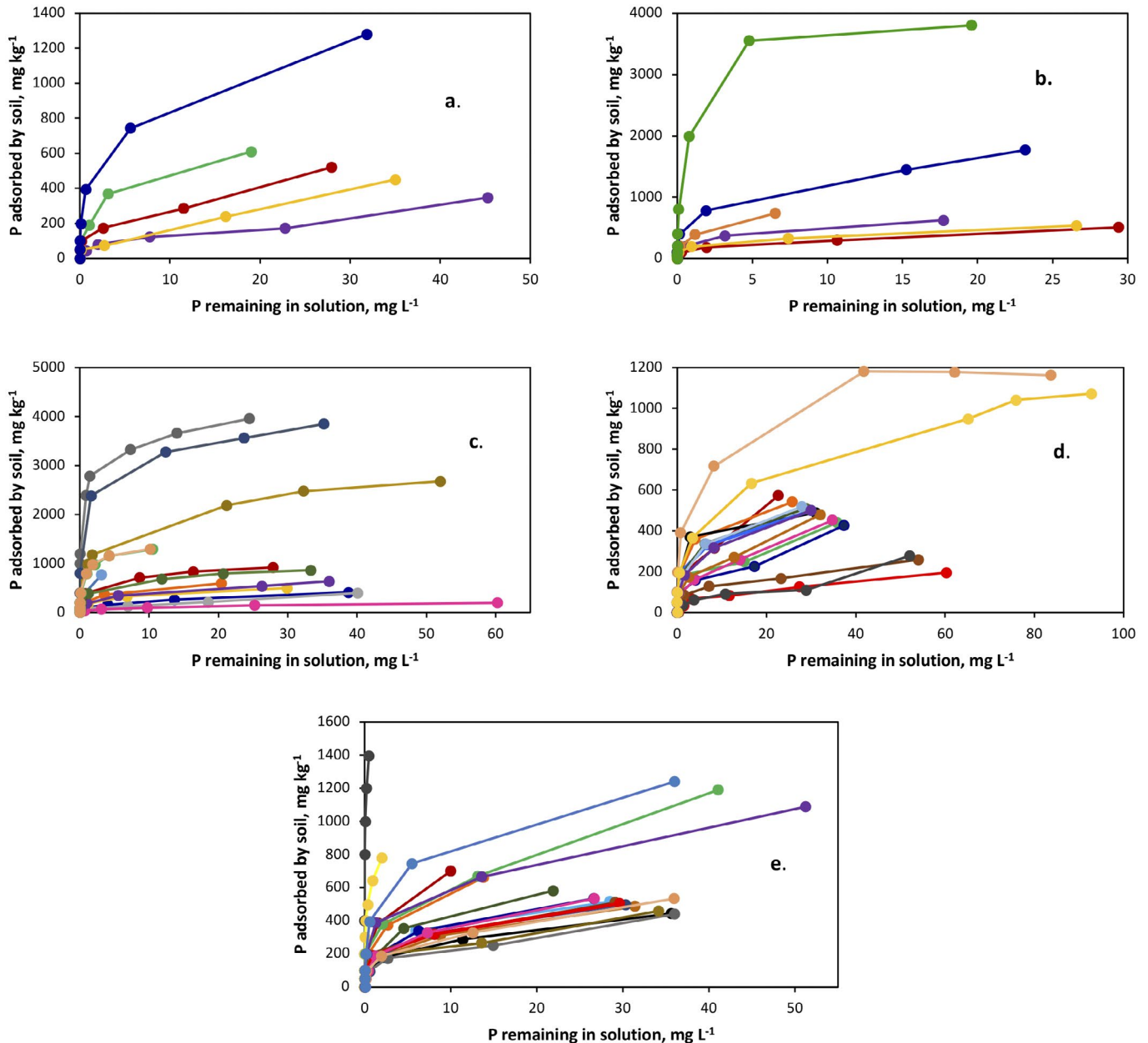


Figure 2: Phosphorus adsorption isotherms obtained for the five soil units evaluated: **a.** La Cristalina (n = 5), **b.** Saladoblanco (n = 6), **c.** San Simón (n = 14), **d.** Campoalegre (n = 16) and **e.** El Recreo (n = 19).

3.3 Phosphorus adsorption by soil unit

As a whole, the relationship between soil unit and P fixation capacity was not found. San Simón soil unit was statistically different from Campoalegre for q , and Saladoblanco and San Simón differed from Campoalegre for b (Table 4). San Simón and El Recreo units presented extreme values for q and classifications between various ranges. In contrast, Campoalegre and La Cristalina units exhibited similar behavior and very low and low capacities. Regarding the maximum adsorption capacity, Saladoblanco and San Simón had the highest capacity, reaching 3,916 and 3,731 mg kg^{-1} , respectively.

3.4 Relationship between phosphorus adsorption and soil chemical properties

The results of the correlation analysis between the P adsorption parameters and soil properties with which the effect occurred are shown in Figure 3. The adsorption of P at 0.2mg L^{-1} in solution (q) and the maximum of adsorption (b) were significantly ($P < 0.0001$) and directly correlated with Al^{3+} content and aluminum saturation, and inversely with base saturation, pH, Ca^{2+} , and Mg^{2+} .

Table 3: Chemical properties of soils according to soil unit from the department of Huila. The data correspond to mean \pm SD (median).

No.	Soil unit	Linear Langmuir isotherm						Nonlinear Langmuir isotherm					
		q ^a	b ^b	K	R ² adj	RMSE	BIC	q	b	K	R ² adj	RMSE	BIC
1	LC	99	636	0.92	0.98	0.0018	-70.45	48	692	0.38	0.96	35.35	65.19
2	LC	38	511	0.40	0.87	0.0084	-52.30	11	739	0.07	0.89	52.61	69.96
3	LC	8	345	0.12	0.75	0.0291	-37.38	3	662	0.02	0.88	34.36	64.85
4	LC	13	475	0.15	0.73	0.0169	-43.90	6	698	0.04	0.90	41.67	67.16
5	LC	202	1303	0.92	0.98	0.0012	-88.93	98	1292	0.41	0.93	103.85	90.70
6	SB	121	643	1.16	0.98	0.0015	-73.15	69	652	0.59	0.95	42.40	67.37
7	SB	43	507	0.46	0.92	0.0067	-54.95	19	557	0.18	0.89	49.88	69.32
8	SB	182	799	1.47	0.96	0.0006	-83.70	126	847	0.87	0.97	37.12	65.77
9	SB	366	1711	1.36	0.98	0.0008	-110.19	154	1787	0.47	0.95	136.37	107.59
10	SB	1022	3916	1.77	1.00	0.0001	-161.20	916	3951	1.51	0.99	130.61	119.83
11	SB	74	539	0.80	0.96	0.0039	-61.57	44	523	0.46	0.89	53.42	70.14
12	SS	373	796	4.40	0.95	0.0004	-89.84	193	931	1.31	0.92	64.99	72.49
13	SS	26	423	0.32	0.94	0.0091	-51.30	11	479	0.12	0.92	34.99	65.06
14	SS	14	395	0.18	0.78	0.0206	-41.53	4	792	0.02	0.89	38.64	66.25
15	SS	68	513	0.77	0.98	0.0031	-64.37	40	509	0.43	0.95	36.13	65.45
16	SS	121	611	1.24	0.99	0.0016	-72.34	73	603	0.69	0.95	43.66	67.72
17	SS	62	630	0.55	0.98	0.0036	-73.82	35	645	0.29	0.96	44.02	78.69
18	SS	212	910	1.52	0.99	0.0011	-104.48	153	881	1.05	0.96	63.54	95.37
19	SS	8	206	0.19	0.96	0.0222	-40.65	5	210	0.12	0.95	13.56	53.69
20	SS	1093	3731	2.07	0.98	0.0001	-207.68	1785	3344	5.73	0.95	304.72	178.77
21	SS	440	2628	1.01	0.99	0.0006	-159.00	276	2571	0.60	0.96	172.24	151.69
22	SS	1165	3771	2.24	1.00	0.0002	-164.56	694	3720	1.15	0.96	283.82	148.25
23	SS	169	855	1.24	0.99	0.0014	-100.05	123	828	0.87	0.96	59.75	94.39
24	SS	487	1312	2.95	0.99	0.0002	-147.40	370	1283	2.03	0.98	65.80	107.49
25	SS	534	1408	3.06	0.98	0.0004	-153.68	352	1413	1.66	0.95	112.97	129.83
26	CA	67	563	0.67	0.90	0.0052	-58.03	28	616	0.24	0.86	65.17	72.53
27	CA	5	205	0.12	0.89	0.0400	-33.55	3	230	0.06	0.90	17.85	56.99
28	CA	37	424	0.48	0.90	0.0113	-48.72	47	371	0.73	0.83	53.44	70.14
29	CA	22	409	0.28	0.84	0.0158	-44.69	7	556	0.06	0.83	51.10	69.61
30	CA	129	551	1.54	0.99	0.0017	-71.79	77	534	0.84	0.92	47.71	68.79
31	CA	24	458	0.27	0.89	0.0105	-49.60	9	580	0.08	0.91	39.46	66.51
32	CA	119	499	1.57	1.00	0.0009	-79.27	87	498	1.06	0.99	18.50	57.41
33	CA	12	260	0.24	0.93	0.0216	-40.98	10	244	0.22	0.88	26.41	61.69
34	CA	10	117	0.46	0.98	0.0145	-37.12	6	124	0.27	0.99	3.20	30.64
35	CA	94	504	1.15	0.98	0.0030	-64.68	91	451	1.26	0.89	51.81	69.77
36	CA	31	481	0.34	0.90	0.0087	-51.82	15	534	0.14	0.89	46.78	68.55
37	CA	75	523	0.84	0.98	0.0027	-65.90	47	512	0.50	0.94	39.26	66.44
38	CA	63	537	0.66	0.98	0.0030	-64.70	34	552	0.33	0.95	34.69	64.96
39	CA	160	1189	0.78	1.00	0.0015	-11.,21	86	1186	0.39	0.96	93.64	113.84
40	CA	50	515	0.54	0.97	0.0041	-60.82	28	526	0.28	0.94	36.74	65.65
41	CA	54	1073	0.26	0.99	0.0041	-94.14	25	1124	0.11	0.97	69.63	108.51

Continue.

Table 3: Continuation.

No.	Soil unit	Linear Langmuir isotherm						Nonlinear Langmuir isotherm					
		q ^a	b ^b	K	R ² adj	RMSE	BIC	q	b	K	R ² adj	RMSE	BIC
42	ER	52	542	0.53	0.98	0.0028	-65.35	30	570	0.28	0.98	23.52	60.29
43	ER	206	725	1.99	0.98	0.0007	-81.30	124	736	1.01	0.93	54.90	70.47
44	ER	79	604	0.76	0.97	0.0025	-66.67	36	664	0.29	0.96	36.85	65.68
45	ER	129	691	1.15	0.98	0.0012	-75.15	76	712	0.60	0.96	43.16	67.58
46	ER	77	545	0.82	0.97	0.0031	-64.21	37	563	0.35	0.93	44.55	67.96
47	ER	1330	1380	133.15	0.99	0.0000	-141.92	1253	1355	61.67	0.89	158.66	123.33
48	ER	44	503	0.48	0.97	0.0042	-60.57	28	503	0.30	0.95	33.42	64.51
49	ER	593	770	16.85	0.98	0.0001	-157.65	502	723	11.40	0.84	93.85	113.88
50	ER	38	453	0.46	0.96	0.0061	-56.19	24	446	0.29	0.93	36.35	65.52
51	ER	85	508	1,01	0.97	0.0042	-60.58	137	431	2.34	0.88	53.46	70.15
52	ER	29	433	0.36	0.90	0.0109	-49.13	18	431	0.22	0.86	48.36	68.95
53	ER	51	440	0.65	0.91	0.0095	-50.80	98	372	1.78	0.83	56.71	70.86
54	ER	44	521	0.46	0.98	0.0034	-63.23	31	522	0.31	0.97	25.13	61.09
55	ER	62	513	0.69	0.97	0.0039	-61.62	54	470	0.65	0.92	43.13	67.57
56	ER	50	556	0.50	0.97	0.0035	-62.80	34	556	0.32	0.95	36.08	65.43
57	ER	40	441	0.49	0.95	0.0074	-53.80	29	416	0.38	0.88	46.78	68.55
58	ER	103	1174	0.48	0.93	0.0036	-73.99	26	1430	0.09	0.91	111.40	91.69
59	ER	110	1087	0.56	0.97	0.0032	-75.68	80	989	0.44	0.90	104.02	90.73
60	ER	191	1265	0.89	0.99	0.0011	-90.56	124	1196	0.58	0.94	94.71	89.41

^aq = P adsorbed per unit soil mass at an equilibrium concentration of 0.2mg L⁻¹, mg kg⁻¹ of soil.

^bb = P maximum fixation capacity, mg kg⁻¹ of soil. K_L = binding energy constant between phosphate ions and the surface of soil particles, mg L⁻¹.

Table 4: Descriptive statistic for P fixation capacity at a 0.2mg L⁻¹ concentration of P in solution, q (mg kg⁻¹ of soil), and maximum fixation capacity of P, b (mg kg⁻¹ of soil), per soil unit. Non-common letters indicate significant differences in the means of least squares according to the t-test at 5%.

Parameter	Value	Soil unit									
		CA	ER	LC	SB	SS	CA	ER	LC	SB	SS
q	Mean	59.32		174.41		72.19		301.32		340.91	
	Median	51.84	B	76.83	BA	38.03	BA	151.22	BA	190.86	A
	SE	11,52		70.51		36.28		151.49		101.59	
b	Mean	519.26		692.10		654.12		1352.52		1299.17	
	Median	501.24	B	545.19	BA	511.38	BA	721.05	A	825.23	A
	SE	68.10		69.42		168.64		544.29		320.77	

4 DISCUSSION

Results showed that samples of the soil units were contrasting in their properties, reflecting the high variability that can exist in the study zone, even when they are classified in the same soil unit, as also mentioned by Sadeghian et al. (2019) (Figure 2).

Concerning the phosphorus adsorption isotherms, the two models described the P adsorption phenomenon satisfactorily (Table 3); the R² adj values obtained for the

linear form were slightly higher in most cases. Additionally, the RMSE and BIC values were lower for this model, thus suggesting a better fit. Related to this topic, it is essential to highlight that although the adjR² provides information about the degree of reliability of the model, this measure is not enough to determine the real distribution of the error and, therefore, it cannot be considered a unique criterion for defining the fit degree. From there, the weight in the model selection is mainly given by the RMSE and BIC criteria (Khandelwal et al., 2020;

Rahman et al., 2019; Rahman et al., 2018). These criteria coincide with those reported by Hidayat et al. (2021), who, through the RMSE and χ^2 (chi-square) criteria, indicated that the Langmuir linear model is adequate than the nonlinear form to represent the experimental adsorption data studied.

According to *b* and *q* values obtained for the linear Langmuir model, it can be stated that between 5 and 55% of total analyzed samples showed very low and low P fixation (*q* values between 3 and 99 mg kg⁻¹), so with the application of the element through fertilization, the most significant part of the nutrient will be available to be absorbed by plants roots. Thus, 30% of the samples showed medium fixation (*q* values between 103 and 487 mg kg⁻¹), 3% high (*q* values between 534 and 593 mg kg⁻¹), and 7% very high (*q* values between 1022 and 1330 mg kg⁻¹). The previous corroborates that the P fixation measure allows understanding that its availability for plants does not necessarily depend on its soil concentration (Muindi et al., 2015). For the case of samples with high and

very high fixation capacity that presented values of *b* between 770 and 3,916 mg kg⁻¹, the P liberation to soil solution will be determined by the binding energy between phosphate ions and soil surface, which present values of *K* between 1.3 and 133.15 mg L⁻¹, being the last one, the highest reached value.

The high values of maximum fixation capacity found in some soil samples coincide with what was reported by Díaz-Poveda and Sadeghian (2017) in a study developed in the Colombian coffee zone, where this parameter varied between 118 and 3,333 mg kg⁻¹ and, for a sample of Huila's department the value was 1,000 mg kg⁻¹. For other countries and crops, lower values are reported; in Cameroon, for maize and plantain, the P fixation was site-specific and revealed that soil can adsorb until 175 mg P kg⁻¹ (Mbene et al., 2017); in Kenya, in maize, the maximum adsorption varied between 771 and 1,796 mg kg⁻¹ (Muindi et al., 2015) and in Ethiopia, the maximum adsorption varies between 297 mg P kg⁻¹ in Fluvisoles and 820 mg P kg⁻¹ in Vertisoles (Hadgu et al., 2014).

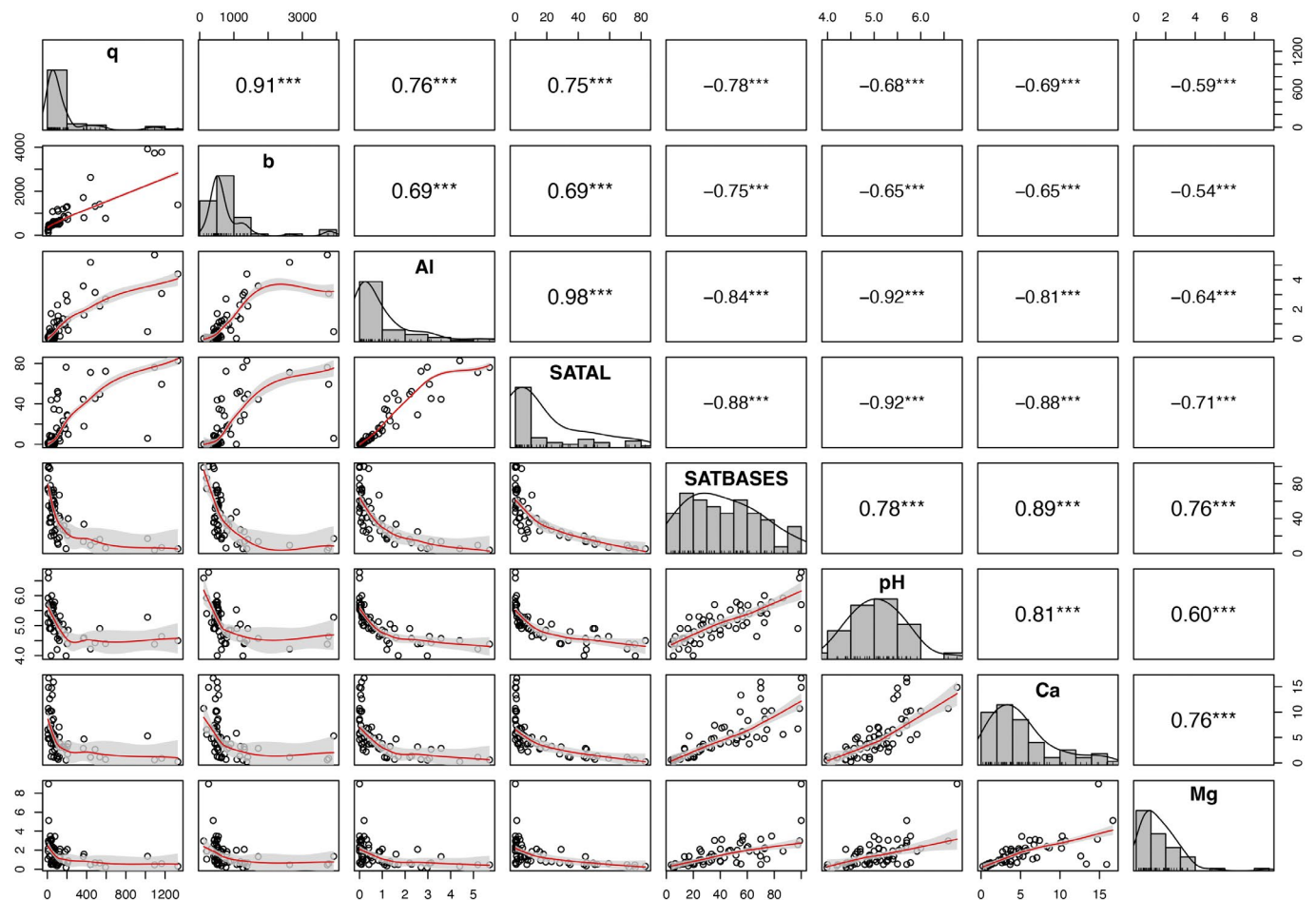


Figure 3: Spearman correlation coefficients between the combinations: adsorb P per soil mass unit at an equilibrium concentration of 0.2 mg L⁻¹ (*q*), maximum fixation capacity of P (*b*), exchangeable aluminum (Al), aluminum saturation (SatAl), base saturation (Satbases), pH, Ca and Mg (n=60). The coefficients above the diagonal of the matrix indicate the degree of correlation and the asterisk's significance (***) *p* < 0.0001). The scatterplots between the associated variables are shown below the diagonal of the matrix.

It is specified that the soil cartographic units, defined by the National Federation of Coffee Growers (FNC), are directly related to the presence of dominant, codominant, or associated soil typologies. For example, El Recreo unit is characterized by several present typologies at the subgroup level; consequently, there is variability in the soils' chemical and physical characteristics (Lince-Salazar; Sadeghian, 2021) and their P fixation capacity (Table 1). These facts can explain the differences, as shown in Table 4.

The correlation analysis between the P adsorption parameters and soil properties shows the relationship between Al^{3+} and P fixation. It has been reported as a good indicator of phosphorus soil retention due to its direct relationship with clay mineralogy (Bonomelli et al., 2003). In this same sense, Gunjigake and Wada (1981) concluded that P adsorption capacity increases with the levels of Al extractable with pyrophosphate. According to Mahdi et al. (2012), the hydroxyl phosphate that is formed is slightly soluble because it has a greater surface area exposed to the soil solution and, consequently, the P is initially available to some extent for plants, but, over time, this compound becomes less soluble and unavailable to plants.

The negative correlation with pH is a consequence, in part, of its same relationship with Al^{3+} . At greater pH values than 5.5, the activity of this cation tends to be zero (Li et al., 2022), so the adsorption of P is reduced (Mbene et al., 2017). On the other hand, Fe/Al oxides also reduce their ability to fix P as soil pH increases. In acid soils, the surface of these minerals has a net positive charge that adsorbs phosphate anions (Havlin et al., 2017). Additionally, there is an inverse relationship between the contents of Al^{3+} and those of Ca^{2+} and Mg^{2+} (Sadeghian; Díaz, 2020); hence the negative relationship between P fixation and these two exchangeable bases, a response reported by Moazed et al. (2010). In this aspect, Hadgu et al. (2014) argue that most soil properties are interrelated, so it is sometimes difficult to identify the principal components contributing to P availability in soils.

Similar studies have found that P fixation is also related to CEC, clay content, and exchangeable Ca^{2+} and Al^{3+} (Mbene et al., 2017; Moazed et al., 2010), contents of amorphous clays, OM (Díaz-Poveda; Sadeghian, 2017), clay content and CEC (Hadgu et al., 2014), aluminum saturation, extractable P, clay content, electrical conductivity and pH (Muindi et al., 2015), among others.

On the other hand, the correlation between P fixation and OM content was relatively low but significant ($r=0.39$, $p=0.0018$ for q and $r=0.38$, $p=0.0025$ for b), as has already been reported for some soils from the Colombian coffee zone (Díaz-Poveda; Sadeghian, 2017; Bravo; Montoya; Menjivar, 2013). This relationship may be because the soils studied in this work belong to the Entisol and Inceptisol orders (Table 1) and are the Andisols that have been identified as correlating

with OM contents (Villareal-Núñez et al., 2017; Bravo; Marquez; Potosi, 2007; Espinosa, 2004).

These results show the need for development research focusing on understanding soil chemical and physical P reactions according to their specific characteristics, which can vary between soils of the same zone and have completely different behaviors between countries.

5 CONCLUSIONS

The results of this study indicate that the Langmuir model, in its linear and nonlinear forms, describes the process of P adsorption in soils of the coffee zone of the department of Huila; however, the linear form fits the data better. The soils of Huila's coffee zone department exhibit different P fixation capacities. Of the total samples analyzed, 5% presented very low capacity, 55% low, 30% medium, 3% high, and 7% very high. No relationship was found between P adsorption and soil cartographic units. P fixation at 0.2 mg L^{-1} in solution and P maximum adsorption were significantly and positively correlated with Al^{3+} and Al saturation and negatively with pH, exchangeable Ca and Mg, and base saturation.

6 AUTHOR CONTRIBUTIONS

VCDP and SS wrote the manuscript, VCDP designed experiments, VCDP performed experiments, VCDP analyzed the data, VCDP and SS conducted statistical analyses, VCDP and SS review and approval of the final version of the work.

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