



THE INFLUENCE OF ORGANIC MATTER ON PHOSPHORUS FIXATION IN SOILS FROM THE EASTERN FLANK OF MOUNT CAMEROON

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ABSTRACT: *The maximum phosphate fixation (K_F) and phosphorus sorption capacity (PSC) of soil samples collected from the surface and sub-surface horizons of five volcanic soil profiles from the eastern flank of Mount Cameroon were investigated before and after organic matter removal. The aim of this research was to investigate the influence of soil organic matter (OM) on phosphorus (P) fixation. The removal of soil OM from the soil samples was accomplished by the use of sodium hypochlorite. Phosphorus fixation studies were performed on the treated and untreated soil samples using calcium chloride as the background electrolyte. Fixation data were interpreted with Freundlich adsorption isotherm. The results indicated that the removal of OM had an influence on both K_F and PSC. Removal of soil OM decreased PSC and increased K_F for all soils. The inhibition of aluminium oxide and the reduction of soil surface area after the removal of OM were the justifications for the increase in P fixation.*

KEYWORDS: Phosphorus fixation; Freundlich isotherm; organic matter removal; volcanic soils; Mount Cameroon.



INTRODUCTION

Phosphorus (P) is one of the plant growth-limiting nutrients and it is considered as the most important element in plant nutrition. It is responsible for plant growth and development as it plays key roles in plant metabolism, structure, and energy transformation (Malhotra et al., 2018). Phosphorus found in the soil can either be in organic or inorganic form, but it is taken up by plants only in anionic forms as H_2PO_4^- and HPO_4^{2-} . Inorganic P is fixed on clay minerals and on iron (Fe) and aluminium (Al) oxides as an inner sphere complex through ligand exchange with hydroxide surface groups (Almasri et al., 2019). This is the main reason that accounts for the low efficiency (15-30%) of P fertilization and is a common problem in agriculture, due to strong P fixation through sorption or precipitation reactions in soils (Daly et al., 2015). Hence, these reactions immobilize P in the soil and cause a deficiency of available P for plants, leading to an increase in the application rates of P fertilizers in agricultural systems to maintain soil fertility. Application of P fertilizer without proper soil testing will lead to the accumulation of excess amounts of P in soils that could enhance eutrophication in aquatic ecosystems if carried away during run-offs (Scalenghe et al., 2007).

Soil organic matter (SOM), among others, plays an important indirect role in P sorption as it is the main constituent of the soil sorption complex which is responsible for the binding of anions in the soil material. Soil organic matter consists of humus, fulvic acid (FA), humatmelanic acid, humic acid (HA), and their hydroxybenzoic acid derivatives (Tan, 1986). Fulvic acid and HA are higher in humified organic acids than in non-humified organic acids and they play an important role in soil chemistry due to the presence and position of functional groups (especially carbonyl and phenolic hydroxyl groups) which make the former very effective in cation exchange and complexation reactions in soils (Tan, 1986). Fulvic acid and HA may form metal complexes of high stability through chelation, where metal ions are bound to bidentate ligands such as carbonyls and phenolic hydroxyl groups. These groups can form stable complexes with Al and Fe metal ions. The chelation of Al and Fe in the surface mineral soil will eventually lead to leaching and this reduces the number of P adsorption sites (Tan, 1986).

According to Hunt et al. (2007), the effect of soil organic matter on P sorption can involve four processes: competition between organic matter and P for mineral adsorption sites; complexation of surface metals and release of these metals into the solution, thereby removing adsorption sites; increased repulsion of phosphate anions by sorption OM to positive sorption sites; and formation of cation bridges leading to an increase in P sorption sites. Guppy et al. (2005) in a review discussed the uncertainty of the mechanisms involved in P-OM interactions in soils, but the impact of SOM on P-sorption has not been clearly explained till present especially in soils from this region. Although the influence of organic matter on P sorption has been abundantly investigated under different experimental conditions on sorption processes (Kang et al., 2009; Winarso et al., 2011; Debicka et al., 2016), they had different results. While Winarso et al. (2011) and Sibanda and Young (1986) found that OM in solution from added sources strongly decreased P sorption onto Al and Fe oxides on soil surface, Appelt et al. (1975) found no change in P adsorption on soil after the addition of dissolved OM. Debicka et al. (2016) later found out that the removal of OM with hydrogen peroxide (H_2O_2) led to an increase in P desorption. This behaviour was linked to the role of OM as a binding agent for P in soil thereby hindering its



availability. Darke and Walbridge (2000) investigated the impact of organic matter on P sorption and concluded that OM was strongly held with the content of Al and Fe, which confirmed their role in P fixation in soil.

Volcanic soils are found over extensive agricultural areas in South West Region of Cameroon. However, they are especially vulnerable to P deficiency due to strong sorption properties and enhanced P leaching from surface horizons in soils with high P levels. The objective of the study was to examine the effects of soil organic matter on P fixation in volcanic soils.

MATERIALS AND METHODS

Study Site

The study area lies on the lower slopes of the South-South Eastern flank of Mount Cameroon volcano, the highest mountain in west and central Africa, which is located within latitudes 4°00'–4°13'N and longitudes 9°00'–9°30'E (Figure 1).

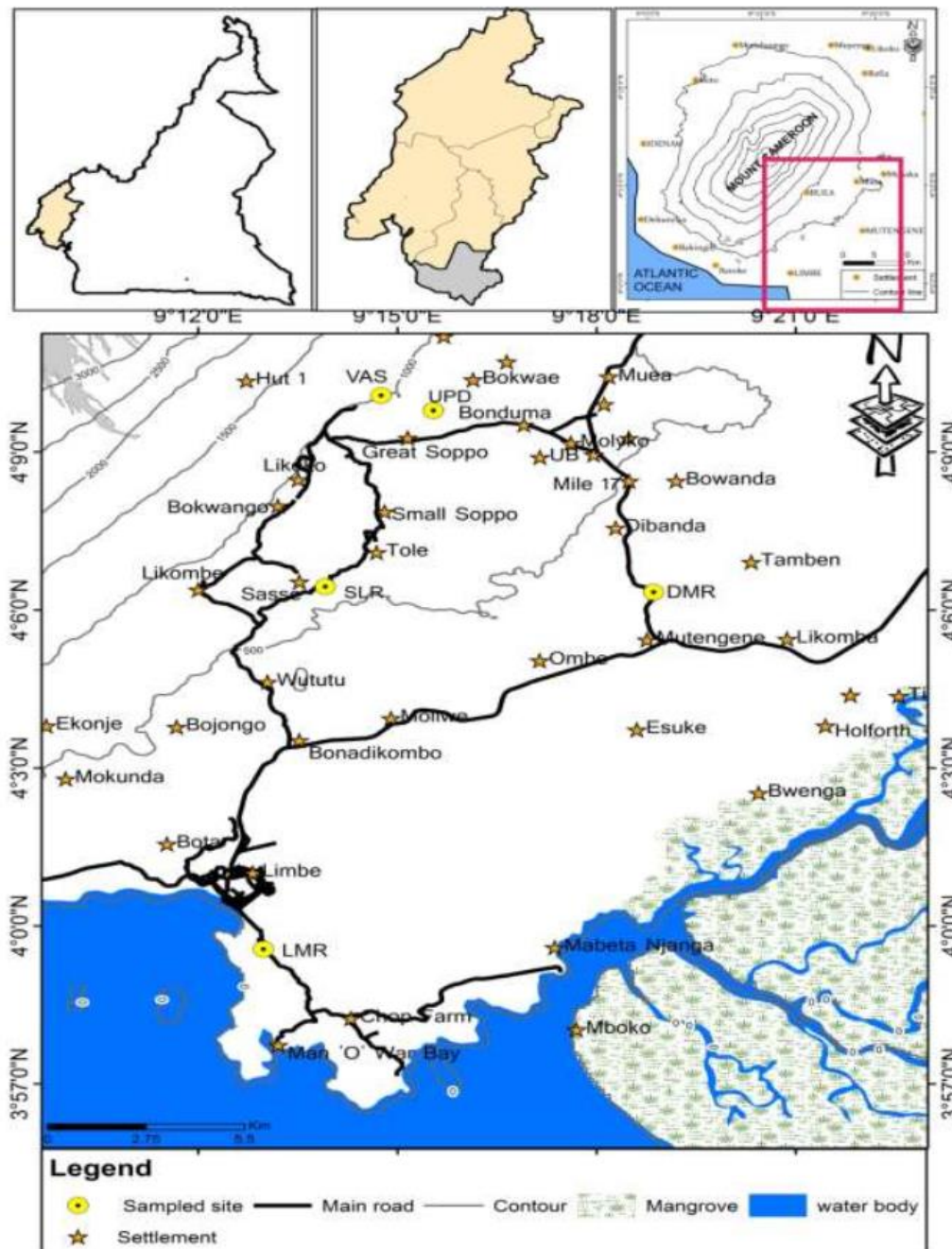


Figure 1: Location and sample distribution map. Inset is the map of Cameroon showing the SW Region, Mount Cameroon, and Mount Cameroon with a zoom on the study area



The soils of this region are developed from a basaltic rock (Manga et al., 2014). These soils have been weathered and partly covered by more recent deposits; thus, the soils are mostly black and are well drained due to the generally hilly nature of the terrain. Climatic conditions such as temperature (20°C to 28°C), and annual rainfall (3000 mm–5000 mm) (Manga et al., 2014) are favourable for agricultural practices.

Soil Sampling and Preparation

Sampling sites were selected to represent the different human activities and altitudes (Table 1) and samples were collected in March 2015, just before the commencement of the raining season.

Table 1: Soil sampling site description along the eastern flank of Mount Cameroon

Sample site	Sample code	Latitude	Longitude	Altitude (m)	Soil depth (cm)	Human Activity
Vasingi	VAS	N04° 10.076'	E009° 14.755'	1006	0-40 40-100	Plantains farm
Upper Boduma	UPD	N04° 09.789'	E009° 15.542'	786	0-30 30-70	Maize, beans, cassava farm
Sasse-Limbe Road	SLR	N04° 06.443'	E009° 13.915'	603	0-30 30-80	Maize, beans, cassava farm
Dibanda-Mutengene Road	DMR	N04° 06.340'	E009° 18.861'	351	0-20 20-40	Plantains, maize, beans, cassava farm
Limbe-Man or War Bay Road	LMR	N03° 59.559'	E009° 12.982'	36	0-20 20-40	Cassava, maize farm

Soil samples were collected from the horizons of five soil profiles in five different locations with different altitudinal gradients (Table 1). Only the surface and immediate subsurface horizon samples were involved in this investigation. The research was conducted on the basis of a comparison of different soil horizons of five soil profiles collected at different altitudes, as well as on the comparison of the P fixation abilities in natural (untreated) and treated top and subsurface soils with sodium hypochlorite (NaOCl) to remove soil organic matter.

The samples were air-dried for one week in the chemistry laboratory of the University of Buea. The organic materials (roots) were removed. Mineral fractions were ground and sieved using a 2 mm stainless steel sieve.



Soil Sample Characteristics

Soil fractions smaller than 2 mm were analysed following the standard methods described by Pansu and Gautheyrou (2007) to characterize the following basic properties: soil colours were identified using Munsell Soil Colour Charts, soil pH and electrical conductivity (EC) were measured in 1:5 soil to water ratio, and bulk density and moisture content were determined following the oven-dry method. Organic carbon (% C), exchangeable bases and exchangeable acidity were analysed according to the procedures described by Pansu and Gautheyrou (2007). Effective cation exchange capacity (ECEC) was determined by summation (sum of the exchangeable bases and exchange acidity). Available P was determined by Bray method. Total Nitrogen (%N) was determined by exploiting the Kjeldahl's distillation method. Both wet sieving (for the fraction > 80 μm) and gravity dimension (for the fraction < 80 μm) techniques were used to determine particle size, according to (ASTM D 422-63, 2003) standard methods.

Removal of Organic Matter

Soil organic matter was removed from the soil samples, according to Cassidy and Mankin (1960), and the procedure described with slight modifications by Anderson (1961). A 25 mL aliquot of NaOCl solution freshly prepared at 3.8% and adjusted to pH 8.5 was added to about five grams soil sample in 50 cm^3 centrifuge tubes and shaken for 4 hours at 220 tpm in an electrical shaker. The content was centrifuged at 4000 rpm for 20 min, the supernatant was discarded, and the treatment was repeated over five times. The content was washed with distilled water in replacement with NaOCl and the supernatant was tested with drops of 0.1 M AgNO_3 , until complete disappearance of the white precipitate in the treated soil sample. Samples were air dried, ground, and then used for analysis as treated samples.

Oxalate and Dithionite Citrate–Bicarbonate-extractable Al and Fe for Both Treated and Untreated Soil Samples

Oxalate-extractable aluminium and iron (Al_{ox} , Fe_{ox}) were determined after extraction for 2 hours with 0.2 M ammonium oxalate at pH 3 in the dark (Schwertmann et al., 1968). Dithionite citrate–bicarbonate-extractable aluminium and iron (Al_{dith} , Fe_{dith}) were determined after two extractions for 15 min at 70°C, as described by Mehra and Jackson (1960). The concentrations of the elements in the clear extracts were determined by flame atomic absorption spectroscopy. This same measurement was done on the treated samples and their corresponding values were denoted with “primes” such as Al'_{ox} to denote oxalate extractable Al. The summed amounts of Al_{ox} and Fe_{ox} were widely used to calculate the maximum amount of P that can be retained in soil – the P sorption capacity (PSC), which is an important factor in regulating the release of P from soil to water (Kang et al., 2009; Debicka et al., 2016). The values of PSC were calculated according to the following equation (Equation 1) (Debicka et al., 2016):



$$\text{PSC} = 0.5 ([\text{Fe}_{\text{ox}}] + [\text{Al}_{\text{ox}}]), \dots \dots \dots (1)$$

Phosphorus Fixation Studies on Both Treated and Untreated Soil Samples

In the fixation study, about 5 g air-dried soil samples were weighed in triplicates into 50 mL polypropylene centrifuge tubes and were equilibrated with 25 mL of KH_2PO_4 in 0.01 M CaCl_2 containing 0, 10, 50, 100, 250, and 500 mg P/L. Two drops of chloroform were added to each tube to act as a microbial inhibitor. The tubes were set in a mechanical shaker for 16 hours at 20 turns per minute. Following equilibration, the soil suspensions were centrifuged at 4000 rotations per minute for 20 minutes and filtered through Whatman No. 5 filter paper to obtain a clear solution. The inorganic P was determined by the phosphomolybdate blue method of Murphy and Riley (Murphy & Riley, 1962). The amount of P fixed by the soil (P_{fix}) was calculated from the difference between the initial concentration (P_0) and the equilibrium concentration (P_{eq}). Phosphorus fixation data for the soils used in this study were fitted into the linearized form of the Freundlich equations proposed by Muindi et al. (2015.). The difference between phosphate concentrations before and after shaking with soil samples was used to calculate the amount of phosphate fixed by both treated and untreated soil samples.

The Freundlich equation is described in its linear form as:

$$\log X = \log K_F + n_F \log C \dots \dots \dots (2)$$

where:

C = Equilibrium concentration of phosphorus in solution (mg P L^{-1})

X = mg of P fixed (mg P kg^{-1})

n_F = Empirical constant related to binding energy of soil with phosphate

K_F = Proportionality constant for Freundlich model (mg P kg^{-1}).

The Phosphate adsorption isotherms of soils in the five study sites were determined by plotting the equilibrium concentration of phosphate (C) against the amount of phosphate adsorbed (X). In order to understand competition existing between physicochemical parameters and adsorption models, simple regression analysis shall be generated on maximum adsorbed phosphate for treated and untreated soil samples and some specific soil properties such as OM, available P, exchangeable Al and Fe, extractable Al and Fe.

Statistical Analysis

The data from the experiments were analyzed using the Statistical Package for Social Science (SPSS-20) and Excel-2007 software. Soil data were subjected to correlation analysis to establish the relationship between maximum P fixed and some soil properties, and between the maximum P fixed by Freundlich model for the treated and untreated soil samples.



RESULTS

Basic Soil Properties

Particle size analysis (< 2 mm fraction) showed that these soils are rich in clay (> 30%) in both horizons for all profiles except for VAS where the clay content was lower (< 25%). The clay content was found to increase with a decrease in the soil profile elevation where the VAS profile at the highest elevation exhibited the smallest amount of clay, while DMR and LMR with the least elevation had the highest amount of clay (Table 2). Generally, we can say that: silt content > clay content > sand content, and that the clay content increases with decrease in altitude while the silt content decreases with decrease in altitude.

Table 2: Some physical properties of soil samples along the eastern flank of Mount Cameroon

Sample Ref	Depth cm	Soil Colour	Particle Size distribution			Textural Class
			% Sand	% Silt	% Clay	
VAS	0-40	2.5YR3/4	41.2	42.0	16.8	Loam
	40-100	2.5YR5/6	25.0	54.9	20.1	Silt Loam
UPD	0-30	5YR3/2	24.8	45.8	29.4	Clay Loam
	30-70	7.5YR3/2	16.5	42.0	41.5	Silt Loam
SLR	0-30	5YR3/2	23.0	41.9	35.1	Clay Loam
	30-80	7.5YR3/2	21.7	36.8	41.5	Clay
DMR	0-20	5YR3/2	19.6	40.0	40.4	Clay
	20-40	5YR3/4	9.8	20.5	69.7	Clay
LMR	0-20	2.5YR8/6	29.4	32.1	38.5	Clay Loam
	20-40	7.5YR6/8	16.7	29	54.3	Clay

The effective cation exchange capacity (ECEC) varied from 3.28 to 15.67 cmol/kg (Table 3) with the highest average value in the highest elevation profile, VAS, and the lowest average value in the least elevation profile LMR.

The pH (H₂O) values of the soils were moderately acidic to strongly acidic (Table 3). The average pH of the soil profiles also reflected their elevation variation as the highest elevated soil profile (VAS) was moderately acidic with an average pH of 5.5 just like in UPD. This was closely followed by SLR with an average pH of 5.0 and the lowest elevation profiles like LMR and DMR were strongly acidic with an average pH of 4.8 (Table 3).

The available P measured by Bray 1 method showed that P was very low for all the sites studied and necessitates P fertilizer amendment to improve the soil fertility. Although P was known to be very low in all samples, there was a decrease in the amount of P down the soil profile and it also decreased with a decrease in altitude, with the highest altitude, VAS (1000 m), having the highest amount of available P (0.787 mg/kg) and the lowest altitude, LMR (36 m), having the least available P (0.361 mg/kg) for the surface samples (Table 3).



Table 3: Some selected soil physicochemical properties of soil samples along the eastern flank of Mount Cameroon

Sample Ref	Depth (cm)	pH(H ₂ O)	pH(KCl)	EC (μS/cm)	Exchangeable Bases				Exch. Acidity	ECEC	Org C -----(%)-----	OM	Avail. P (mg/kg)
					Ca	Mg	K	Na					
VAS	0-40	5.6	4.3	38	8.65	4.32	1.91	0.11	0.68	15.67	2.93	5.63	0.787
	40-100	5.4	4.1	13	6.36	2.91	0.08	0.16	0.38	9.88	1.04	2.23	0.519
UPD	0-30	5.3	4.1	19	4.52	1.65	0.07	0.13	0.14	6.51	1.75	3.81	0.675
	30-70	5.9	4.4	28	7.76	1.36	0.04	0.13	0.31	9.60	1.73	3.46	0.675
SLR	0-30	5.2	4.6	22	3.96	1.77	0.07	0.10	0.87	6.77	2.56	4.95	0.724
	30-80	4.7	4.1	26	2.35	1.25	0.11	0.11	0.31	4.13	2.20	4.30	0.675
DMR	0-20	4.8	3.6	24	3.13	2.01	0.09	0.10	1.13	6.46	1.92	3.80	0.361
	20-40	4.8	3.5	17	3.13	1.20	0.05	0.13	1.30	5.81	1.32	2.73	0.361
LMR	0-20	4.7	4.1	18	2.01	1.47	0.19	0.13	8.28	5.07	2.02	3.98	0.361
	20-40	4.9	4.2	12	0.90	0.58	0.04	0.12	8.64	3.28	1.47	3.10	0.204



Calcium (Ca) concentrations were the highest followed by magnesium (Mg) concentrations, and they were more variable than potassium (K) and sodium (Na), which occurred in smaller concentrations. The concentrations of these exchangeable cations increased with increase in elevation, with VAS being the highest in altitude having the greatest concentrations (8.65 cmol/kg) of these exchangeable cations, whereas LMR with the lowest altitude had the least concentrations (2.01 cmol/kg) of the exchangeable cations. The relative quantities of the exchangeable cations were typical for the soils formed and varied in the order ($\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+, \text{Na}^+$) (Table 3). The soil OM presented a marked decrease from surface to sub surface in all the sites studied. The highest altitude VAS contained the greatest OM (5.63%) and the lowest altitude had the least OM (3.98%) (Table 3). Phosphorus sorption capacity increased down the profile for VAS, DMR and LMR, and decreased down the profile for UPD and was constant for SLR. The least PSC was recorded for DMR (1.28%) and the greatest with SLR (2.29%). The variation of PSC was not regular with respect to altitudes (Table 4).

Al and Fe Extractible Fractions

The concentrations of dithionite extractible Al (Al_{dith}) and oxalate extractible (Al_{ox}) are very similar for the untreated and treated soil samples (Table 4). The Al_{ox} values ranged from 2.28% to 3.48% for untreated soil samples and 1.28% to 3.38% for treated samples. The Al_{dith} values ranged from 4.68% to 5.15% for the untreated samples and 3.17% to 5.94% for the treated samples. The Al_{ox} and Al_{dith} values for both untreated and treated samples did not show any significant variation with altitude even though the highest altitude still had the greatest while the lowest altitude had the least values of extractible Al fractions. Oxalate extractible Fe (Fe_{ox}) values had a marked difference as its corresponding dithionite extractible (Fe_{dith}) values. The Fe_{dith} contents almost doubled the Al_{dith} contents of all profiles, and was almost the same for both treated and untreated samples.



Table 4: Proportion of extractable Al and Fe fractions in soils (< 2mm-fraction) for untreated and treated soil samples

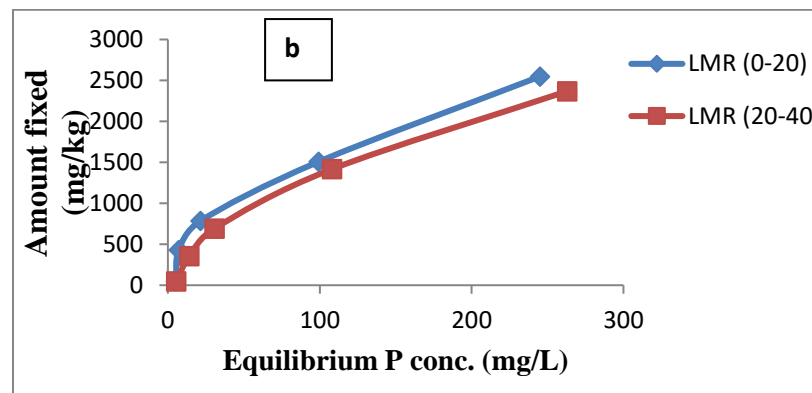
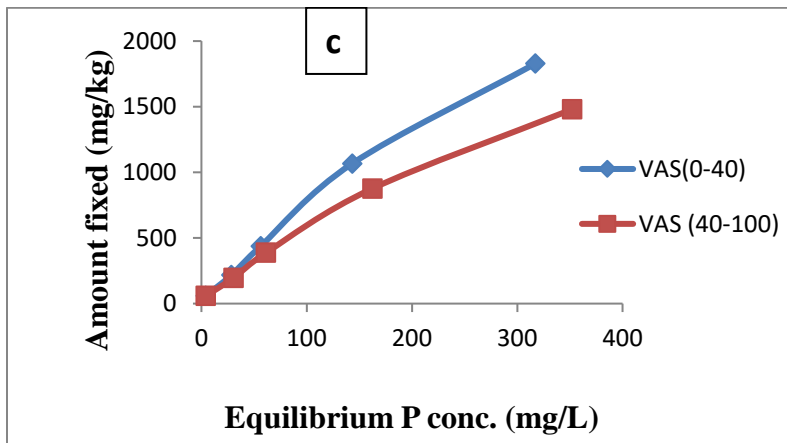
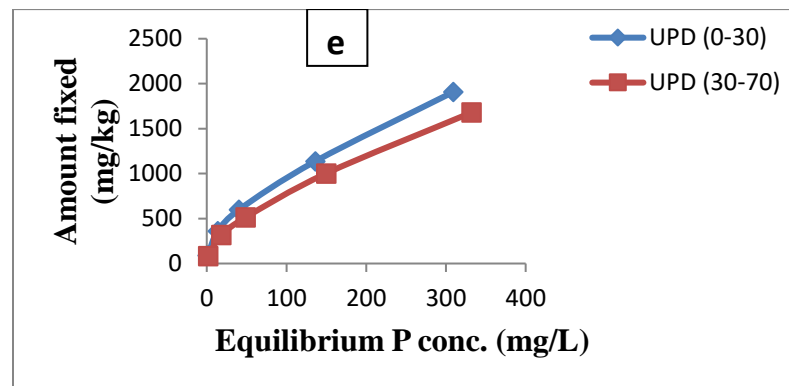
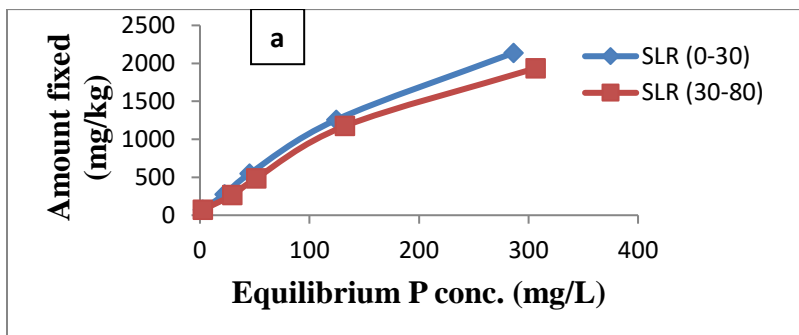
Sample Ref	Depth cm	Untreated (with SOM) samples				PSC# %	Treated (without SOM) samples				PSC'
		Fe [#] _{ox} (%)	Al [#] _{ox} (%)	Fe [#] _{dith} (%)	Al [#] _{dith} (%)		Fe' _{ox} (%)	Al' _{ox} (%)	Fe' _{dith} (%)	Al' _{dith} (%)	
VAS	0-40	1.34	3.17	9.62	4.96	2.26	1.35	2.16	8.73	4.42	1.76
	40-100	1.29	3.14	9.83	4.97	2.22	1.3	3.04	8.59	4.05	2.17
UPD	0-30	1.41	2.28	9.16	4.87	1.85	1.32	2.30	8.94	4.71	1.81
	30-70	1.39	2.31	8.79	4.82	1.85	1.24	2.34	8.61	4.63	1.79
SLR	0-30	1.38	3.43	9.86	5.12	2.41	1.26	3.31	9.17	5.94	2.29
	30-80	1.32	3.48	9.79	4.78	2.40	1.19	3.38	9.42	3.17	2.29
DMR	0-20	1.31	2.29	10.84	5.15	1.80	1.28	1.28	8.65	4.55	1.28
	20-40	1.29	3.18	10.89	4.97	2.24	1.17	2.15	8.69	4.37	1.66
LMR	0-20	1.27	2.97	8.73	4.68	2.12	1.21	1.52	8.65	3.94	1.37
	20-40	1.29	2.86	8.77	4.71	2.08	1.22	1.94	8.66	3.86	1.58

#Untreated soil samples; 'Treated soil samples

PSC = Phosphorus sorption capacity; Fe_{ox} = Oxalate-extractable iron; Al_{ox} = Oxalate-extractable aluminium; Fe_{dith} = dithionite extractible iron; Al_{dith} = dithionite extractible aluminium

Phosphate Fixation

The phosphorus fixation maxima were determined by fitting the solution P concentrations and fixation P values (Figure 2) in to Freundlich equations, as plotted in Figure 3. The highest P fixation maxima (Table 5) for the five untreated and treated soil profiles, according to Freundlich (KF), followed the order VAS (16.877 mg/kg) < DMR (24.717 mg/kg) < SLR (34.1219 mg/kg) < UPD (88.105 mg/kg) < LMR (174.58 mg/kg) for surface untreated soil samples and VAS (34.119 mg/kg) < SLR (47.313 mg/kg) < DMR (50.816 mg/kg) < UPD (114.551 mg/kg) < LMR (195.434 mg/kg) for surface treated soil samples. The phosphate adsorption isotherms gave a good fit for Freundlich ($r^2 = 0.98$ to 0.99) for untreated and treated soil samples.



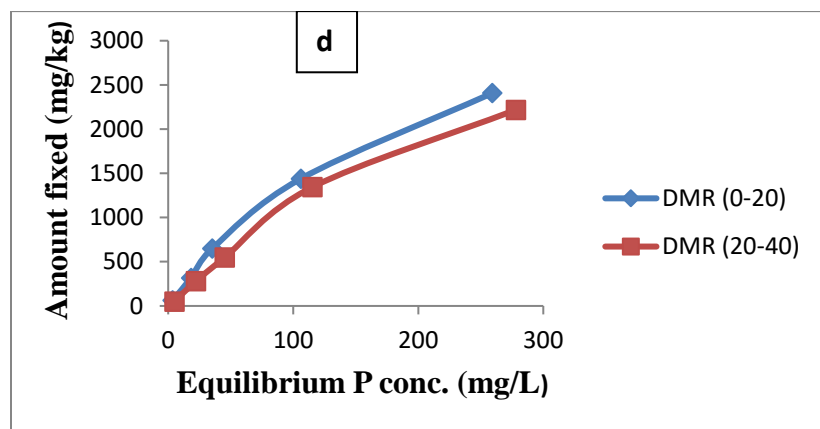
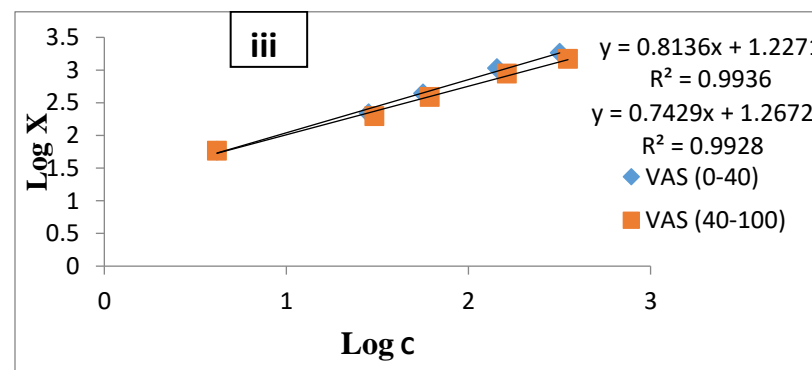
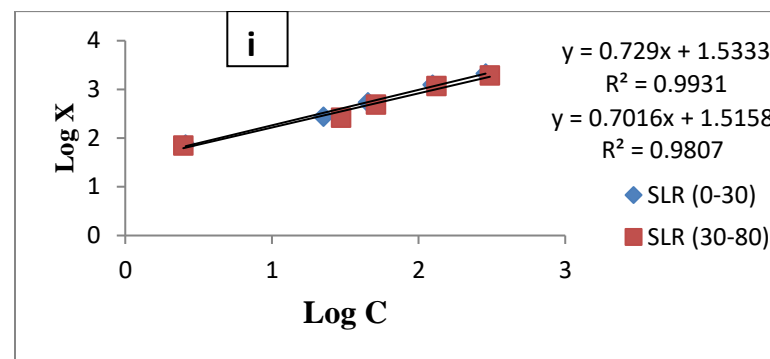


Figure 2: Processes of P fixation of the five untreated surface and subsurface soils studied [a: (SLR), b: (LMR), c: (VAS), d: (DMR) and e: (UPD)]



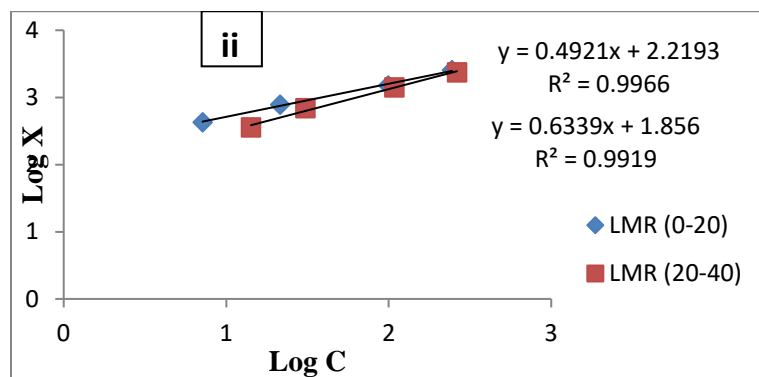
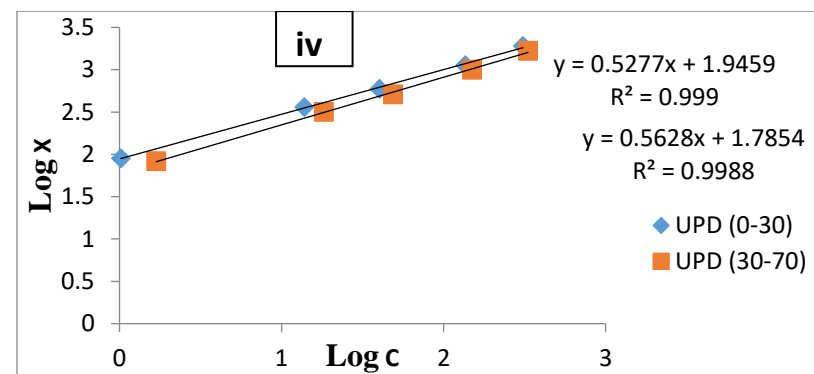
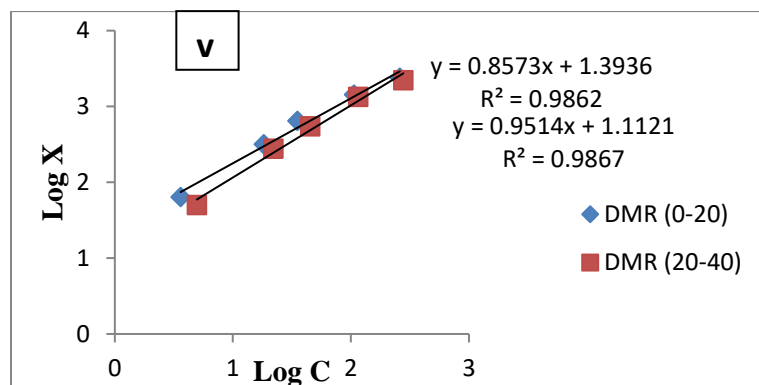


Figure 3: Freundlich models for phosphorus fixation of the five untreated surface and subsurface soils studied [i: (SLR), ii: (LMR), iii: (VAS), iv: (UPD), v: (DMR)]

**Table 5: Freundlich isotherm parameters for treated and untreated soil samples**

Sample Ref	depth cm	Freundlich parameters untreated				Freundlich parameters treated			
		Equation	n [#]	k _F [#]	R ^{2#}	Equation	n'	k _F '	R ^{2'}
VAS	0-40	0.813x +1.227	0.813	16.866	0.993	0.748x +1.533	0.748	34.119	0.980
	40-100	0.742x +1.267	0.742	18.493	0.992	0.736x +1.365	0.736	23.174	0.997
UPD	0-30	0.527x +1.945	0.527	88.105	0.999	0.524x +2.059	0.524	114.551	0.996
	30-70	0.562x +1.785	0.562	60.954	0.998	0.537x +1.926	0.537	84.333	0.994
SLR	0-30	0.729x +1.533	0.729	34.119	0.993	0.726x +1.675	0.726	47.315	0.994
	30-80	0.701x +1.515	0.701	32.734	0.980	0.748x +1.525	0.748	33.497	0.998
DMR	0-20	0.857x +1.393	0.857	24.717	0.986	0.765x +1.706	0.765	50.816	0.971
	20-40	0.951x +1.112	0.951	12.942	0.986	0.898x +1.322	0.898	20.989	0.980
LMR	0-20	0.492x +2.219	0.492	165.577	0.996	0.497x +2.291	0.497	195.434	0.995
	20-40	0.633x +1.856	0.633	71.779	0.991	0.585x +2.036	0.585	108.643	0.987

K_F = proportionality constant for Freundlich model; n = equilibrium constant related to binding energy

#Untreated soil samples

'Treated soil samples

Competition between Basic Soil Properties

Simple correlation coefficients (r) between selected soil properties and maximum adsorbed phosphate for untreated and treated soil samples were generated to better understand the relationship existing among soil chemical properties (Table 6).

Table 6: Simple correlation coefficients (r) between selected soil properties and maximum adsorbed phosphate for untreated and treated soil samples

	K _F [#]	K _F '	PSC [#]	PSC'
k _F	1			
K _F '	0.986**	1		
PSC	-0.291	-0.39	1	
PSC'	-0.413	-0.509	0.650*	1
Al _{ox}	-0.27	-0.369	0.995**	0.591
Al _{ox} '	-0.401	-0.500	0.667*	0.997**
Fe _{ox}	-0.086	-0.064	-0.257	0.352
Fe _{ox} '	-0.186	-0.133	-0.246	0.054
Al _{dith}	-0.681*	-0.650*	0.035	0.136



Al_{dith}'	-0.148	-0.103	-0.072	0.115
Fe_{dith}	-0.713*	-0.721*	0.176	0.016
Fe_{dith}'	-0.145	-0.225	0.537	0.673*
OM	0.009	0.014	0.275	0.119
pH(KCl)	-0.609	-0.392	-0.041	0.640
Avail. P	-0.270	-0.324	0.248	0.637*
ECEC	-0.375	-0.370	0.023	0.183

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

#Untreated soil samples

'Treated soil samples

Simple correlation coefficients (r) between selected soil properties and extractable Al and Fe for untreated and treated soil samples were generated to better understand the relationship existing among soil chemical properties (Table 7).

Table 7: Simple correlation coefficients (r) between selected soil properties and extractible Al and Fe for untreated and treated soil samples

	Al_{ox}#	Al_{ox}'	Fe_{ox}#	Fe_{ox}'	Al_{dith}#	Al_{dith}'	Fe_{dith}#	Fe_{dith}'
Al_{ox}	1							
Al_{ox}'	0.612	1						
Fe_{ox}#	-0.356	0.317	1					
Fe_{ox}'	-0.289	-0.028	0.44	1				
Al_{dith}#	0.007	0.104	0.225	0.402	1			
Al_{dith}'	-0.136	0.086	0.597	0.358	0.651*	1		
Fe_{dith}#	0.192	0.022	-0.208	-0.061	0.770**	0.15	1	
Fe_{dith}'#	0.486	0.685*	0.341	-0.172	0.033	0.005	0.087	1
OM	0.226	0.084	0.392	0.356	0.164	0.305	-0.085	0.47
pH(KCl)	0.020	-0.391	0.671	-0.210	-0.401	0.307	-0.501	-0.360
PSC	-0.200	0.241	0.759*	0.308	0.308	0.509	0.217	0.495
Avail. P	0.162	0.595	0.739*	0.494	0.24	0.342	-0.079	0.505
ECEC	-0.017	0.122	0.343	0.739*	0.321	0.235	0.013	-0.226

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

#Untreated soil samples

'Treated soil samples



DISCUSSION

All soil samples based on their pH (H₂O) are in the range of strongly acidic, as per ratings by Pansu and Gautheyrou (2007). The acidity of these soils may be associated with the high rainfall, coupled with the porous nature of the soils, resulting in leaching of bases. The increase of pH with altitude could be attributed to the decrease in temperature with altitude leading to decrease in rainfall. Electrical conductivity was very low for all samples according to the ratings established by Pansu and Gautheyrou (2007). Low range of EC indicates that tolerant crops and sensitive crops will not be affected if cultivated in these soils. The desired range for ECEC is between 5 and 25 cmol/kg (Landon, 2014). Therefore, ECEC was in the desirable range for all soils and is normally satisfactory for agriculture with average fertilizer application. One reason for the moderate ECEC may be that there is enough ionization of the functional groups of the OM to develop a great number of negative charges. Another possibility is that a great part of the organic charges might not have strongly interacted with the inorganic fraction, decreasing the effective negative charge.

These concentrations of exchangeable bases are quite low (especially for K⁺ and Na⁺), low for Mg²⁺ and vary from low to medium for Ca²⁺ ions, according to Landon Landon, (2014). These low concentrations may be as a result of the porous nature of the composite surface samples that are prone to base leaching. These low concentrations can also be explained from the prevalence of pH values of less than 5.5, where these cations are deficient (Tan, 1986).

All samples from the study area were in the range of low available plant phosphorus, as per ratings established by Pansu and Gautheyrou (2007). These low P concentrations may be associated with the acidic nature of the soils (pH < 5.5). At these pH values, Al, Fe and Mg are highly soluble and will react with the phosphate ions (H₂PO₄⁻) to form hydroxyl-phosphate which is insoluble and unavailable for plants. The low contents of available P observed in the soils of the study area were in agreement with the studies made by Mbene et al. (2017) on soils collected within this region. There is a relationship between adsorption and soil physicochemical properties.

According to Baldock and Skjemstad (1999), the amount of OM was either high or moderate judged according to their corresponding textural class for the selected soil samples. The results of this investigation clearly showed that the removal of organic matter altered the maximum fixation of phosphate in these soils. The maximum adsorption of phosphate was found to increase for both untreated soils compared to the treated soils. The phosphate sorption capacity (PSC), the amount of extractable aluminium and iron (Table 4) decreased after the removal of the organic matter content, confirming the fact that the destruction of the organic matter alters phosphate adsorption (Table 5). Sibanda and Young (1986) also found that added organic matter from other organic sources strongly competed with phosphate for adsorption sites, particularly at low pH. This may be due to the fact that the net charge on the organic matter at low pH is positive and therefore could attract the negatively charged phosphate.

In contrast, Appelt et al. (1975) found organic matter from added organic sources unable to compete with phosphate for adsorption sites on andisols. Borggaard et al. (1990) investigated the



impact of organic matter on phosphate adsorption using calcium acetate as a background electrolyte before and after removing organic matter from the soil and they concluded that OM had no direct influence on phosphate adsorption. Similarly, Debicka et al. (2016) carried out a similar investigation like Borggaard et al. (1990) but used calcium chloride as the background electrolyte and concluded that OM was the main soil constituent, which increased P binding and limited P leaching from sandy soils. The interpretation of the results, therefore, could be that the organic matter in the soil solution might have blocked P adsorption sites (Hunt et al., 2007; Mbene et al., 2017), even though its removal slightly affected these binding sites (Table 4) but it increased the soil surface area which is responsible for the increase in P maximum adsorption (Table 5). Since calcium was the dominant cation (Table 3) in these cultivated soils, phosphate behaviour in volcanic soils should be better simulated in the present study.

These results are important from agricultural (by knowing the necessary amount of P to be added to attain the soil fertility status), geological (by using the ratio of Fe_{ox}/Fe_{dith} to predict the degree of crystallinity or age which reflects the degree of soil development in volcanic soils) (Lü et al., 2017) or environmental (limit excess application of P and reduce eutrophication of water bodies) point of view, since they suggest that optimal phosphate fertilization of volcanic soils may be estimated from extractable aluminium and iron while considering the organic matter content.

The concentrations of Al_{ox} and Fe_{ox} were taken to indicate amorphous and poorly crystalline forms, including organically bound Fe and Al, which are dissolved during extraction (McLaughlin et al., 1981; Arduin et al., 1986). The similarities between Al_{ox} and Fe_{ox} values and Al_{dith} and Fe_{dith} are a clear indication that the oxides were poorly crystalline or amorphous. The formation of crystalline iron oxides may be inhibited in the presence of certain organic matter. However, the interaction between organic matter and iron seems weak in these soils regarding their pH values (Table 3). This may be the main reason why there was no correlation between PSC with Fe_{ox} before and after treatment. This was not the case with Al because PSC had a strong positively correlation with Al_{ox} ($P < 0.01$) and ($P < 0.05$) before and after treatment, respectively. The negative correlations ($P < 0.05$) between maximum phosphate adsorption (Table 6) before and after treatment with Al_{dith} and Fe_{dith} may be due to the poor crystallinity of the soil samples used in this investigation. Furthermore, the highly significant ($P < 0.01$) positive correlation coefficients between maximum (K_F) before and after OM removal indicate that K_F is unaffected by organic matter removal. This suggests that there is inhibition of adsorption sites for phosphate in one way or the other.

The crystallinity of the aluminium oxides seems very poor as a result of Al_{ox} , which is similar to Al_{dith} (Table 4), probably because of the strong interaction between aluminium and organic matter similar to the judgment of Borggaard et al. (1990). Considering the amount of OM in these soils (Table 3), they tend to behave like organic matter hydroxyaluminium polymers. These polymers can retain phosphate by ligand exchange with hydroxyl groups, indicating that the organic matter did not block the fixation sites but provided new fixation sites with lower reactivity to the phosphates. This may be the justification for OM not correlating with any of the extractable oxides (Table 7). Therefore, the changes in maximum phosphate fixation may be due to the increase in adsorbent surface area. This strongly suggests that organic matter affects phosphate adsorption indirectly by decreasing the adsorbent surface area, but not directly by



competing for adsorption sites, especially when the organic matter was not added from other sources during investigation.

Adsorbents

In the volcanic soils investigated, aluminium and iron oxides are the main adsorbents. Iron oxides and aluminium oxides retain phosphate by ligand exchange, where singly coordinated hydroxyl groups on the oxides (adsorbent) are replaced by phosphate ions (adsorbate); each phosphate replaces a pair of contiguous hydroxyl groups on iron oxides (Borggaard et al., 1990; Lü et al., 2017; Mateus et al., 2020). McLaughlin et al. (1981) stated that the adsorption capacity depends very much on the specific surface area of the oxides but appears independent of the mineral form. Therefore, any soil property that can affect the soil surface area and soil surface oxides will definitely affect P sorption capacity. In soils, only organic matter can double play this function on the adsorbent. This may be the main reason why the removal of organic matter caused an increase in P adsorption on treated samples.

CONCLUSION

Volcanic soils are used for agriculture world-wide and conservation of soil OM additions will prevent P loss and contribute to P availability for crop plants, thus decreasing P fertilization needs. The P sorption capacity observed in surface soils was predominantly higher than in the subsurface soil horizons. Phosphorus sorption capacity values decreased with decreased SOM, with an increase in P fixation as revealed by its K_F value. The removal of SOM from the surface and subsurface samples resulted in a considerably increased K_F' value ($K_F' > K_F$), and a decrease in the P sorption capacity in most of the examined samples. This caused a higher dependence of P sorption on other soil properties. A higher P fixation was observed as a consequence of SOM removal in most top soils. Our results showed a better fit for Freundlich isotherm. Similarly, the K_f parameter values were also higher in top soil as compared with subsoil before and after SOM removal. Our results indicated a considerable impact of SOM on P sorption in volcanic soils, but also the dependence on the specific conditions generated by soil properties ($Fe_{(ox)}$, $Al_{(ox)}$, Fe_{dith} and Al_{dith}), which are often related to soil parent material and anthropogenic activities.

Therefore, activities like liming of the Al oxides in these soils should be encouraged so that these oxides will no longer play a major role in retaining phosphates and P availability to plants will be assured. Improving the organic matter content in these soils should be emphasized as it influences phosphate fixation indirectly without competing with phosphates for fixation sites. Freundlich isotherm can adequately be used to determine the maximum phosphate adsorption in soils and give precise advice to better fertilizer management in volcanic soils. Other aspects of P sorption are still worth undertaking, for example, the relations between the capacity for P sorption and specific fractions of soil organic matter, and the influence of the activity of Fe and Al fractions on the process tested across different soil properties and SOM content.



CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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