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The Behavior of Phosphorus Adsorption on Soil in the Geological Formation of Ranau Tuff Using the Langmuir Isothermic Model to Support Food Security

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Abstract. In tropical soils, phosphorus (P) adsorption is one of the main processes that control the availability of P for plant growth. Soils that develop from volcanic material have a high P uptake as the mineral composition contains a lot of active colloids of Fe and Al which play a crucial role to adsorb P in soil complex. Soils which have a high capacity of P adsorption, potentially decrease the efficiency of P fertilizers into the soil as it is unavailable for plant growth. Langmuir Isothermic Model is a mathematical model that can be used to determine the capacity adsorption (X_{max}) and the relative energy (K_L) of phosphorus in the soil. This study was therefore aimed to obtain the information on the maximum phosphorus absorption capacity in the soil samples of Tufa Ranau Geological Formation (TRGF). The basic information from this research provided the valuable information of P nutrients management in the soil to support the efficiency of P fertilizer and food security. Soil samples were collected from TRGF area at three zones in West Lampung Regency (1. ± 40 km; 2. ± 30 km; and 3. ± 20 km in the southern area of Lake Ranau). Soil samples were collected from two depth of soils (0 – 20 cm and 20 – 40 cm). This research was an experimental study that has been conducted in the Laboratory of Soil Science, Faculty of Agriculture, University of Lampung to analysis the behavior of P adsorption with Langmuir Isothermic Model. Then the Student-t test was performed to see the difference between the maximum absorption of phosphorus and the relative energy of phosphorus adsorption in each treatment. The results showed that soil in Balik Bukit has a maximum adsorption P value (X_{max}) which is higher than that of the soil in Sekincau and Batu Brak on TRGF. The high value of X_{max} is because Balik Bukit may have to do with a high Fe content of 35.95 mg kg-1, since Fe is one of the causes of high P sorption in the soil. The relative energy of phosphorus adsorption value (K_L) in subsurface horizons is relatively higher than that of in surface horizon so that P in subsurface horizons is relatively difficult to be available when compared to surface horizons, because the higher K_L value makes P more difficult to be available to plants.

INTRODUCTION

Phosphorus (P) adsorption or sorption is defined as the net accumulation of P at the interface between the soil solids and the water soluble phase [1], which is determined by the availability of soil P and the amount of P added through fertilization [2]. When soluble P compounds are applied to soil, it undergoes a series of complex reactions that can reduce the availability of P to plants. P compounds generally often react rapidly with other soil minerals through

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precipitation reactions and adsorption to the surface of solid soil particles [2]. The adsorption reaction is one of the main processes involved in P retention at the soil surface.

The main factors affect the maximum of soil P adsorption capacity include pH, clay mineral type, Fe and Al oxide content, particle size distribution, soil oxide crystallinity, quality and quantity of soil organic matter. P-uptake tends to increase in tropical soils with low pH and the presence of kaolinite and Fe and Al oxides in the clay fraction [3]. Fink *et al.* [4] reported P adsorption tends to increase in tropical soils with low pH and the prevalence of kaolinite and Fe and Al oxides in the clay fraction. When Fe and Al oxides react with soluble phosphate in the soil, it will form a solubility complex which will reduce the amount of available phosphorus [5]. Fe and Al oxides found on the soil surface of soils are specific adsorption sites of phosphorus [6], [7].

The Langmuir isothermic model can be used to determine the maximum adsorption and relative bond energy of phosphorus in the soil. Hanyabui *et al*. [3] reported that the method of determining phosphorus adsorption using the Langmuir equation is a good model for determining P adsorption in tropical soils. This method is useful for separating soil and solution easily and the solution to be analyzed for its phosphorus adsorption capacity is available in sufficient quantities [8], [9]. The maximum absorption of phosphorus can be shown by the calculated phosphorus concentration in the soil. However, the relative value of phosphorus binding energy is a Langmuir isothermic parameter that describes the energy of phosphorus nutrient binding in soil colloids [10]. So that from the maximum adsorption value and relative phosphorus bond energy, it can be determined the value of phosphorus nutrient uptake in the soil sorption complex (soil colloid).

In this study, samples from the Tuff Ranau Geological Formation (TRGF) were used. TRGF is the result of a pile of tuff material that comes from the results of an ancient volcanic eruption of a quarter age. The uniqueness of the soil in the Tufa Ranau distribution is that it has undergone further development and has an alteration horizon so that it can be classified into the order Inceptisols [11]. Hence, it is necessary to do this research to determine the capacity or how much maximum P adsorption in soil formed from parent material in TRGF soil (soil that has undergone advanced development). Shoeji *et al*. [12] reported that the uniqueness found in soils developed from volcanic ash is that the mineral composition contains a lot of active colloids Al and Fe, both in non-crystalline and para-crystalline forms. The presence of a large number of active compounds Al and Fe in the soil developed from volcanic ash causes P to be strongly adsorbed [13], [14] in mineral structures or bound to positively charged OH or H functional groups [15]. According to [16] that the volcanic soil in Chile has high acidity and Ex-Al, so that the efficiency of P fertilization is low. Egawa [17] reported that only 10% of the applied P fertilizer could be used by plants. The high percentage of P loss is a serious problem that is often found in volcanic soils. Therefore, this research is very important considering the high P sorption in soils developed from volcanic material and the absence of data on P sorption in the TRGF volcanic area. In addition, considering that phosphorus is a limiting factor in crop production. So it is important to analyze the behavior of phosphorus adsorption using the Langmuir isothermic model.

MATERIALS AND METHODS

This research was an experimental research conducted in a laboratory. Phosphorus adsorption analysis was carried out using the Langmuir isothermic model on TRGF samples. This Langmuir isothermic parameter taken used to determine the maximum adsorption and relative energy of phosphorus bonds in the soil. Soil samples used in this study were derived from TRGF. TRGF soil sampling was taken from three points in West Lampung Regency with a radius of ± 20-40 km in the southern region of Lake Ranau. Disturbed soil samples were taken at a depth of 0 – 20 cm (surface) and 20 – 40 cm (subsurface). Soil sampling was carried out simultaneously with observations of the physical environment of the study area. The map of the location of the soil sampling can be seen in Figure 1.

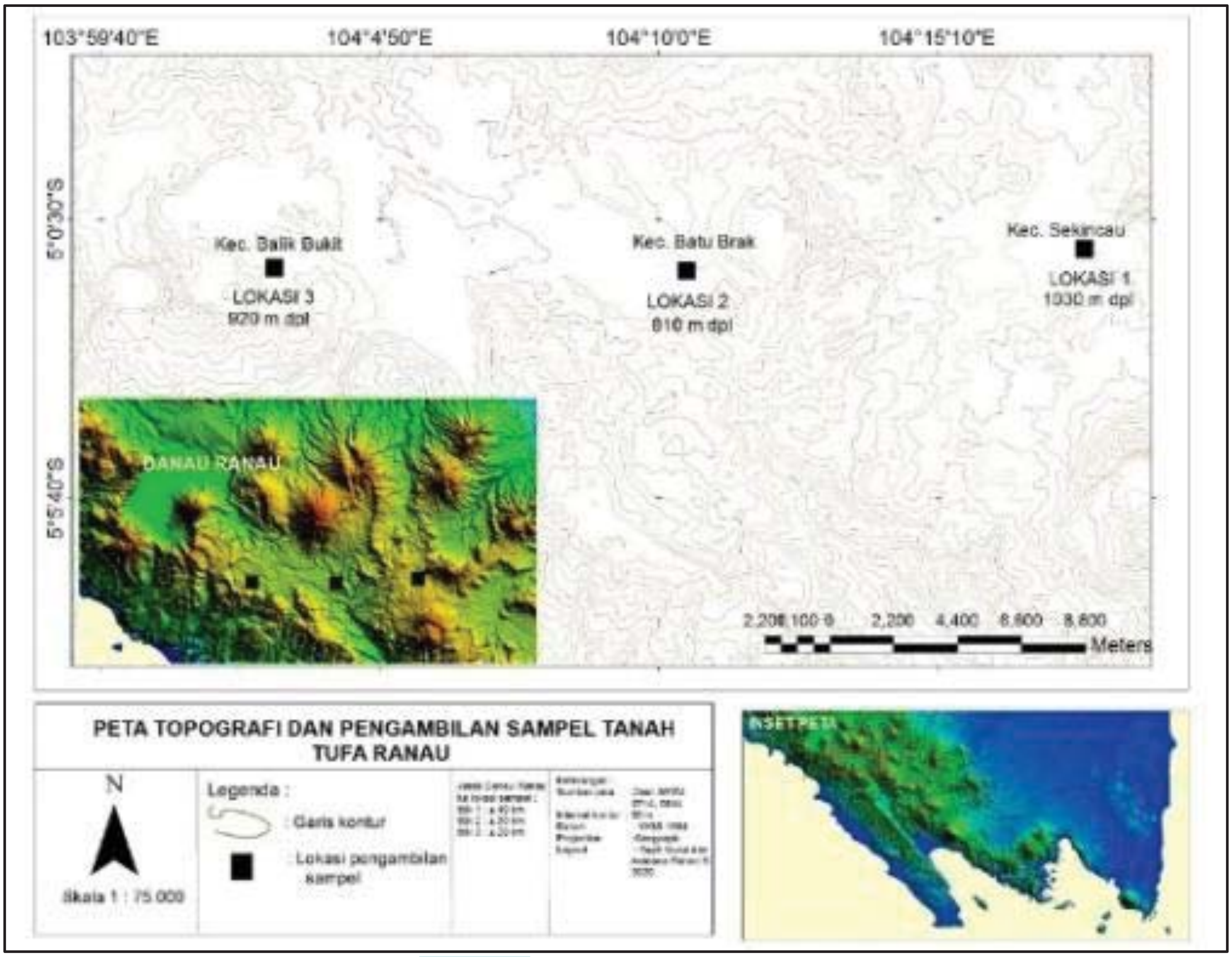

FIGURE 1. Location of sampling TRGF

The experimental procedure of the Langmuir isothermic model was adapted from [18], [19], [20] which modifies the manufacture of the P series solution. The serial solutions made in this study were 0 ppm P, 10 ppm P, 25 ppm P, 50 ppm P, 100 ppm P, and 200 ppm P. The steps for making 10 ppm, 25 ppm, 50 ppm, 100 ppm, and 200 ppm serial solutions are to enter 10 ml, 25 ml, 50 ml, 10 ml and 200 ml KH_2PO_4 solution 1000 ppm P respectively into a volumetric flask (size 1 L), then continued by adding 10 ml of 1 M $CaCl_2$ solution and distilled water up to 1 L.

The procedure for determining phosphorus adsorption on soil samples using the Langmuir isothermic model was conducted by weighting each soil sample as much as 3 g and put into a shaker bottle (100 ml size). Then, each soil sample was added with a series solution (0, 10, 20, 50, 100, and 200 ppm) as much as 30 ml. The suspension of the soil sample was shaken using a shaker for ± 2 hours. After that, the soil sample suspension was centrifuged at 3000 rpm for 10 minutes.. The clear extract from the centrifuge was used in the measurement of phosphorus using a spectrophotometer with a wavelength of 720 nm. While the phosphorus that was absorbed in the soil is the difference between the concentration of the phosphorus solution given and the phosphorus in equilibrium. The data obtained is calculated based on the equations and curves of the Langmuir equation can be seen in Figure 3.

$$\frac{C}{X} = \frac{1}{K_L X_{max}} + \frac{1}{X_{max}} C \quad (1)$$

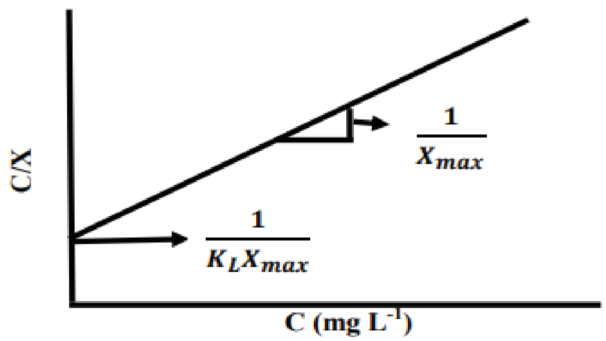

FIGURE 2. Langmuir's equation curve

The description [21]:
C/X = Adsorption index P
Xmax = maximum adsorption (mg P kg-1)
KL = Relative bond energy to determine phosphorus adsorption
C = Concentration of phosphorus in equilibrium solution (mg P L-1)
X = Amount of phosphorus adsorbed (mg P kg-1).

Maximum adsorption with the Langmuir isothermic equation shows the ability of the soil to bind or absorb P nutrients in the adsorption complex or soil colloid. Meanwhile, K_L (relative bond energy value) shows the bond energy of P nutrients in adsorption complexes or soil colloids in the Langmuir equilibrium constant which is related to the heat of adsorption [10]. Harianti [22] reported that the higher the maximum phosphorus uptake in the soil, the lower the P uptake by plants and the lower the available P content in the soil. The implication is that if the soil has a P adsorption capacity and a high relative value of bond energy, it will cause the addition of fertilizer to the soil to be difficult to be available to plants. The Xmax value is obtained from the slope of the equation or the slope of the line, while the K_L value is obtained from the point of intersection of the line on the Y axis (intercept) as shown in Figure 2.

Soil analysis data obtained from the laboratory are displayed in the form of tables and graphs. The data will show the comparison of phosphorus adsorption using the Langmuir isothermic model on three different samples from TRGF. Phosphorus adsorption model is determined by using Langmuir isothermic equation model. Then the Student-t test was performed to see the difference between each maximum phosphorus adsorption in each treatment and the relative phosphorus adsorption energy in each treatment using the Langmuir isothermic model.

RESULTS AND DISCUSSION

Charateristics of Soil on TRGF

Table 2 shows physical and chemical properties of the soils in Sekinsacau, Batu Brak and Balik Bukit. The soil in Sekincau had a particle size distribution of 34.27% sand, 33.41% silt, and 32.32% clay classified to clayey loam class by USDA. While soil in Batu Brak had a particle size distribution of 40.02% sand, 29.43% silt, and 30.55% clay classified to clayey loam class by USDA. The soil in Balik Bukit had a particle size distribution of 51.63% sand, 31.76% silt, and 16.62% clay so that it belongs to the texture class, namely clay.

Chemically, the soil in Sekincau has an acidic pH of 4.52, low levels of organic-C, CEC, and ex-Mg which are 1.64%, 14.82 $cmol_c\ kg^{-1}$, and 0.48 $cmol_c\ kg^{-1}$, respectively. and has a Fe content which is classified as moderate (13.28 $mg\ kg^{-1}$). In addition, soil in the Sekincau has a very low content of available-P, and ex-Ca. Soil in Batu Brak has a slightly acidic pH of 6.16, has low levels of organic-C, CEC, and ex-Mg and has very low levels of available-P, and ex-Ca, but has a high Fe content of 20.32 $mg\ kg^{-1}$. While the land in the Balik Bukit has an acidic pH of 4.78, and a high Fe content of 35.95 $mg\ kg^{-1}$.

TABLE 1. Physical and chemical properties of the TRGF soils in Sekincau, Batu Brak and Balik Bukit

Parameter	Unit	Sekincau	Category*	Baru Brak	Category*	Balik Bukit	Category*
Physical Properties							
Texture							
Sand	%	34.27	Clayey loam	40.02	Clayey loam	51.63	Clay
Silt	%	33.41		29.43		31.76	
Clay	%	32.32		30.55		16.62	
Chemical Properties							
pH	-	4.52	Acid	6.16	Slightly acid	4.78	Acid
C-organic	%	1.64	Low	1.14	Low	4.00	High
P-available	mg kg^{-1} P_2O_5	0.53	Very Low	1.56	Very Low	2.82	Very Low
CEC	cmolc kg^{-1}	14.82	Low	12.40	Low	16.56	Moderate
Ex-Ca	cmolc kg^{-1}	0.85	Very low	1.60	Very Low	0.99	Very Low
Ex-Mg	cmolc kg^{-1}	0.48	Low	0.89	Low	0.82	Low
Fe	mg kg^{-1}	13.28	Moderate	20.32	High	35.95	High

Note: Data Source [23]

* Criteria based on the standards of Indonesian Soils Research Institute (2012)

Soil Phosphorus Adsorption on TRGF Using the Langmuir Isothermic Model

The results of the analysis of P measurements in the series solution obtained the initial P content while the extracted P results in each treatment were P content at equilibrium conditions or available in the soil solution (C). The difference between the two values is the absorbed P value (X). Plotting the values of C and C/X will produce the Langmuir Equation Curve which has presented in Figure 4 and the Langmuir linear equation is presented in Table 2. Figure 3 shows that the P value in equilibrium (C) is inversely proportional to the adsorption value of P (X) in the soil. The higher the P value in equilibrium, the lower the adsorbed P value, and vice versa.

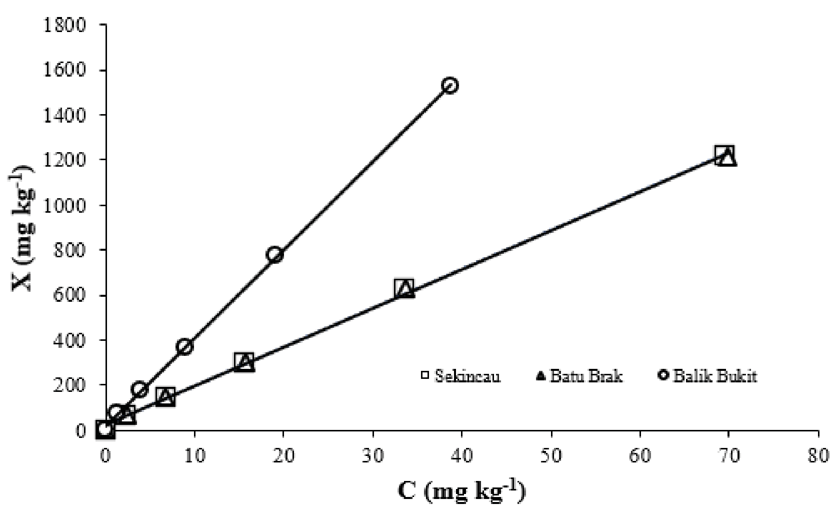

FIGURE 3. Graph of the relationship between the amount of adsorbed P (X) and the concentration of P in the equilibrium solution (C) in the soil TRGF.

Figure 4 shows the relationship between the P adsorption index (C/X) and the concentration of P in the equilibrium solution (C) in two soil layers at three soil sampling points (Sekincau, Batu Brak, and Balik Bukit) are in TRGF. The soil in Balik Bukit has a relatively low C/X value compared to Sekincau and Batu Brak both on the surface and subsurface so that the soil of Balik Bukit has the highest maximum adsorption value (X_{max}) (Figure 3). This can be seen in Table 2 which shows that the soil in Balik Bukit has a X_{max} value of 5,000 mg kg^{-1} in surface and 1,429 mg kg^{-1} in subsurface. The high X_{max} value is due to the soil in Balik Bukit has a high Fe content of 35.95 mg kg-1 (Table 1), where Fe is one of the causes of high P sorption in the soil. The lowest X_{max} value was found on the soil in Batu Brak in subsurface is 625 mg kg^{-1}. This is because the soil in Batu Brak has a higher pH of 6.16 when compared to the pH of the soil samples in Sekincau and Balik Bukit are 4.52 and 4.38, respectively (Table 1). A high pH value causes a decrease in the solubility of Al and Fe, where Al and Fe are the main causes of the high maximum P sorption [24,25].

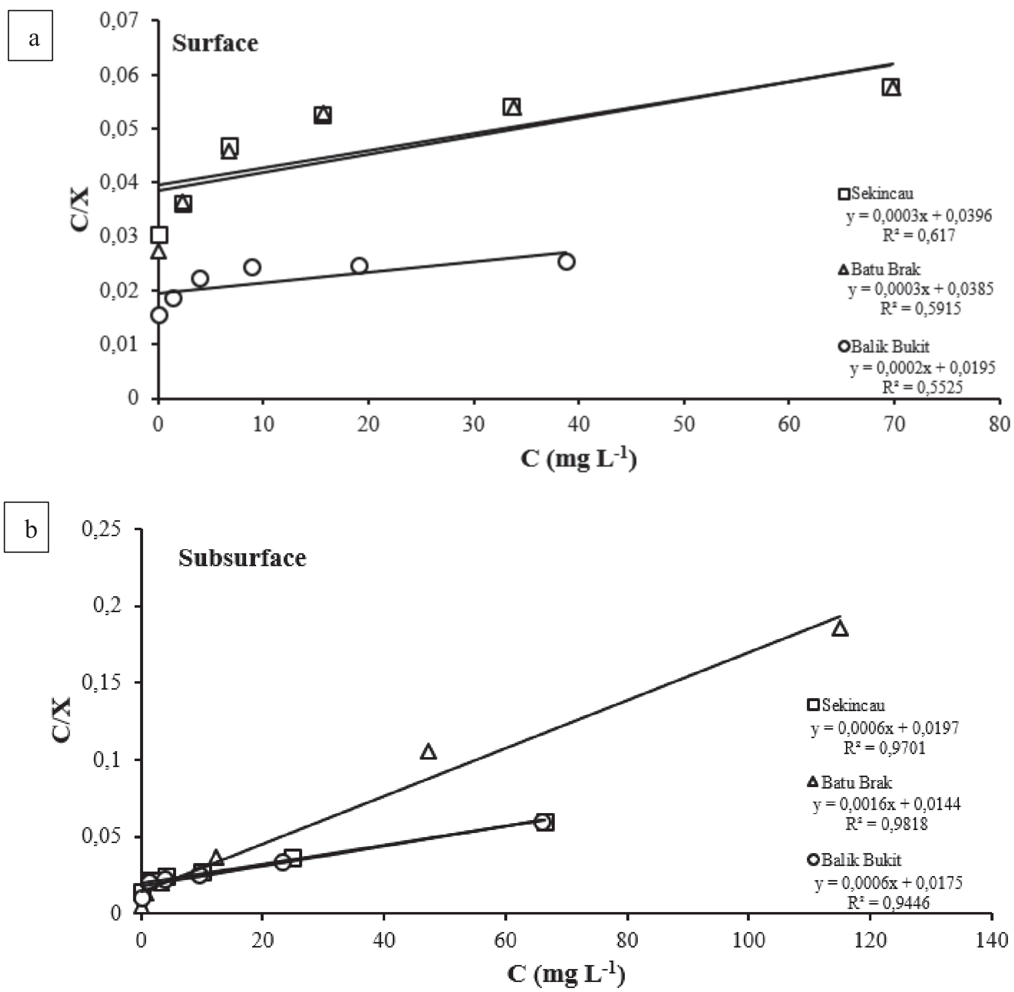

FIGURE 4. (a) Graph of the relationship between the P adsorption index (C/X) and the concentration of P in the equilibrium solution (C) of surface and (b) subsurface of the TRGF.

The bond energy constant (K_L) shows the level of strength of soil colloids to adsorb nutrients which is inversely proportional to the level of ease of nutrient release into the soil solution [24]. The value of K_L in subsurface is relatively higher than that of soil in surface (Table 2). This is in line with the results of research by Fiantis [18], that the value of sorption affinity (K) tends to increase with soil depth, which means that the energy to bind P is greater in the lower horizon than the surface horizon. Thus, the higher the K_L value, the more difficult P is available to plants.

TABLE 2. Langmuir Isothermic Linear Equation Adsorption P in each sample

Soil Sample	Regression Equation	R^2	X_{max} (mg kg^{-1})	K_L
AL1	y= 0,0003x + 0,0313	0,684	3333	0,080
AL2	y= 0.0006x+0.0177	0,965	1667	0,030
BL1	y=0,0004x + 0,0382	0,629	3333	0,080
BL2	y= 0,0016x + 0,0159	0,987	625	0,111
CL1	y=0,0002x + 0,0161	0,572	5000	0,010
CL2	y= 0,0007x + 0,0163	0,911	1429	0,034

Note: A = Sekincau; B= Batu Brak; C= Balik Bukit; L1= surface; L2= subsurface.

Table 3 shows that the maximum adsorption (X_{max}) on the soil in Balik Bukit is significantly higher that of the soil in Sekincau and Batu Brak. This is probably due to the high content of Fe in the soil in Balik Bukit is 35.95 mg kg^{-1}, when compared to the Fe content in the soil in Sekincau and Batu Brak, respectively, only amounted to 13.28 and 20.32 mg kg^{-1} (Table 1). These findings are consistent with those of Nanzyo [27] which stated that phosphate fixation attributable mainly to active species of aluminium and iron. Gonzalez-Rodriguez *et al*. [15] reported that the presence of active forms of aluminium and iron, such as oxides, oxyhydroxides, short-range order silicates (allophane, imogolite), Al(Fe)-humus complexes, is a characteristic of volcanic soils. These materials confer the soil the ability to adsorb phosphate. The table above also shows that the X_{max} value in surface is significantly higher than that in subsurface. According to Nursyamsi & Setyorini, [26] that the X_{max} value (maximum adsorption) indicates the ability of the soil to store nutrients in soil colloids. In general, the soil in surface has a higher ability to store nutrients in the soil colloid than the soil in subsurface.

TABLE 3. Student-t test on maximum adsorption parameters P (X_{max}) and relative bond energy P (K_L)

Soil Sample	*t*		Sig. (2-tailed)	
	X_{max} (mg kg^{-1})	K_L	X_{max} (mg kg^{-1})	K_L
AL1 vs AL2	nc	0.072ns	nc	0.949
AL1 vs BL1	1.000ns	-710ns	0.423	0.551
AL1 vs BL2	127.952**	-785ns	0,000	0.515
AL1 vs CL1	nc	-272ns	nc	0.811
AL1 vs CL2	15.000*	-119ns	0.004	0.916
AL2 vs BL1	-3000ns	-753ns	0.095	0.530
AL2 vs BL2	48.619**	-822ns	0.000	0.497
AL2 vs CL1	nc	-372ns	nc	0.745
AL2 vs CL2	1.000tn	-239ns	0.423	0.834
BL1 vs BL2	5.444*	-122ns	0.032	0.914
BL1 vs CL1	-5.002*	0.576ns	0.038	0.623
BL1 vs CL2	3.159ns	0.682ns	0.087	0.566
BL2 vs CL1	-207.333**	0.666ns	0.000	0.574
BL2 vs CL2	-7.464*	0.760ns	0.017	0.527
CL1 vs CL2	29.008**	0.200ns	0.001	0.864

Note : The *t-student* analysis was carried out using the SPSS Statistics 25 application. Nc = cannot be computed, **= very significant 1%, *= significant 5%, dan ns=not significant. A = Sekincau; B= Batu Brak; C= Balik Bukit; L1=Surface; L2= Subsurface.

CONCLUSION

The findings in this study were that the soil in Balik Bukit has a maximum adsorption value (Xmax) being higher than that of the soil in Sekincau and Batu Brak on TRGF. The high value of Xmax is because the soil in Balik Bukit has a high Fe content, where Fe is one of the causes of high P sorption in the soil. The K_L value in subsurface is relatively higher than surface so that P in subsurface is relatively difficult to be available when compared to surface, because the higher K_L value makes P more difficult to be available to plants. The Strong phosphate absorption by the soil under study is a serious limiting factor for plant growth, which requires phosphorus fertilizer management that carefully, including proper management of organic materials. This finding is needed to be applied in field to test the fertilizer efficiency for crop production.

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