

RESEARCH ARTICLE



Amelioration of Potassium Humate as Ligand Exchanger for Adsorbed P Fractions and their Relationships with Chemical Properties of an Indonesian Andisol

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ABSTRACT

Andisols are specifically characterized by a very high P adsorption capacity owing to their acidic reaction and dominance of variable-charged clay minerals. This crop cultivation problem can be overcome by potassium humate amelioration intended to exchange the adsorbed soil P fractions into the more available (labile) forms. This study aims to evaluate the effects of potassium humate application at 0, 20, 40, and 60 kg ha⁻¹ on the dynamics of P fractions and their relationships with the chemical properties of an Indonesian Andisol. Using the Tiessen and Moir procedure, P_{H2O}, P_{NaHCO3-Pi-Po}, P_{NaOH-Pi-Po}, and P_{HCl} fractions were obtained in topsoil (0–30 cm) and subsoil (30–60 cm) samples 16 weeks after the treatment. The organic soil P (P_{po}) fractions tended to increase and were attributed positively to total P and negatively to base saturation (BS) at the topsoil, whilst the subsoil P_{po} fractions tended to increase with the decreasing soil BS. At 60 kg ha⁻¹, the potassium humate application effectively decreased P_{po} and increased P_{pi} fractions in the subsoil. The results also revealed that humic acid component of potassium humate was an effective organic ligand exchanger for the adsorbed P_{po} fractions that simultaneously altered soil anion-cation equilibrium in the studied Andisol. As an implication, soil P availability was increasing.

Introduction

Pagar Alam City is a part of the Bukit Barisan highlands of South Sumatera Province, Indonesia. The existence of Mt. Dempo, an active volcano, extensively influences the natural fertility of soil, which is dominated by Andisols [1]. The main crop cultivation problem in Andisols is the high soil adsorption capacity for phosphate (P) owing to the dominance of nanocrystalline allophane and paracrystalline imogolite, as well as ferrihydrite and hydrated Al and Fe oxides as the forming clay minerals. These clay minerals can adsorb up to 97.8% of soil P [2] through the formation of an inner-sphere complex with phosphate as the main ligand [3,4].

The colloidal surface reactivity of Andisols originates from the functional groups of the dominant clay minerals, especially the reactive sites of aluminol (Al-OH), which have variable or pH-dependent charge characteristics [5]. In highland areas, soils tend to develop an acidic reaction [6]; hence, the aluminol reactive sites of Andisols are deprotonated and produce a dominantly positive charge. It is therefore most anions, particularly phosphate, are strongly adsorbed by the chemisorption mechanism [7], making them unavailable for plant root absorption. As a result, the response of cultivated crops to P fertilization in tropical Andisols is tremendously low [8].

Without an attempt to decrease the P adsorption capacity, the P fertilizer dose to achieve optimum crop productivity in Andisols will be immense, inefficient, and tend to cause environmental problems [9]. This is one of the reasons why Pagar Alam City, one of the agribusiness sub-terminals in South Sumatera, is challenged to sustainably increase the productivity of its crops, especially vegetables [10]. One prospective

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effort that necessitates the assessment of its effectiveness in decreasing P adsorption capacity in Andisols is the application of potassium humate. Potassium humate is a potassium (K) salt of humic acid. In this case, the humic acid component of the potassium humate is expected to function as a ligand exchanger to displace phosphate at the soil colloidal adsorption site; hence, soil P will be dominated by labile fractions that are more available for plant root absorption.

According to Tiessen and Moir [11], soil P consists of five fractions that are related to the level of plant availability: P_{Resin} (very quickly available), $P_{\text{NaHCO}_3\text{-Pi-Po}}$ (rapidly available), $P_{\text{NaOH-Pi-Po}}$ (slightly available), P_{HCl} (slowly available), and P_{Residual} (potentially available). Humic acid is a base-soluble organic compound that is difficult to decompose further and therefore tends to form a relatively stable colloid [12]. Humic acid has a polyphenol or quinone aromatic core as well as carboxyl, phenol, and carbonyl functional groups, including sugars and peptide fragments, whilst its sub-entities can be associated with the $-\text{O}-$, $-\text{CH}_2-$, $=\text{CH}-$, and/or $-\text{NH}-$ as well as $-\text{S}-\text{S}-$, and other similar groups [13]. The adsorption affinity of clay minerals in Andisols for humic acid is greater than that of phosphate; therefore, phosphate as an adsorbed ligand complex can be displaced. Hence, phosphate is released into the soil solution as plant-available P [14].

The application of potassium humate can also increase the availability of soil K and the negative charge of soil colloids, thereby decreasing anion adsorption, including phosphate, through a negative adsorption mechanism [15,16]. This study aimed to evaluate the effects of potassium humate amelioration on the dynamics of soil P fractions and their relationships with the chemical properties of an Andisol in Pagar Alam, South Sumatera, Indonesia. In an effort to achieve a sustainable soil resource management option, the results of this study will be useful for determining the recommended dose of potassium humate for productive crop cultivation in Andisols.

Materials and Methods

Experimental Design

A field experiment was conducted from May to August 2023 on the farmers' land in Gunung Agung Pauh Village, Pagar Alam City, North Dempo Regency, South Sumatera Province, Indonesia, which is located at an altitude of 1,100 to 1,300 m above sea level with Andisol as the soil order. Based on interviews with farmers, in the growing season preceding the experiment, the land was cultivated for potatoes with a low productivity (18 t ha^{-1}). After the harvest, the plots had been ameliorated with 15 t ha^{-1} chicken manure. One week later a mixture of 650 kg ha^{-1} Biophosphate (P) and 350 kg ha^{-1} Vigo Amino (N) as basic fertilizers, as well as potassium humate powder according to the treatment dose levels, were spread over the unplanted experimental plots. One month later, 350 kg ha^{-1} NPK 16-16-16 was applied as supplemental fertilizer. Except for potassium humate, chicken manure and fertilizers doses followed local farmers' decisions.

Soil samples were taken compositely from five subsamples of topsoil (0–30 cm) and subsoil (30–60 cm) of each experimental plot one day before and 16 weeks after the application of potassium humate as a single treatment according to a Randomized Block Design. The dimension of each experimental plot was 3 x 2 m. The treatment consisted of 4 levels of potassium humate application (kg ha^{-1}), $P_0 = 0$ (control), $P_1 = 20$, $P_2 = 40$, and $P_3 = 60$, each with 3 replications. Soil samples were air-dried, separated from litter and roots, and passed through a 2 mm sieve for laboratory analysis.

Soil Analysis

Soil analyses were carried out on texture (3 fractions) using Pipette method and chemical properties as presented in Table 1. The modification performed in the P fractionation analysis was to change resin with aquadest to obtain the quickly available fraction, designated as $P_{\text{H}_2\text{O}}$. Soil P fractionation was only carried out on soil samples taken 16 weeks after the initial application of the treatment to obtain $P_{\text{H}_2\text{O}}$ (instead of P_{Resin}), $P_{\text{NaHCO}_3\text{-Pi-Po}}$, $P_{\text{NaOH-Pi-Po}}$, and P_{HCl} fractions, whereas P_{Residual} was calculated as the difference between total P and $P_{\text{H}_2\text{O}} + P_{\text{NaHCO}_3\text{-Pi-Po}} + P_{\text{NaOH-Pi-Po}} + P_{\text{HCl}}$. The P_{Pi} and P_{Po} attributes indicated the soil inorganic and organic P fractions, respectively.

Data Analysis

The relationships between potassium humate treatment doses, soil chemical properties, and soil P fraction dynamics are presented graphically and descriptively. The significance levels of the treatment effects on the soil P fractions were based on the results of the linear regression analysis. Data analysis was also performed to determine the multiple linear regression equations ($Y = a + b_1X_1 + b_2X_2 + b_nX_n$) using a backward stepwise

procedure, and to analyze the relationship between the soil P fractions as the dependent variable (Y) and the soil chemical properties as independent variables (X_{i-n}) using MS Excel and SPSS software. In this article, the $P_{Residual}$ data were not presented or discussed because they were not significantly affected by the treatment or related to the chemical properties of the soil.

Table 1. Methods of soil analysis.

Soil analysis	Extraction methods	Determinations
pH H ₂ O	H ₂ O Extract [17]	pH-meter
pH NaF	N NaF Extract [18]	pH-meter
Exch. Al (ppm)	N KCl Extract [19]	HCl Titration
Organic C (%)	Walkley & Black 1934 [20]	Titration
Total N (%)	Kjeldahl 1883 [21]	Titration
Total P (mg 100 g ⁻¹)	HCl 25% Extract [22]	Spectrophotometer
Exch. Bases (K, Na, Ca, Mg) (cmol _c kg ⁻¹)	N NH ₄ OA _c pH 7.0 Extract [23]	Atomic Absorption Spectrophotometer
Cation Exchange Capacity (CEC) (cmol _c kg ⁻¹)	N NH ₄ OA _c pH 7.0 Extract [23]	Atomic Absorption Spectrophotometer
P Fractions (%)	Tiessen and Moir [11] modified by Sudadi et al. [24]	Spectrophotometer
Base saturation (%)	Ratio of sum of exch. bases to CEC	Calculation
Al Saturation (%)	Ratio of exch. Al to (CEC + exch. Al)	Calculation

Results and Discussion

Initial Soil Chemical Properties

Andisols are generally characterized by low bulk density. Andisol at the study site, however, had a clay textural class (clay content > 50%) in both topsoil and subsoil. This was related to the mechanical mixing process performed by the farmers during land preparation before planting potatoes in the preceding growing seasons. Table 2 shows that the soil pH NaF was > 11, indicating that the soil colloids were dominated by allophane, one of the specific characteristics of an Andisol [25]. The soil pH H₂O was categorized as slightly acidic in both soil layers with low Al saturation levels. The most common range of pH H₂O values for Andisols is 4.5 to 6.5 [26].

The organic C levels (< 1%) were very low in both soil layers even after ameliorated with 15 t ha⁻¹ chicken manure. This indicated that the soil organic matter content before the amelioration of chicken manure was already low due to leaching and erosion processes, as the soil slope in the study site was slightly steep and rainfall intensity was high [27]. Besides, the soil organic C level was decreasing due to decomposition or mineralization of the soil organic matter [28]. The soil total P was very high because it had been fertilized with 650 kg ha⁻¹ biophosphate, while soil CEC was very high with low to medium exchangeable bases, which resulted in a very low soil Base Saturation (BS).

Table 2. Average soil chemical properties of Andisol Pagar Alam before ameliorated with potassium humate*.

Soil Layer (cm)	pH NaF	pH H ₂ O	Al Saturation (%)	Organic C (%)	Total P (mg 100g ⁻¹)	Exchangeable (cmol _c kg ⁻¹)				CEC	BS (%)
						K	Na	Ca	Mg		
0 – 30	11.33	5.85 sa	0.2 vl	0.87 vl	202.22 vh	0.48 m	0.12 l	7.10 m	0.83 l	43.07 vh	19.8 vl
30 – 60	11.39	5.85 sa	0.3 vl	0.70 vl	162.89 vh	0.25 l	0.12 l	4.78 l	0.50 l	42.56 vh	13.3 vl

* Based on soil chemical properties assessment criteria [22]: sa = slightly acidic, vl = very low, l = low, m = medium, vh = very high.

Effects of the Treatment on Soil P Fractions Dynamics

The average percentages of soil P fractions to the total P concentration after potassium humate amelioration and fertilizer application are presented in Table 3. The average percentage levels of soil P_{H₂O}, P_{NaHCO₃-Po}, and P_{NaOH-Po} fractions were higher in the subsoil than in the topsoil, whereas P_{NaHCO₃-Pi}, P_{NaOH-Pi}, and P_{HCl} were the opposite. In the subsoil, the application of potassium humate was highly significant ($p < 0.01$) and negatively affected soil P_{H₂O}, P_{NaHCO₃-Po}, and P_{NaOH-Po} fractions, but positively affected soil P_{NaHCO₃-Pi}, P_{NaOH-Pi}, and P_{HCl} fractions. However, the total values of P_{H₂O} + P_{NaHCO₃-Po} + P_{NaOH-Po} fractions in the subsoil at the highest dose of potassium humate application (60 kg ha⁻¹) were still relatively high, at 52.4% of the total soil P.

Table 3. Average P fractions percentage in Andisol Pagar Alam after ameliorated with potassium humate and applied with basic fertilizers for 16 weeks and supplemental fertilizer for 12 weeks*.

Potassium humate dose (kg ha ⁻¹)	Soil layer (cm)	Soil P fractions (% to total P concentration)					Total P (ppm)	
		P _{H2O}	P _{NaHCO3}		P _{NaOH}			P _{HCl}
			P _o	P _i	P _o	P _i		
0	0 – 30	2.0	5.7	7.7	35.7	25.4	22.0	1,301.5
	30 – 60	3.6	12.5	3.7	54.3	18.5	16.6	921.4
20	0 – 30	2.5	4.9	6.0	31.5	30.0	23.0	1,124.8
	30 – 60	2.9	8.8	4.4	51.5	17.9	17.3	1,280.7
40	0 – 30	1.8	5.2	6.1	40.3	22.7	20.2	1,200.5
	30 – 60	2.2	6.7	4.3	50.0	19.1	17.4	1,157.1
60	0 – 30	2.1	5.0	7.9	39.8	24.5	22.1	1,295.7
	30 – 60	2.3	5.4	5.7	44.7	19.6	20.7	1,223.0
Average	0 – 30	2.1	5.2	6.9	36.8	25.7	21.8	1,230.6
	30 – 60	2.8	8.4	4.5	50.1	18.8	18.0	1,145.6

*Doses of the basic and supplemental fertilizers were 650 kg ha⁻¹ Biophosphate, 350 kg ha⁻¹ Vigo Amino and 350 kg ha⁻¹ NPK 16-16-16.

The soil organic P fraction (P_{Po}) is positively correlated with soil organic matter content [29]. In this study, the average percentage of P_{Po} fraction concentration was higher in the subsoil than in the topsoil, while the soil organic C content was the opposite. This was related more to the very high porosity of the soil; therefore, the soil P_{Po} fractions that have a low molecular weight were very easily leached from the topsoil and accumulated in the deeper soil layers (subsoil), except in the rainy season [30]. The field experiment in this study was conducted from May to August 2023 with an average monthly rainfall that ranged above normal, 158 to 161 mm [31-34], and was higher than that occurring in the same period during the last six years [35], so that the leaching process became very intensive. Because inorganic P (P_{Pi}) fractions are naturally non-mobile in the soil system, they do not easily leach [36] and remain relatively in the topsoil.

The average percentage of rapidly available P fractions (P_{NaHCO3-Po-Pi}), especially P_{NaHCO3-Po}, in the subsoil decreased with increasing doses of potassium humate (Figure 1). Ren et al. [37] reported the same pattern, in which the application of potassium humate can also reduce the soil available P levels by up to 80%; therefore, a site-specific and precise assessment is needed to determine the recommended dose of potassium humate application.

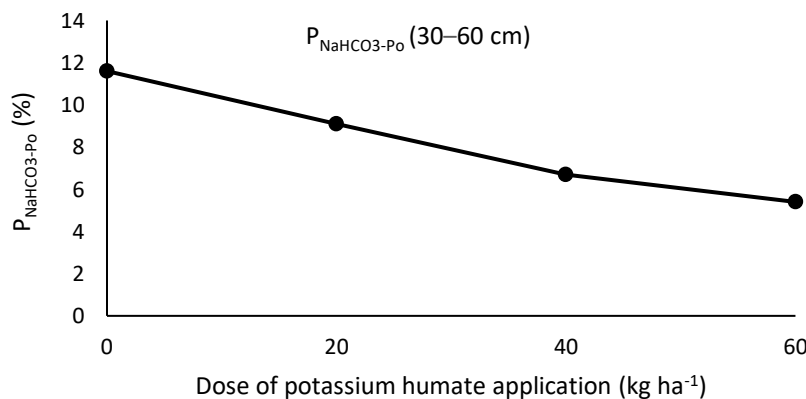


Figure 1. Effects of potassium humate amelioration on the rapidly available soil P fractions (P_{NaHCO3-Po}) in the subsoil of Andisol Pagar Alam, South Sumatera.

Figure 2 shows that the average percentage of the slightly available P fractions (P_{NaOH-Po-Pi}) in the subsoil decreased for the organic fractions (P_{NaOH-Po}) and increased for the inorganic fractions (P_{NaOH-Pi}) with increasing doses of potassium humate application. This indicated the occurrence of the mineralization process of P_{NaOH-Po} into P_{NaOH-Pi}, which was catalyzed by the soil phosphatase enzyme, resulting in a decrease in soil P_{NaOH-Po} and an increase in soil P_{NaOH-Pi} fractions [38].

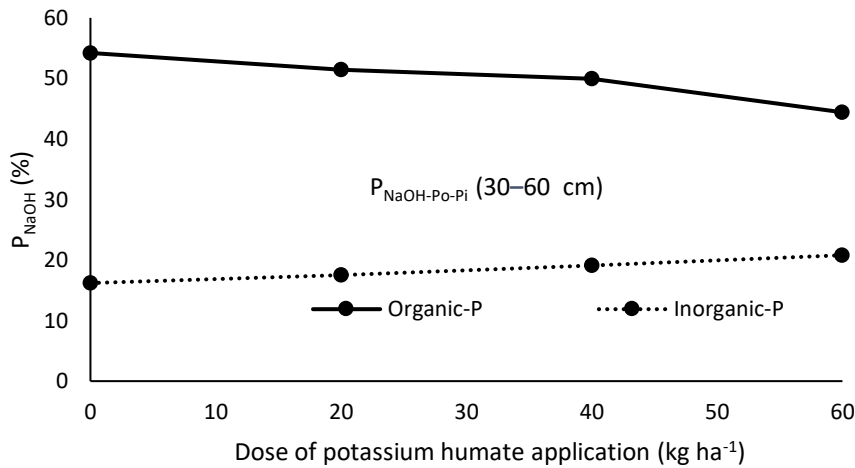


Figure 2. Effects of potassium humate amelioration on the slightly available soil P fraction ($P_{\text{NaOH-Po-Pi}}$) in the subsoil of Andisol Pagar Alam, South Sumatera.

The average percentage of slowly available P fractions (P_{HCl}) in the subsoil increased with increasing doses of potassium humate (Figure 3). This could be due to direct adsorption, precipitation, or accumulation processes originating from the mineralization of soil organic matter [39].

Slightly available P (P_{NaOH}) dominated the soil P fractions in the Andisol Pagar Alam. According to Takamoto et al. [40], the adsorbed soil P fractions at the allophane reactive sites of andisols were dominated by the NaOH-extracted fractions, which showed the considerable influence of Al and Fe oxides and aluminosilicate clays on the soil P adsorption process. The results of this study also showed that the soil P availability was mainly attributed to the resultant of the inorganic P (P_{Pi}) and the slowly available P fractions (P_{HCl}) in topsoil, as well as the quickly available P ($P_{\text{H}_2\text{O}}$) and the organic P fractions (P_{Po}) in the subsoil.

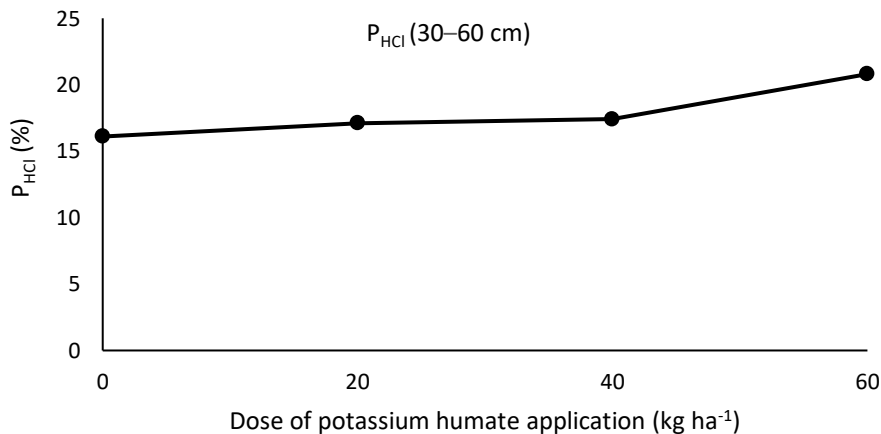


Figure 3. Effects of potassium humate amelioration on the slowly available soil P fraction (P_{HCl}) in the subsoil of Andisol Pagar Alam, South Sumatera.

Relationships between Soil P Fractions and Chemical Properties

The average values of soil chemical properties after potassium humate amelioration and fertilizers application are given in Table 4. Based on the results of multiple linear regression analysis, the soil chemical properties that performed significant effects on the soil P fractions dynamics were pH H_2O , exch. Al , total P, and BS. On average, soil chemical properties after the treatment decreased compared to those of the initial ones (Table 2), especially for the soil total P, indicating the occurrence of a leaching process on soil organic matter and, accordingly, to the soil organic P fractions.

Table 4. Average values of chemical properties of Andisol Pagar Alam after ameliorated with potassium humate and applied with basic fertilizers for 16 weeks and supplemental fertilizer for 12 weeks*.

Potassium humate Dose (kg ha ⁻¹)	Soil layer (cm)	pH H ₂ O	Exch. Al (cmol _c kg ⁻¹)	Total P (mg 100g ⁻¹)	Exch. K (cmol _c kg ⁻¹)	Exch. Na (cmol _c kg ⁻¹)	Exch. Ca (cmol _c kg ⁻¹)	Exch. Mg (cmol _c kg ⁻¹)	CEC	BS (%)
0	0 – 30	5.55	0.03	130.15	0.71	0.20	12.19	1.22	58.53	24.13
	30 – 60	5.29	0.09	92.14	0.36	0.20	3.19	0.51	52.88	8.11
20	0 – 30	5.31	0.10	112.48	0.40	0.23	6.54	0.70	50.86	16.37
	30 – 60	5.09	0.16	128.07	0.29	0.22	3.76	0.51	62.34	7.50
40	0 – 30	5.28	0.06	120.05	0.32	0.26	7.30	0.74	55.75	15.35
	30 – 60	5.09	0.05	115.71	0.23	0.18	3.76	0.51	55.92	8.43
60	0 – 30	5.54	0.05	129.57	0.46	0.18	10.74	1.09	58.40	21.63
	30 – 60	5.32	0.11	122.30	0.24	0.19	7.57	0.73	62.87	15.36
Average	0 – 30	5.42	0.06	123.06	0.47	0.22	9.19	0.94	55.89	19.37
	30 – 60	5.20	0.10	114.56	0.28	0.20	4.57	0.57	58.50	9.85

*See Table 3.

The soil chemical properties that performed significant effects on the P fraction dynamics in topsoil were pH H₂O, exch. Al, total P, and BS, with the lowest *p*-value (most significant) found in the relationships of soil BS and total P with the organic P fractions (Table 5, equation 2: $Y = 96.051 - 0.811 BS + 0.028 \text{ total P}$, $R^2 = 0.55$; $p = 0.027$). This equation shows that a 1% reduction in soil BS increases the P_{Po} fractions by 0.811%. The decrease in soil BS was related to the decrease in exchangeable base cations (mainly K, Ca, and Mg), whereas the soil CEC was relatively constant. In addition, an increase of 1 ppm in total soil P increases the P_{Po} fraction by 0.028%. According to Zarif et al. [41], total P had a significant effect on all soil P fractions, whereas soil BS affected more soil inorganic P fractions. Therefore, in this study, decreasing soil BS had a greater effect in reducing the inorganic P fractions, which in turn indirectly increased the proportion of soil organic P fractions.

Table 5. Multiple linear-regression equations between P fractions (Y) and soil chemical properties (X) with significant coefficient of determination in Andisol Pagar Alam after ameliorated with potassium humate and applied with basic fertilizers for 16 weeks and supplemental fertilizer for 12 weeks*.

Y	Equation*	R ²	<i>p</i>
Topsoil			
P _{H₂O+NaHCO₃-Pi+ NaOH-Pi+HCl}	$Y_{(1)} = -1.277 + 12.216 \text{ pH H}_2\text{O} + 0.933 \text{ BS} + 100.961 \text{ exch. Al} - 0.028 \text{ total P}$	0.74	0.032
P _{H₂O+NaHCO₃-Po+ NaOH-Po}	$Y_{(2)} = 96.051 - 0.811 \text{ BS} + 0.028 \text{ total P}$	0.55	0.027
P _{NaHCO₃-Pi+NaOH-Pi}	$Y_{(3)} = 0.838 + 7.156 \text{ pH H}_2\text{O} + 0.462 \text{ BS} - 72.824 \text{ exch. Al}$	0.59	0.057
P _{NaHCO₃-Po+NaOH-Po}	$Y_{(4)} = 101.277 - 12.216 \text{ pH H}_2\text{O} - 0.933 \text{ BS} - 100.961 \text{ exch. Al} + 0.028 \text{ total P}$	0.74	0.032
Subsoil			
P _{H₂O+NaHCO₃-Pi+ NaOH-Pi+HCl}	$Y_{(5)} = 79.309 + 0.831 \text{ BS}$	0.38	0.032
P _{H₂O+NaHCO₃-Po+ NaOH-Po}	$Y_{(6)} = 50.293 - 0.705 \text{ BS}$	0.41	0.025
P _{NaHCO₃-Po+NaOH-Po}	$Y_{(8)} = 20.691 - 0.831 \text{ BS}$	0.38	0.032

*See Table 3, n = 12.

The chemical properties of the subsoil with the most significant effects (with the lowest *p*-value) on the dynamics of soil P fractions were soil BS in its relationship with the organic P fractions (Table 5, equation 6: $Y = 50.293 - 0.705 BS$, $R^2 = 0.41$; $p = 0.025$). This indicates that a 1% reduction in soil BS increases the soil P_{Po} fraction by 0.705%. The decrease in soil BS could be associated with the decrease in exchangeable bases, especially K, which might be leached into the deeper soil layers owing to its interaction with the organic fraction from the potassium humate application, especially with abnormally high rainfall during the field experiment [42]. As a result, the subsoil pH H₂O decreased, the soil colloidal exchange sites were protonated, and their positive charge increased. Thus, the soil was more likely to retain anions, including the P fractions. In addition to causing alterations in the anion-cation equilibrium in the soil colloidal reactive sites, this result also revealed that BS was a soil factor that could directly influence the dynamics of soil P fractions and indicated that a decrease in BS increased the soil adsorption affinity for phosphate, particularly the P_{Pi}.

Conclusions

The P_{H_2O} and organic P (P_{Po}) fraction levels in Andisol Pagar Alam were higher in the subsoil, whereas the inorganic P fractions (P_{Pi}) were the opposite. At a dose of 60 kg ha^{-1} , potassium humate application significantly increased P_{Pi} fractions and decreased P_{Po} fractions in the subsoil. In general, using potassium humate as a ligand exchanger effectively increased soil P availability in the studied Andisol, in the form of P_{Pi} in the topsoil and P_{Po} fractions in the subsoil. The soil P_{Po} fractions increased with increasing total P in the topsoil and decreasing BS in both the soil layers. The results also indicate an alteration in the anion-cation equilibrium at the soil colloidal reactive sites. As an implication, soil P availability was increasing. A similar study should be conducted at the same experimental site by cultivating food or horticultural crops with additional doses of potassium humate, higher than 60 kg ha^{-1} , to determine the recommended dose more precisely.

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