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The Influence of Organic and Inorganic Amendments on Phosphorus Chemistry in Two Acidic Soils of Southwestern Ghana

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ABSTRACT

A study in southwestern Ghana compared the effects of organic and inorganic additives on P availability and related factors in two acidic soils, Ankasa and Abenia. Different amounts of P as KH_2PO_4 were applied: 0.067 g kg^{-1} for Abenia and 0.041 g kg^{-1} for Ankasa. Soil samples were treated with cow dung, *Chromolaena odorata*, and poultry droppings for six weeks to increase standard P requirement and neutralize exchangeable Aluminum. Data analysis was performed using GenStat (version 14). An analysis of variance (ANOVA) was conducted for the soil amendments, followed by Tukey's comparison test at a 5% significance level to identify significant differences among the soil amendments. The result showed that higher rates of organic amendments significantly increased pH, available P (Bray 1 and $NaHCO_3$-P), NaOH-P, and reduced exchangeable Al concentration. Poultry droppings and cow dung impact notably improved soil quality. At the same time, $CaCO_3$ had similar effects on soil pH. However, it did not significantly affect P availability or NaOH-extractable P. $CaSO_4$ and $CaCO_3$ had minimal impact on phosphorus distribution, suggesting that altering pH or exchangeable Al does not necessarily change P fractions. Poultry droppings, rich in P, could be a potential alternative to lime in enhancing P availability and reducing soil acidity.

Keywords: Acidic soil, exchangeable Aluminum, organic and inorganic amendments, phosphorus fractions

INTRODUCTION

The soil in southwestern Ghana, accounting for 10-15% of the country's land, is predominantly acidic despite favorable topography and hydrology, leading to low crop production (Ofori-Sarpong & Amankwah, 2019; Agegnehu *et al.*, 2021). Numerous investigations conducted over the years have consistently shown that adding phosphate fertilizer to tropical soils results in a substantial portion of the fertilizer being adsorbed onto colloidal surfaces in configurations that are not easily accessible to crops. This phenomenon leads to only a modest proportion, approximately 10-20%, of the applied fertilizer being effectively utilized by crops (Mabagala, 2022; Hanyabui, 2020).

The occurrence of sorbed phosphorus is common in weathered soils like Ultisols and Oxisols and volcanic soils with high amorphous compounds, primarily due to Al and Fe oxides and hydroxides (Reed *et al.,* 2011; Amadou *et al.*, 2022). Contemporary approaches to soil management for mitigating P sorption include applying liming agents (such as $CaCO_3$), integrating P, or introducing organic amendments into soils with high P sorption capacity (Fan *et al.*, 2022). The latter approach is notably appealing in developing and developed nations, serving as a cost-efficient and environmentally friendly alternative to traditional inorganic P fertilizers and liming amendment (Huck *et al.,* 2014). Studies show conflicting results on the impact of organic amendments on P sorption and desorption in high P sorbing soils (Huck *et al.*, 2014; Servesh *et al.,* 2015; Nobile *et al.,* 2020).

The results are due to the competition of organic acids, like citrate or malate, for sorption sites on A1 and Fe, leading to the production of organic acids. Conversely, Yan *et al.* (2013) documented increased P sorption when incorporating organic amendments with low P content. Yusran (2018) also documented a positive relationship between soil organic matter content and P adsorption. The phenomenon is due to organic matter decomposition, where microorganisms absorb P as lipids and nucleoproteins, making it accessible upon their death and decay. Research on phosphorus sorption in organic amendment-added soils is limited, lacking comparisons with inorganic amendments like $CaCO_3$ and $CaSO_4$, which increase pH and enhance P availability (Servesh et al., 2015; Melese & Yli-Halla, 2016).

However, the presence of $CaSO_4$ enhances the accessibility of P by displacing exchangeable Al and Fe while causing minimal alteration to the pH levels (Lizarralde *et al*., 2021). This research aimed to compare the effects of organic and inorganic amendments on P desorption, pH, and exchangeable Al in two acidic soils of southwestern Ghana.

MATERIAL AND METHODS

Soil samples and amendment materials

Two acid soils of agricultural importance, such as the Abenia and Ankasa of Southwestern Ghana, were chosen for the study. The soils are designated as Typic Hapludox by soil taxonomy (Soil Survey Staff, 1994), originate from biotite granite schist, and are found on the upper slope of the landscape. Surface soil (0-15 cm) was collected under a virgin tropical evergreen rainforest with an average rainfall of 1800 and 2000 mm per annum. The sampled soils were air-dried and sieved using a 2 mm sieve before analysis. Three organic amendments were used: cow dung, *Chromolaena odorata*, and poultry droppings. After air-drying, the materials underwent oven-drying at 60 °C for 24 hours before being ground and sieved through a 0.5 mm mesh. The sieved materials were then stored in white polyethylene bags before chemical analysis.

Laboratory analysis

Soil pH was assessed in distilled water at a soil-to-solution ratio of 1:2.5 using a Suntex pH meter (Table 1). The total C content was quantified through the wet oxidation technique developed by Walkley and Black (1934). The total N content in both soil and organic amendments was determined utilizing the Kjeldah1 method. Additionally, extractable P levels were determined through the Bray 1 method (0.03M NH_3F and 0.25 M HCl solution), $NaHCO_3$-P (Olsen *et al*., 1954), and NaOH-P using a 0.1M NaOH solution. Total P was quantified by digesting the soil and organic samples with concentrated HNO_3-$HC1O_4$ until the solution became colorless. Subsequently, the ascorbic acid molybdate method developed by Watanabe and Olsen (1965) was employed following cooling and filtration. The color intensity was then assessed using a spectrophotometer set at a wavelength of 712 nm.

Exchangeable A1 and acidity were extracted with 1M KCl solution (Barnhise1 & Bertsch, 1982). Exchangeable bases were identified using 1 M NH_4OAc solution at a pH 7. The particle size analysis involved the complete breakdown of organic matter with a 1:1 mixture of soil and H_2O_2. Subsequently, the soil particles were dispersed using a 0.01 M calgon $(NaPO_3)_6$) solution, followed by a five-minute mixing period with a motor mixer. Silt content was determined after five minutes using a hydrometer, while the clay fraction was assessed over 5 hours.

Incubation studies

Based on the standard P requirement of these soils, P as KH_2PO_4 was initially incubated at rates of 0.067 g kg^{-1} and 0.041 g kg^{-1} in Abenia and Ankasa, respectively. The fertilizer was mixed thoroughly and then incubated for six weeks at room temperature (26 °C). Throughout the incubation period, samples were subjected to drying and wetting cycles after seven days, maintaining moisture content gravimetrically at 60% water holding capacity. Stirring was done every other day. Following the completion of the incubation period, the soil samples were air-dried and grounded for further laboratory testing.

Table 1. Chemical analysis of organic amendments.

Organic Materials	Chemical analysis						
	pH soil: H_2O 1:2.5	cmol kg^{-1}			N %	Bray 1 (ppm) P	Organic C (%)
		Ca	K	Mg			
Cowdung	7.2	13.5	0.8	2.6	0.73	78	18.6
Chromolaena Odorata	7.5	28.4	1.82	5.86	2.23	80	20.23
Poultry droppings	8.2	30.36	1.65	5.43	2.35	264.8	23.73

Organic amendments (Cowdung, *Chromolaena odorata*, and Layer poultry droppings) were each added to the treated soil samples at an increasing rate of 0 (Control), 1% (Low), 2.5% (Medium), and 5% (High) (wt/wt). Another group of samples was treated with inorganic amendments ($CaCO_3$ and $CaSO_4$) at levels of 1.0 x (low), 1.5 x (medium), and 3.0 x (high) the quantity of $CaCO_3$ and $CaSO_4$ required to offset the exchangeable Al present in the soils. The amended soil samples were mixed thoroughly and made up to a moisture level of 60% water retention capacity using deionized water. All the samples were further incubated in triplicate at room temperature (26 °C) for six weeks.

The specimens were aerated on alternate days, and the water content was consistently monitored gravimetrically. After six weeks, the incubated samples underwent a process of air drying and grinding and were subsequently stored in zipped polyethylene bags for the determination of pH, exchangeable A1, available P (Bray 1, $NaHCO_3$-P), and NaOH-P. All analyses were carried out in triplicates.

Statistical analysis

Data were analyzed using analysis of variance (ANOVA) using Genstat (version 14). Post-hoc tests were employed to separate the means at a 5% probability level, while Microsoft Excel was used for the graphical representation of the data.

RESULTS

Impact of organic and inorganic amendments on soil acidity levels

The application of various organic amendments resulted in significant ($p<0.05$) increases in soil pH compared to the control group. Cow dung exhibited the least impact on soil pH among the amendments in both types. The highest increase in pH was caused by *Chromolaena odorata* and poultry droppings. It was observed that increasing amounts of organic amendments caused a corresponding increase in pH in both soils. Interestingly, $CaCO_3$ and poultry droppings affected a similar magnitude of decreasing acidity in the two soils. In addition, increasing rates of $CaSO_4$ led to a proportional drop in pH. However, there was no statistically significant difference in the alteration of both soils. The order of effectiveness in decreasing soil acidity for organic and inorganic amendments was poultry droppings > $CaCO_3$ > *Chromolaena odorata* > cow dung > control > $CaSO_4$ (Figure 1).

Variation in exchangeable $A1^{3+}$ concentration due to amendments

The impact of organic and inorganic amendments on exchangeable Al (Al^{3+}) in the two soils is shown in Table 2. The findings indicated that $CaSO_4$ had a minimal impact on decreasing the

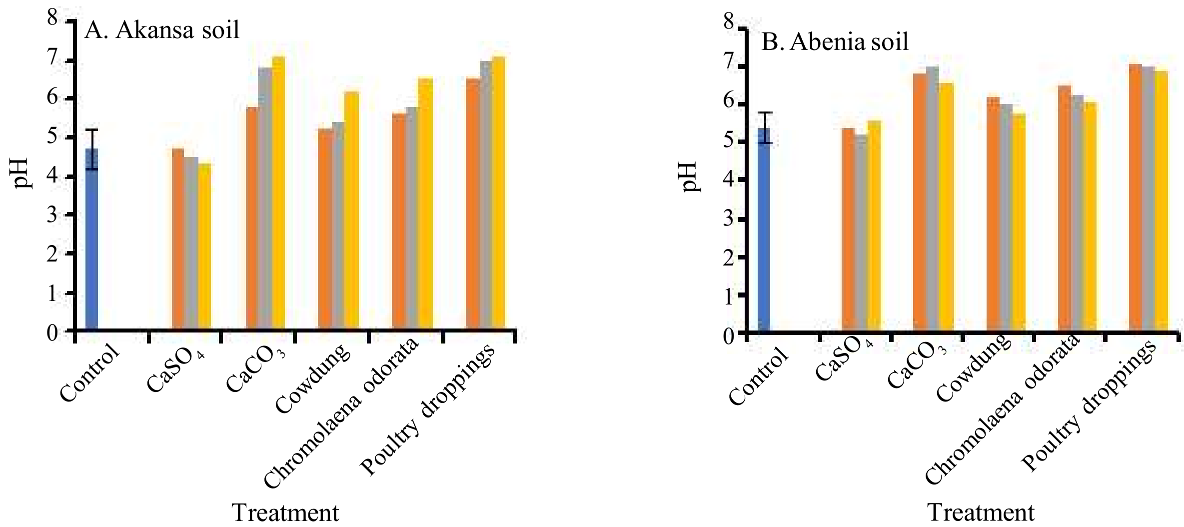

Figure 1. Impact of organic and inorganic amendments on soil pH of two acidic soils of southwestern Ghana. ■ : 0%, ■ : 1%, ■ : 2.50%, ■ : 5%.

Table 2. Impact of organic and inorganic amendments on exchangeable Aluminum ($A1^{3+}$) in two acidic soils of Southwestern Ghana.

Treatments / Levels																
Soils	Control (cmol+kg^{-1})	CaSO$_4$ (cmol + kg^{-1})			CaCO$_3$ (cmol + kg^{-1})			Cow dung (cmol + kg^{-1})			Chromolaena odorota (cmol + kg^{-1})			Poultry droppings (cmol + kg^{-1})		
	0%	1x	1.5x	3x	1x	1.5	3x	1%	2.5%	5%	1%	2.5%	5%	1%	2.5%	5%
Ankasa	2.00^a	2.00^a	2.20^a	2.50^b	nd	nd	nd	1.20^c	0.68^c	0.30^e	0.70^c	0.50^d	nd	nd	nd	nd
Abenia	0.81^a	0.87^a	0.88^a	1.20^b	nd	nd	nd	0.33^c	0.25^c	nd	nd	nd	nd	nd	nd	nd

LSD (P=0.05): P=0.093 in Abenia soil, P=0.16 in Ankasa soil, and = no exchangeable A1 detected after six weeks of incubation. It means that letters bearing the same letters are not significantly different. X = time the quantity of $CaCO_3$ or $CaSO_4$ required to neutralize exchangeable Aluminum.

concentration of Al^{3+} in both soils, whereas $CaCO_3$ had the most significant effect, reducing Al^{3+} levels by up to 100%. The lowest level of $CaCO_3$ was optimal for ultimately reducing $A1^{3+}$ in both soils. Generally, the addition of $CaSO_4$ did not result in a statistically significant ($p>0.05$) decrease in the concentration of Al^{3+} in the control group.

However, at the highest level (3x), $CaSO_4$ in both soils was found to increase the exchangeable A1 significantly ($P<0.05$). The organic amendments significantly ($P<0.05$) reduce $A1^{3+}$ compared to the control. Poultry droppings affected a 100% reduction in the concentration of $A1^{3+}$, followed by *Chromolaena odorata* (80-100%) and cow dung (70-100%). Increasing rates for all the organic amendments reduced the concentration of exchangeable A1 (Table 2). The order of effectiveness in reducing the exchangeable A1 followed the trend of poultry droppings > *Chromolaena odorata* > cow dung and control.

Impact of organic and inorganic amendments on P availability

In this study, Bray 1 and $NaHCO_3$-P were used as indices of P availability. The impact of $CaCO_3$ and $CaSO_4$ on availability P did not show a significant difference ($P>0.05$) from the control at lower application rates. However, at the highest level of $CaSO_4$ in both soils, there was a decrease in $NaHCO_3$. Whereas the observed decrease was significant ($P<0.05$) in Ankasa, it was insignificant in the Abenia soil. Abenia soil $CaCO_3$, at the highest level, caused a decrease in available P. However, there was not a statistically significant ($P>0.05$) difference in the effect.

On the other hand, the medium (1.5x) and highest (3x) levels of $CaCO_3$ in Ankasa soil exhibited a significant ($P<0.05$) increase from the control. Incorporating various organic amendments leads to a notable increase in the P availability in both soil

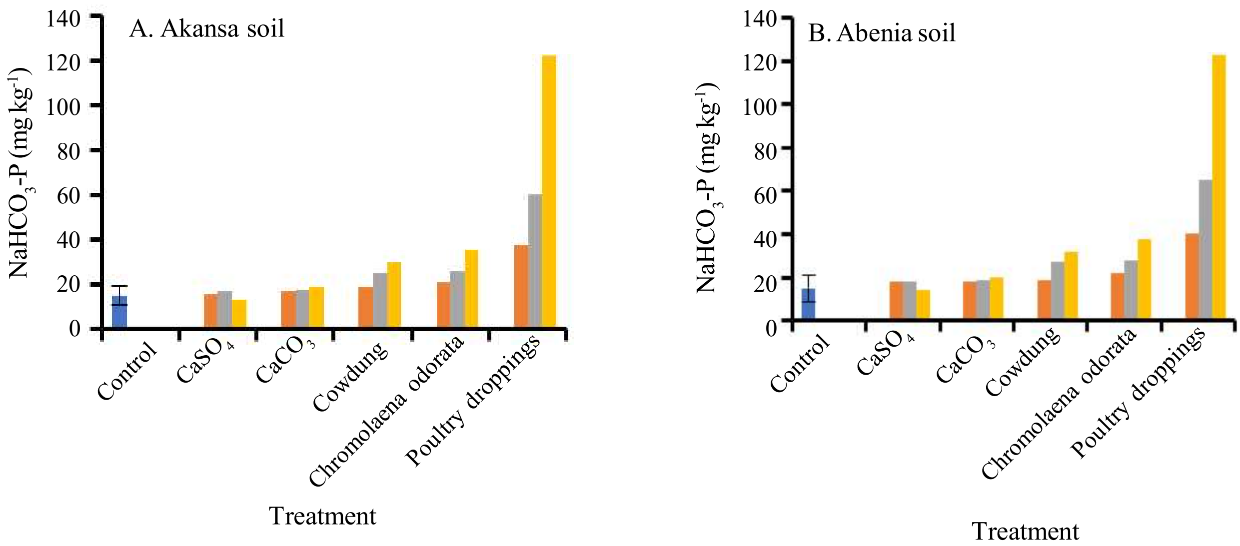

Figure 2. Impact of organic and inorganic amendments on P availability on two acidic soils of southwestern Ghana. ■ : 0%, ■ : 1%, ■ : 2.50%, ■: 5%.

types. Unlike poultry droppings, the cow dung and *Chromolaena odorata* were ineffective in Abenia soil at the lower level of incorporation; however, in Ankasa soil, *Chromolaena odorata* at 1% was effective in increasing available P. Increasing rates of organic amendments increased available P. The order of effectiveness in increasing available P among the organic amendments followed the trend of poultry droppings > *Chromolaena odorata* > cow dung and control (Figure 2).

Impact of organic and inorganic amendments on NaOH extractable P

Soils amended with poultry droppings gave the highest increase in NaHO-P fraction, followed by *Chromolaena odorata* and cow dung. Increasing rates of the organic amendments led to a corresponding significant ($P<0.05$) increase in NaOH-P fraction. In Ankasa soil, the lowest levels of *Chromolaena odorata* and cow dung resulted in a statistically significant ($P<0.05$) elevation in NaOH-P levels. Applying inorganic amendments to the soils showed minimal impact on NaOH-P levels. Both $CaSO_4$ and $CaCO_3$ at low and medium levels did not significantly ($P>0.05$) affect NAOH-P. However, it was observed that whereas $CaCO_3$ increased NaOH-P at the same level, $CaSO_4$ decreased NaOH-P. At the highest level, $CaSO_4$ significantly decreased NaOH-P in the Abenia soil but not in Ankasa (Figure 3). On the other hand, $CaCO_3$ significantly decreased and increased NaOH-P in Abenia and Ankasa, respectively.

DISCUSSION

The substantial increase in soil pH due to organic amendments in both soil types is significant for the reaction of P in acidic soils, as shown by the statistical significance level of $P<0.05$. The elevation of pH levels leads to the precipitation of exchangeable Al and Fe, consequently diminishing the capacity for sorption of HPO_4^{2-}.

The rise in levels resulting from the use of organic additives can be credited to self-neutralization caused by the breakdown of C, the liberation of essential positively charged ions, or the release of hydroxide ions because of the decrease in Mn, Fe, and Al at oxygen-deprived microenvironments (Fageria & Nascente, 2014). High pH values of organic materials and high basic cations contribute to the rise in soil pH. The results are therefore consistent with the observation made by Huck *et al*. (2014). Alternatively, the rise in soil pH may be linked to generating OH^- ions through the ligand exchange process involving organic acids and hydroxyl ions of Al and Fe in the soil (Sokolova,

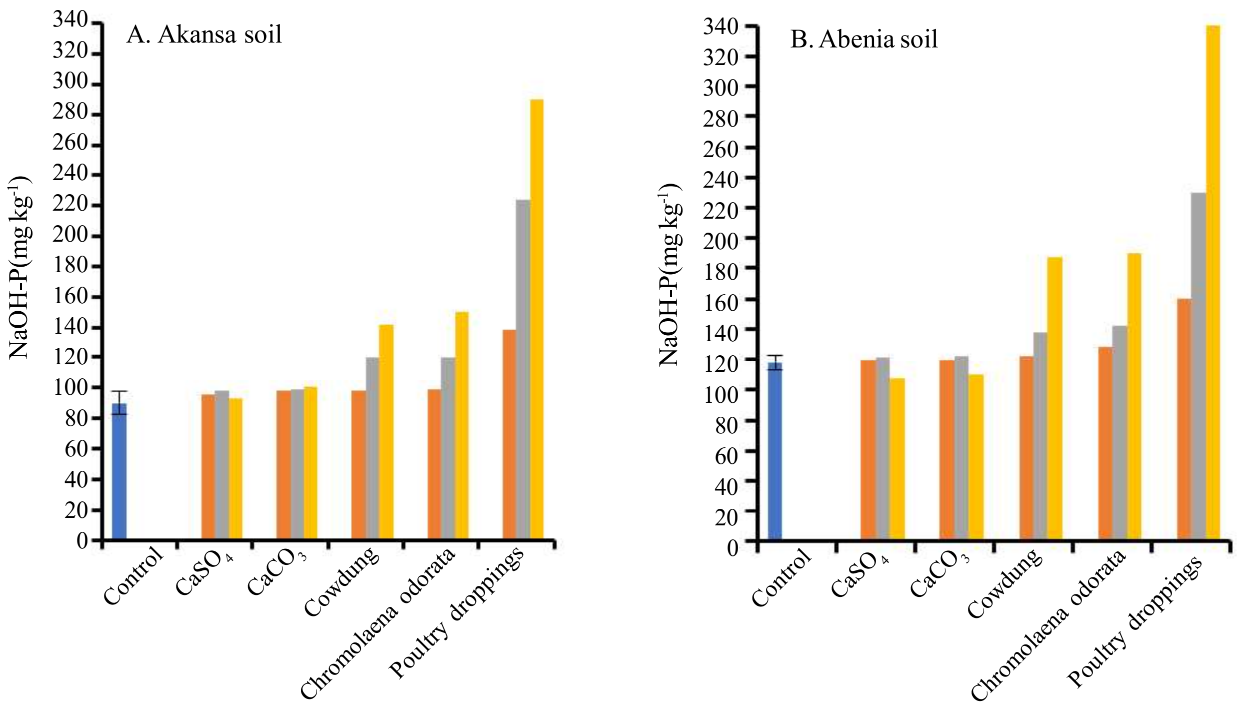

Figure 3. Impact of organic and inorganic amendments on NaOH extractable P on two acidic soils of southwestern Ghana. ■ : 0%, ■ : 1%, ■ : 2.50%, ■ : 5%.

2020). Nonetheless, a rise in soil pH by $CaCO_3$ could be due to the production of OH when it interacts with water in the soil. The resulting OH causes an increase in the pH by neutralizing the effect of the potential acidity in the soil (Mabagala, 2022). The decline in pH with increasing $CaSO_4$ may also be attributed to the formation of H_2SO_4 as CaSO4 interacts with H_2O.

Under normal circumstances, the Ca ion is expected to produce more OH- ions to neutralize the effect of H_2SO_4, but the reverse is the case, indicating that more H_2SO_4 was produced such that the OH^- produced by $CaSO_4$, even at the highest level of application was insufficient to neutralize it. The reduction of exchangeable A1 because of organic amendments and $CaCO_3$ in the two soils may be partly a result of an increase in soil pH (Figures 1a and 1b). Huck *et al*. (2014) and Nobile *et al*. (2020) have also documented comparable findings. pH determines the activity of A1 in each soil; at low pH, more $A1^{3+}$ comes into the soil solution, while at high pH, little or no $A1^{3+}$ comes into the solution (Mabagala, 2022). Alternatively, the decrease could also be ascribed to the formation of A1 ions due to the OH^- ions being discharged from the substitution of ligands among organic anions and terminal hydroxyl of Fe and A1 oxides or the binding of A1 by organic compounds (Servesh *et al*., 2015; Melese & Yli-Halla, 2016). Concerning $CaSO_4$ the increase in $A1^{3+}$ at the highest level may be attributed to the lowering of the pH in both soils (Figures 1 and 2). As pH decreases, more $A1^{3+}$ comes into the soil solution, resulting in a higher $A1^{3+}$ concentration. The impact of $CaSO_4$ on soil pH is consistent with findings reported by Zhao *et al*. (2022).

The available P indices (Bray 1 and $NaHCO_3$-P) in both soil samples showed a notable rise in P levels at a significant level ($p<0.05$) when the concentration reached 2.5% of organic amendments incorporation. The increase in available P by organic amendments may be credited to creating enduring complexes between A1 and anions generated from the breakdown of organic substances. During the mineralization of organic amendments, organic acids like citrate, malate, or tartaric acid are liberated into soil solution and their anions complex A1, resulting in more P in solution (Philips, 2002; Sindhu *et al*., 2022). The increase may also be a result of $H_2PO_4^-$ anion by humate ions and the formation of a protective cover by humus around particles, leading to a decrease in the soil's phosphate sorption capacity (Huck *et al*., 2014; Nobile *et al.,* 2020). Moreover, the increased level of accessible P due to organic amendments implies a more significant mineralization of P and the subsequent release of P to interact with P on the adsorption sites of A1, ultimately resulting in an augmentation in P in the soil solution (Sarvest *et al*., 2015; Sokolova, 2020). The increase may also be a result of the change in soil chemistry. These factors are recognized to significantly influence the availability of P and their absence or reduction in the soil system, especially $A1^{3+}$, and an increase in pH will increase available P. The high increase in P by poultry droppings in Abenia is at a 5% level, despite the pH values rising to about 7.51, possibly because poultry droppings are known to produce many citrates that can chelate exchangeable Al (Bauer, 2019).

Generally, the phosphorus-rich remains of poultry waste led to a notable rise in biologically accessible P1 (Bray 1 and $NaHCO_3$-P). The findings are consistent with the results of Huck *et al.* (2014) and Nobile *et al.* (2020). $CaSO_4$ and $CaCO_3$ did not significantly impact the availability of phosphorus, despite $CaCO_3$ causing an increase at all levels except the highest in Albania. There was a slight decrease in this location, but it was not significant ($P>0.05$). Conversely, there has been a notable reduction in the amount of P by $CaSO_4$ at the highest level in Ankasa soil. It may be attributed to the lowering of soil pH (Figures 1), thereby increasing $A1^{3+}$ activity, as shown in Table 3.

Aluminum can sorb P, rendering P unavailable (Ofori-Sarpong & Amankwah, 2019; Agegnehu *et al*., 2021). The decrease in available P in Abenia soil at the highest level of $CaCO_3$ may be due to precipitation of P by excess Ca in the soil solution enhanced by a rise in soil pH to 7.51, thereby reducing P availability. The NaOH extractant eliminates phosphorus and is not as strongly associated with P uptake by plants as $NaHCO_3$-P (Obikoya, 2016). The fraction under consideration is linked to amorphous and crystalline A1 and Fe-P through chemisorption (Linquist & Ruark, 2011). The rise in chemisorbed P fractions detected in both soil types, as indicated by NaOH-P, is probably due to the introduction of soluble inorganic P into the organic residue and the mineralization of P from the organic P that was added (Verma *et al*. 2005 & Sarvest, 2015).

CONCLUSIONS

Poultry manure affects a particular P fraction that holds significance in P sorption reactions. Incorporating organic residues with high total P content (like poultry droppings) modifies the distribution of P fractions ($NaHCO_3$-p, Bray 1, and NaOH-P). Conversely, $CaCO_3$ and $CaSO_4$ showed limited to no influence on P fractions. Furthermore, the rise in organic amendments applied to high P-fixing soil led to an increase in pH levels and a reduction in exchangeable A1 content. This finding holds significant implications for the behavior of P in soil systems. The optimal level of organic amendments was 2.5%, suggesting that organic additives can be an alternative to traditional inorganic additives such as $CaCO_3$ to improve P availability in acidic soils.

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