

Phosphorus Adsorption Isotherm: A Key Aspect for Soil Phosphorus Fertility Management

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Authors' contributions

This work was carried out in collaboration between all authors. Author LW designed the study, wrote the protocol, wrote the first draft of the manuscript and managed the literature searches and all laboratory analyses. Author KK edited the data, reviewed and edited the manuscript. Authors JJM and FBRR reviewed and edited the protocol and the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Characterization of soils in terms of phosphorus adsorption capacity is fundamental for effective soil phosphorus fertility management and for efficient utilization of phosphorus fertilizers. Thus, this study was conducted to investigate the phosphorus adsorption characteristics of soils of two farms and to elucidate the implication of soil phosphorus adsorption isotherm studies for soil phosphorus fertility management. The two farms, representing the major farming systems of the respective districts, were selected from Adele village in Haramaya district and Bala Langey village in Kersa district in eastern Ethiopia. Soil samples were collected from the crop fields at Adele and Bala Langey farms. Two different P-bearing sources, potassium dihydrogen phosphate (KH_2PO_4) and diammonium phosphate ($\text{DAP}-(\text{NH}_4)_2\text{HPO}_4$), were used for the adsorption isotherm studies. The adsorption data were fitted to the linear and Freundlich adsorption isotherm models. Both models revealed that soils of both farms had different P adsorption capacity from the two P sources. Amount of P adsorbed from DAP solution was higher than the amount of P adsorbed

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from KH_2PO_4 solution in soils of both farms. Phosphorus adsorption capacity of Adele farm soils was higher than that of Bala Langey farm soils. Therefore, soils of the two farms should be managed differently for P fertility. Percentages of P adsorbed (% Pa) and P remained in the equilibrium solution (% EC) were also calculated. By plotting the two percentages i.e. % Pa and % EC against the initial concentration of P (IC), two regions were observed. The two regions were described as P intensity and quantity factor windows. Based on the intensity and quantity factor windows, at currently existing soil condition, between 200 and 500 kg ha^{-1} P should be applied as fertilizer to soils of Adele at 0-30 cm depth for immediate benefits and soil P fertility maintenance.

Keywords: *Phosphorus sources; P-fertility; P- intensity-quantity factor window.*

1. INTRODUCTION

Phosphorus is one of the 17 essential elements for plant growth and reproduction. Plants obtain phosphorus from the soil solution which is either from the weathering of the parent materials or from the applied fertilizers. However, accessibility of phosphorus applied with fertilizers to plant is governed by different factors such as phosphorus adsorption-desorption characteristics of soil, soil texture, soil organic matter content and management practices [1,2]. Therefore, understanding interaction of phosphorus with those factors in soil is crucial for soil phosphorus fertility management and for sustaining phosphorus in pedobiochemical cycle.

In the soil system, phosphorus exists in two forms; the labile form which is weakly adsorbed on the surface of soil particles which is considered as not readily accessible to the plant. The other form is a portion of phosphorus in soil solution which is readily accessible to the plant [3]. The labile phosphorus is in equilibrium with phosphorus in soil solution and may be available to plant. But the rate of release is very slow and may not be available to the plant within the short period of crop reproductive cycle. The equilibrium between labile P and solution P will be disturbed when a phosphate fertilizer is applied to soil. This leads to rapid adsorption of P on the surface of soil particles and makes phosphorus to be more firmly held [4]. As a result, the amount of phosphorus adsorbed on the surface of soil particles increases while the quantity of phosphate ions in soil solution decreases.

The amount of phosphorus adsorbed on the surface of soil particles is termed as the quantity factor and the phosphate ions remaining in soil solution is the intensity factor [5]. These factors are very important for soil phosphorus fertility management. Phosphorus adsorption isotherm describes the interdependence of these two factors i.e. the intensity and the quantity factors. In a simple term, phosphorus adsorption

isotherm is a plot of quantity factor against intensity factor [6]. The ratio of the quantity factor (Q) to intensity factor (I) is the buffering capacity of the soil [5,7]. This governs soil phosphorus supply to plants.

Phosphorus adsorption isotherm is the most useful experimental procedure for studying interaction of phosphate ions with soil constituents [8,4]. It is also a useful parameter to monitor availability of phosphorus to plants. Furthermore, phosphorus adsorption isotherm study can help to describe phosphorus dynamic in the soil system. Characterization of soils in terms of phosphorus adsorption capacity is crucial for effective and efficient utilization of phosphorus fertilizers with respect to quantity, type and placement [9]. Thus, phosphorus adsorption isotherm is a key aspect for soil phosphorus fertility management.

Many workers have investigated phosphorus adsorption characteristic of soils from the environmental sustainability point of views [10,11,12]. Others reported that phosphorus adsorption characteristic of soil is affected by soil clay and organic matter contents [13]. In fact this is directly related to soil fertility. In almost all the studies cited above, KH_2PO_4 was used as phosphorus source for the laboratory studies of soil P adsorption isotherm, which is rarely applied to soil as fertilizer. DAP is commonly being applied as phosphorus fertilizer for soil fertility management in Ethiopia. However, phosphorus adsorption characteristics of soils and impacts of DAP on soil properties when applied as fertilizer have not been studied for soils of eastern Ethiopia.

In general, phosphorus adsorption characteristic of soils of the eastern part of Ethiopia is not well investigated either from the environmental or soil fertility management perspectives. Therefore, the objectives of this study were to investigate the P-adsorption characteristics of soils of the study areas using two different P-bearing sources;

potassium dihydrogen phosphate (KH_2PO_4) and DAP, and to elucidate the implication of soil phosphorus adsorption isotherm for soil phosphorus fertility management.

2. MATERIALS AND METHODS

Soil samples for the study were collected from two farms at Adele in Haramaya district and Bala Langey in Kersa district, Oromia Region, Eastern Ethiopia. Both farms were selected as representatives of the respective farming systems of the districts. From each crop field of the farms 16 sampling sites were selected and soil samples collected from 0-30 cm depth. One composite sample was made from soils collected from the 16 representative sampling sites of the crop fields of each farm. Some properties of the soils are presented in Table 1.

Twenty four, 100 ml capacity plastic bottles were prepared and arranged in two rows, each row containing 12 bottles. One gram air dried soil (<2 mm) from Adele farm was placed in every bottle in each row. The rows were labeled as 1st and 2nd. Every bottle within the row was labeled with the P sources, KH_2PO_4 used for P adsorption study in the laboratory and DAP commonly applied as P fertilizer for crop production in the region.

Twenty five ml of 1.0, 5.0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mgL^{-1} P solution made from KH_2PO_4 and DAP were added to the respective labeled bottles containing the soil. A supporting electrolyte of 10 mM CaCl_2 solution was added to all bottles and the contents in the bottles were shaken for 24 hours at $22 \pm 2^\circ\text{C}$ on an orbital shaker at 300 rpm [14]. After equilibrating time, the contents of each bottle were filtered through Whatman No. 42 filter paper. Three ml of the filtrates were taken for the color development with ammonium molybdate solution containing potassium antimony tartrate and ascorbic acid [15]. The P contents of the filtrates were read on a spectrophotometer (model T80+) at 880nm after the development of the blue color. Same experiment was repeated for the soil from Bala Langey farm.

Adsorbed P was calculated as the difference between initial and final concentration of P in the equilibrium solution. The adsorption data were fitted to the linear model and Freundlich adsorption isotherm model as described below:

$$\text{Linear Model: } x/m = a + bc$$

$$\text{Freundlich Model: } x/m = kfc^{1/n}$$

$$\text{Linear form of Freundlich model: } \log x/m = \log kf + 1/n \log c$$

Where:

c = Concentration of P in equilibrium solution (EPC) (mgL^{-1})

x/m = Amount of P adsorbed (mg kg^{-1})

kf = Proportionality constant for the Freundlich model (mgkg^{-1})

$1/n$ = Slope of the curve, when $\log x/m$ vs $\log c$ was plotted

a = Y-intercept, when x/m vs c was plotted (mgkg^{-1})

b = Slope of line, when x/m vs c was plotted. Slope is the buffering capacity of soils with respect to P and clay contents [16].

Percentages of P adsorbed (Pa) and P in the equilibrium solution (EC) were calculated for the adsorption data of DAP solution as:

$$\%Pa = [(IC - EC) \times 100]/IC$$

$$\%EC = (EC/IC) \times 100$$

Where:

Pa = Phosphorus adsorbed from initial solution (mgL^{-1}) = Quantity factor

IC = Initial phosphorus concentration (mgL^{-1})

EC = Equilibrium phosphorus concentration (mgL^{-1}) = Intensity factor

$\%Pa$ = Percentage of adsorbed phosphorus from initial solution

$\%EC$ = Percentage of phosphorus in equilibrium solution.

Table 1. Some physical and chemical properties of soils from the crop fields of Adele and Bala Langey farms

Sampling sites/crop fields	(%) Sand	(%) Silt	(%) Clay	Textural class	pH	(%) OC	(%) CaCO_3	Olsen P(mg/kg)	Total P (g/kg)
Adele farm	58	17	25	SCL	7.24	1.21	0.45	1.56	28.97
Bala Langey farm	58	13	29	SCL	6.53	1.45	0.15	8.74	17.13

*SCL = Sandy clay loam

Values for the two percentages (%Pa and %EC) were plotted against initial concentration (IC) of P to determine the intensity and quantity factors region or windows for soils of the two farms from DAP adsorption data.

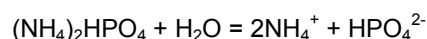
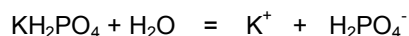
After equilibrating time, pH of the soil suspension to which DAP was added for the adsorption isotherm study was also measured with pH glass electrode. Similarly, pH of soil samples collected from experimental sites established within the crop fields at both farms, where DAP was applied at the rate of 100 kg ha^{-1} for two consecutive cropping seasons, was measured. The soil sampling was done before planting in 2012 and 2013, and after harvesting in 2014. The pH was measured for 1:2.5 soil water suspensions with combined pH glass electrode.

3. RESULTS AND DISCUSSION

3.1 Phosphorus Adsorption Characteristics of the Soils

It was found that the adsorption isotherm data best fit to the linear model and Freundlich adsorption isotherm models. The linear model and Freundlich adsorption model revealed that soils of the two farms have different P adsorption capacity from KH_2PO_4 and DAP solutions used as P sources for the study (Figs. 1a and b). The adsorption isotherm data showed that amount of P adsorbed by soils from both farms increased with the increased concentration of phosphorus

in initial solution of the two P- sources. As shown by Figs.1a and b, at lower concentration amount of P adsorbed from DAP solution is greater than that of P adsorbed from KH_2PO_4 solution by the soils. This can be attributed to the differences in chemical properties of the two compounds used as P-sources. Upon dissolution in water the two compounds yield different phosphate ions as indicate below:



Thus, one phosphate anion is released from 1 mole of KH_2PO_4 and two phosphate anions from 1 mole of $(\text{NH}_4)_2\text{HPO}_4$, which are readily absorbable on the soil anion exchange sites.

The P adsorption capacity of Bala Langey farm soils from DAP was not as high as that for Adele farm soils (Figs. 1a and b). Even though, there was a difference between the two soils from the two farms in P adsorption capacity, more P was adsorbed from DAP solution by the soils of the two farms compared to KH_2PO_4 solution (Figs. 1a and b). This suggests that when phosphorus is applied as fertilizer, its accessibility to plants is threatened by the soil factors and the chemical and physical properties of the fertilizers applied. Therefore, studies of soil phosphorus adsorption characteristics as affected by P sources could be very effective for soil P fertility management and for efficient utilization of P fertilizers.

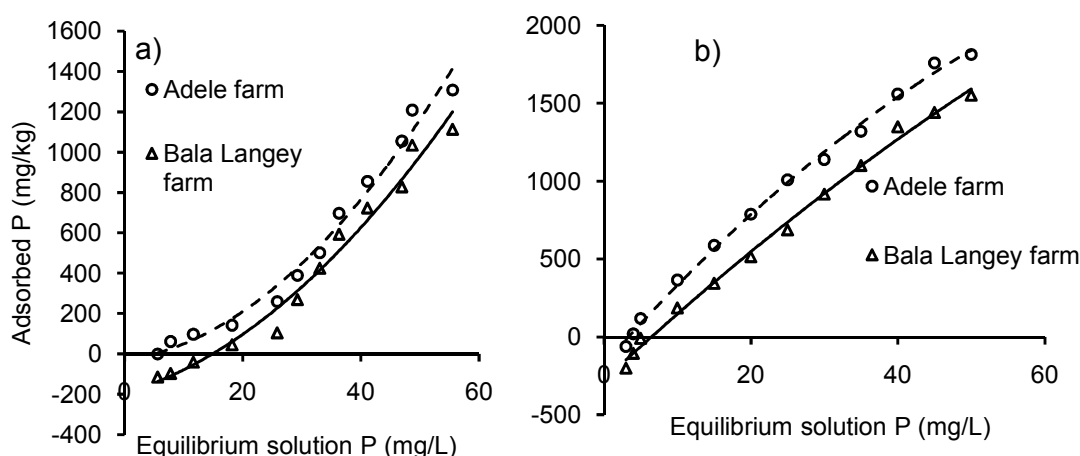


Fig. 1. Phosphorus adsorption characteristics of the soils of the two farms as was affected by different P sources KH_2PO_4 (a) and DAP (b) solutions

Soil organic carbon, clay content and mineralogy, calcium carbonate and soil pH are among the main soil constituents that are responsible for differences in phosphorus adsorption characteristics of soils. It has been reported by several investigators [17,4,1,2,3] that P adsorption is positively correlated with soil clay, calcium carbonate contents and pH, and negatively correlated with soil organic carbon content. Rajput et al. [18] also reported soils with higher available P as well as organic matter content adsorbed less applied P than soils with lower organic matter content. However, soils from Bala Langey farm with relatively higher clay content adsorbed less P than the Adele farm soils (Table 1 and Fig. 1). Therefore, higher P adsorption capacity of Adele farm soils than Bala Langey farm soils can be attributed to its relatively lower organic carbon, higher calcium carbonate and pH value.

The linear and Freundlich models indicate that soils of Adele farm had higher P adsorption capacity from DAP as well as from KH_2PO_4 solutions than Bala Langey farm soils (Figs. 1a and b). These reveal that soils of the two farms demand different P fertility management strategies to increase the soils productivity. Nevertheless, the soil P fertility management strategy of the extension offices of the two districts is 100 kg DAP ha^{-1} which is a blanket recommendation rate for P fertilizer application. These soils should therefore be managed differently for P fertility.

The slopes of the linear model for the Adele farm soil were 40.27 and 27.32, respectively for both P sources, DAP and KH_2PO_4 (Table 2). This describes that for 1 unit increases in P concentration adsorption increases by 40.27 and 27.32 units respectively for the soil. Slopes of Freundlich model were also 0.156 and 0.135 for the same soil, respectively for DAP and KH_2PO_4 . These again indicate an increase in P adsorption by 0.156 and 0.135 for a unit increase in P solution concentration. Therefore, these

clearly show that phosphorus sources have considerable impact on phosphorus adsorption characteristics of soils.

The Y-intercepts of the linear model were -271.30 (KH_2PO_4) and -77.45 (DAP) for soils of Adele farm (Table 2). These suggest that about 271.30 and 77.45 mg kg^{-1} P desorption from the soil when concentration of P is zero in initial solutions. Practically, it is not possible to obtain two observations with such large difference for the same solutions of zero concentration. Therefore, this can be explained as: when the concentration of P in the solutions is very close to zero more P will be desorbed from the soils into KH_2PO_4 solution than into DAP solution. This also indicates soil P-desorption depends on the properties of the P sources applied as fertilizers.

The Y-intercepts for Bala Langey farm soils were also -375.40 (KH_2PO_4) and -230.20 (DAP) (Table 2). As explained above for Adele farm soils, these also show desorption phenomenon at very low concentrations of P. But the Y-intercept values were much higher in magnitude than the Y-intercept values for the Adele farm soils of higher adsorption capacity. This indicates that soils with less adsorption capacity have higher desorption capacity with respect to the phosphorus sources. Therefore, the sorption isotherms clearly depict that phosphorus adsorption/desorption characteristics of soil is a function of soil physico-chemical properties and the chemical and physical properties of fertilizers applied as source of phosphorus.

3.2 Phosphorus Intensity and Quantity Factor Windows of Soils of Adele and Bala Langey farms from Adsorption Isotherm Data of DAP Solution

Phosphorus intensity and Quantity Factor regions (windows) for both farm soils were created from the percentages of adsorption isotherm data i.e. %Pa and %EC. By plotting the

Table 2. Linear model and Freundlich adsorption model parameter for soils of Adele and Bala Langey farms

Soils	P-sources	Linear model parameters			Freundlich model parameters			
		Y-intercept	Slope	R^2	Intercept Log(Kf)	Kf	Slope (1/n)	R^2
Adele farm	KH_2PO_4	-271.30	27.32	0.944	1.79	61.66	0.135	0.95
	DAP	-77.45	40.27	0.990	1.83	67.61	0.156	0.748
Bala Langey farm	KH_2PO_4	-375.40	26.09	0.953	1.78	60.23	0.162	0.868
	DAP	-230.20	37.41	0.993	2.32	208.93	0.109	0.917

two percentages against the initial concentration of P, two regions were observed at the left and right sides of the intersection point in between the line joining the points (Figs. 2a and b).

The region to the left side of the intersection point, with higher percentage of phosphorus in solution represents the intensity factor whereas the region to right side with higher percentage of adsorbed phosphorus represents the quantity factor when P fertilizers are applied to the soil systems. The two regions were described as intensity and quantity factor windows.

The widths of the two windows are interdependent i.e. when the width of intensity factor increases the width of the quantity factor decreases. This exactly demonstrates the P dynamics in the soil systems. The two windows for the study soil revealed the same situation. Adele farm soils with lower available P, higher total P and higher adsorption capacity had narrower intensity factor window and wider quantity factor window (Table 1 and Fig. 2a). Contrary to this, Bala Langey farm soils with relatively higher available P, lower total P and lower adsorption capacity had wider intensity factor window and narrower quantity factor window Table 1 and Fig. 2b.

Furthermore, Figs. 2a and b indicate that the two lines can never cross the Y-axis. This describes the real situation that concentration of P can never be zero in solution and/or in adsorbed form for the materials defined as soil. When the two percentages were plotted against the initial concentration of phosphorus solution, two equilibrium points were also observed. One is at the point where the adsorption line crosses the

X-axis and the other is at the intersection of the two lines (Figs. 2a and b). The 1st equilibrium point indicates concentration of P at which adsorption was exactly equal to desorption. The 2nd equilibrium point also indicates concentration of P at which concentration of adsorbed P was equal to concentration of P in equilibrium solution i.e. 50% of the applied P was adsorbed and the remaining 50% was in the soil solution.

The two equilibrium points have an implication for soil P fertility management. For instance, continuous application of P less than the concentration at the 1st equilibrium point would be resulted in the depletion of native soil P. This is in a way explains the reports by the farmers, “fertilizer is killing our soils”. Even though, it was not recommended based on studies farmers of the study farms apply P less than the blanket recommendation of 100 kg DAP ha⁻¹, which is less than the quantity at the 1st equilibrium point. Thus, application of P fertilizer at a rate adjusted to the concentration of P between the two equilibrium points based on the crop requirements maintain more P in soil solution for immediate benefits. More application of P greater than the concentration at the 2nd equilibrium point ends with soil P build up. The above therefore, gives a baseline for soil P fertility management.

The adsorption isotherms (Figs. 1a and b) could not indicate quantity of P to be applied as fertilizers to alleviate the problems associated with higher P adsorption by the soils or to replenish depleted P. But the intensity and quantity factor windows were able to show the quantity of P to be applied either to be in the intensity factor window or in the quantity factor window.

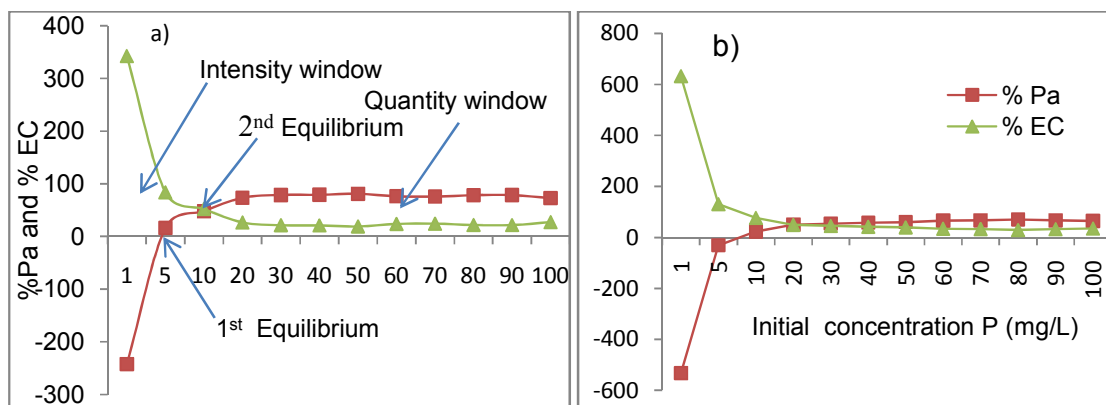


Fig. 2. Intensity and quantity factor windows for soils of Adele (a) and Bala Langey (b) farms from adsorption isotherm data of DAP solution

If the manager of Adele farm is for example, interested in immediate benefits from P application at the currently existing soils conditions, he/she should apply greater than 2.5 ppm (200 kg Pha⁻¹ to the depth of 30 cm) and less than 10 ppm (500 kg Pha⁻¹ to the depth of 30 cm). Therefore, P fertilizer application for the immediate benefits should be in between the 1st and 2nd equilibrium points for the 1st season and then be applied based on quantity of P taken up or exported, and crop requirements per cropping seasons.

This seems unachievable from economic points. But there are options, for instance the values of Pha⁻¹ presented above were calculated from the soil bulk density values. Therefore, if a farmer is able to reduce soil bulk density through organic matter amendment, regardless of the contributions of organic matter to P availability, then he/she could reduce those values calculated above. Because organic matter addition could reduce P adsorption [19,20], which means organic matter amendment can narrow down the quantity factor window and make wider the intensity factor window.

Thus the soil phosphorus intensity and quantity factor windows help the manager of the farm to make a decision. The manager can decide either to deplete his/her soils by applying less amount of phosphorus up to the point that soil will no longer be productive or maintain the soil phosphorus. Soil P maintenance could be achieved through application of adequate and suitable P fertilizers based on the quantity and intensity factor windows of the soils. Similarly, soil P intensity and quantify factor windows can also be established by studying P sorption isotherm of a particular soil. Therefore, soil

phosphorus adsorption isotherm study is a key aspect for soil phosphorus fertility management.

3.3 Impact of Diammonium Phosphate (DAP) Fertilizer on Soil Solution pH

The pH of the equilibrium solution of soils shaken with DAP solution was measured after the equilibrium time to investigate changes in the soil properties induced upon application of DAP to the soil system. Changes in the pH of the equilibrium solution were observed increasing as the concentration of P increased in the initial DAP solution. Changes in pH were rapid for the lower concentration ranges and increased slightly with increased in the P concentration (Fig. 3a). This indicates soil pH buffering capacity against changes in phosphate ions concentration increases with increase in phosphate ions concentrations.

The same was observed for the soil samples collected from the same farms where DAP was applied as P source at the rate of 100 kg ha⁻¹ (18 kg N and 46 kg P₂O₅) over two consecutive cropping seasons (Fig. 3b). 100 kg DAP ha⁻¹ is the blanket rate for the region. But farmers apply about 4 times less than the recommended rate to plots of selected crops.

The pH increased from 7.28 to 8.01 with 0.75 units for soil from Adele farm and from 6.54 to 7.43 with 0.89 units for soil from Bala Lang farm over the two consecutive cropping seasons (Fig. 3b). Change in pH for Bala Langey farm soils with relatively lower initial pH was higher than changes in pH for the Adele farm soils. This shows, soils of Adele farm with higher P adsorption capacity had relatively higher pH buffering capacity against DAP application.

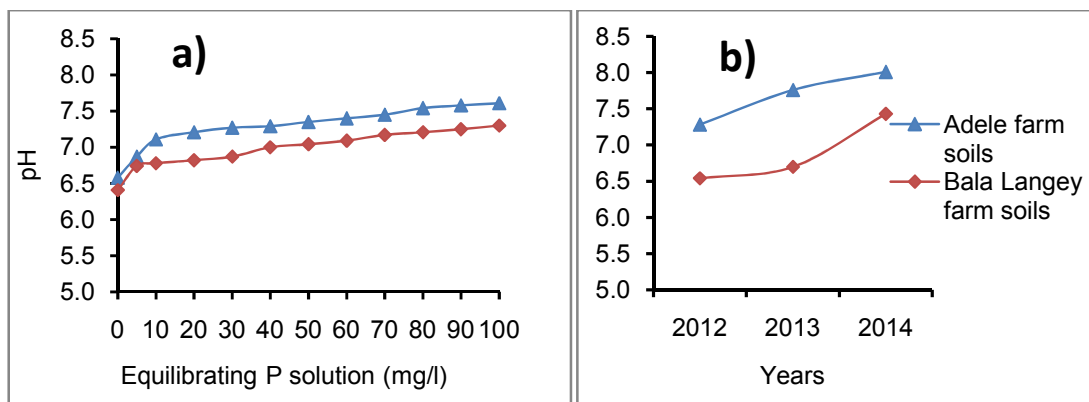


Fig. 3. Changes in pH with increase in P concentration of the equilibrium solution from DAP (a) in laboratory and in soil solution upon application of DAP fertilizer (b) at fields

The pH of equilibrium solutions was also observed increasing as the amount of DAP increased for soil P adsorption characteristics from DAP solution. Similarly, soil pH was also increased upon DAP application at a rate of 100 kg ha⁻¹ for two consecutive cropping seasons. These changes in soil pH over a short periods i.e. two cropping seasons therefore, put under question the suitability of DAP to those soils if the application doses would be increased.

4. CONCLUSION

- Soils of the two farms had different P adsorption capacity from the two P sources DAP and KH₂PO₄.
- More P was adsorbed from DAP solution than from KH₂PO₄ solution by soils of the two farms
- Phosphorus adsorption capacity of Adele farm soils was higher than that of Bala Langey farm soils.
- The soils of the two farms should be managed differently for P fertility.
- Between 200 and 500 kg ha⁻¹ P should be applied as fertilizer to soils of Adele farm at 0-30 cm depth for immediate benefits and soil P fertility maintenance.
- Suitability of DAP as source of phosphorus fertilizer for soils of the study areas should be further investigated at field and in laboratory.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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