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Variable Charge of Ultisols due to Phosphate Application and Incubation Time

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ABSTRACT

Variable Charge Ultisols due to Phosphate Application and Incubation Time (M Mahbub): The laboratory experiment was conducted to study the effect of phosphate (P) application and its incubation time on pHo (pH at the point of zero charge) and variable charge of ultisols . The determined parameters were pHo and variable surface-charges. Soil samples were added by 0, 375 and 1,125 mg P kg^{-1} (or 0, 50 and 150% of the P sorption maximum, respectively). Then, they were incubated for 2, 4, 6 and 8 weeks. The variable surface-charges and pHo were determined by using the activity of potential determining ions (H^+ and OH^-) within two salt concentrations as counter ions (0.1*N* and 0.001*N* $CaCl_2$) through a potentiometric titration method. The results were indicated that the high P sorption and 766 mg P kg^{-1} in maximum sorption were due to high contents in clay fractions and aluminum as well as low pH of experimental soil. Application of P and incubation time were able to decrease pHo and to increase negative surface-charges. Additionals of 375 and 1,125 mg P kg^{-1} incubated for 8 weeks gave the value of pHo 2.86 and 2.69; as well as the magnitude of negative charges 14.48 and 16.76 cmol(-).kg^{-1}, respectively (both for 0.001*N* $CaCl_2$). For pH > pHo (the characteristic of variable charge soils), the higher the salt ($CaCl_2$) concentration and pH solution, the higher the negative surface-charge.

Keywords: Negative variable-charge, pHo, phosphate, salt ($CaCl_2$) concentration, Ultisols

INTRODUCTION

Humid tropical soils are dominated by variable (positively or negatively) charged minerals. The variable charge as soil content materials are: (1) inorganic soil, such as sesquioxides having amphoteric properties, and (2) organic matter. The amphoteric surfaces of colloidal dominates the variable charge soil containing FeOH and/or AlOH such as goethite, ferrihydrite, hematite, gibbsite, imogolite and allophane. The variable charged soils of Andisols, Spodosols, Oxisols, Ultisols and other tropical soils were weathering ultimately (Raij and Peech 1972; Soil Survey Staff 2003).

Oxide surfaces can be charged through adsorption of ions OH^- and H^+. Surface charge properties are very important part in soil management because their reactions more related to soil nutrient availability (Hossner and Juo 1988). Losses of exchangeable cations or nutrients in Ultisols very closely related to low of surface negative charge or cation exchange capacity (CEC). Consequently, a lot of nutrients in form of cations leached and the soil became poor of nutrients.

Soils that have variable charged surfaces can be increased its negative charge by various ways, such as liming, to increase pH and indirectly increase negative charge of soil. The higher the CEC, the larger the quantity of lime that must be added to increase the soil pH (Ketterings *et al.* 2007). In the variable charged soils, pH can not be increased too high (above pH 6.5) because of high of soil capacity. Therefore, the effect of lime on increasing soil pH will be temporary, and back to initial pH condition. This research attempt to increase negative charge of soil by means of lowering pH at zero point of charge (pHo). Addition of organic matter and/or anions into the variable charged soil can decrease pHo (Uehara and Gillman 1981). Application of organic matter (cattle manure) to soil contributed to increase negative charge

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and the increasing was 35% more than application of inorganic fertilizer (TSP) (Jiao *et al.* 2007). Another way is addition of phosphate (P) anion. The P anion specifically adsorbed by soil can neutralize the positive charge (Hossner and Juo 1988) and then increase the negative charge on the soil surface (Parfitt 1980; Hong *et al.* 2009). The objective of this experiment was to determine the effect of addition of P and incubation time on pHo and variable charge of Ultisols.

MATERIALS AND METHODS

Soil Samples

Ultisol soil samples (Soil Survey Staff 2003) from Jasinga area (West Java) were taken by composite at a depth of topsoil (0-30 cm). The properties of soil samples were shown in Table 1. Phosphate materials derived from phosphate fertilizer with 46% P_2O_5 content and grain size of 60 mesh.

P Sorption Analysis

Amount of P sorption maximum was used as a treatment doses of P applied. The value was obtained from former experiment of P sorption isotherm (Okalebo *et al.* 1993) and by using calculation of the Langmuir equation. In describing P sorption, the Langmuir equation fitted better than Freundlich equation (Yusran 2010). The Langmuir equation which modified as (Bohn *et al.* 2001):

$$x/m = (b\ k\ C)/(1 + k\ C) \quad ....[1]$$

where, x/m = amount of P sorption by soil (mg kg^{-1}), C = concentration of P in equilibrium solution (mg L^{-1}), b = P sorption maximum (mg kg^{-1}), k = constant (coefficient related to bonding energy).

Table 1. Soil properties in the experimental site (0-30 cm depth).

Soil properties	Unit	Value
Clay fraction	%	58.36
pH H_2O (1:5)	-	4.32
pH 1 *N* KCl	-	3.60
Exchangable Al (Al_{dd})	cmol(+)kg^{-1}	11.42
Al extracted with Oxalate	%	0.85
Fe extracted with Oxalate	%	0.81
P extracted with P-Bray I	mg kg^{-1}	2.87
P sorption maximum (b)	mg kg^{-1}	766

The result of P sorption isotherm analysis that amount of adsorbed P maximum (b) was 766 mg P kg^{-1} (Figure 2). Therefore, three levels of P treatment which were 0, 375 and 1,125 mg P kg^{-1} (or 0, 50 and 150% P sorption maximum, respectively). Soil samples were added to the soil samples, then were incubated for 2, 4, 6 and 8 weeks. At the end of the incubation time, the treatment soils were air-dried, ground and sieved through 2 mm sieve.

Variable Charge Analysis

Soil pHo and variable charge were determined by a potentiometric titration method (Raij and Peech 1972). The variable charge distribution at various pH was determined by using potentiometric titration curves in the two salt solution (counter ion) at a concentration of 0.1 *N* $CaCl_2$ and 0.001 *N* $CaCl_2$. A potentiometric titration method according to Raij and Peech (1972) and developed by Uehara and Gillman (1981) (as shown in Figure 1), is as follows: Four gram of fine soil samples (oven dry equivalent) were placed into 50-mL beaker as many as 22 beakers sequentially. Then, the beakers were arranged in 2 rows and each row had 11 beakres. The first eleven beakers (series I) were added by 1 mL of 2 *N* $CaCl_2$ respectively and the next eleven beakers (series II) were added by 1 mL of 0.02 *N* $CaCl_2$, respectively. Then beakers at each row were given (in sequence) by the potential determining ions (H^+ and OH^-) : 5 mL, 4 mL, 3 mL, 2 mL, 1 mL of 0.5 *N* H^+ solution and 0 mL, 1 mL, 2 mL, 3 mL, 4 mL, and 5 mL of 0.5 *N* OH^- solution, respectively. A distilled water was added to bring the final volume in each beakers to 20 mL, so that there were 2.5 me (miliequivalent), 2 me, 1.5 me, 1.0 me, 0.5 me H^+; 0 me, 0.5 me, 1.0 me, 1.5 me, 2.0 me, 2.5 me OH^-, respectively in 0.1 *N* $CaCl_2$ solution (series I) and in 0.001 *N* $CaCl_2$ solution (series II). All the beakers with its contents were allowed to reach equilibrium for 4 days, and they were stirring occasionally.

After reaching the equilibrium, pH of suspension was measured with a glass electrode. Then, a blank-curve of the relationship of pH was made. Some amount of H^+ or OH^- was added to the solution of 0.1 *N* and 0.001 *N* $CaCl_2$, respectively without soil addition (blank) and it reached the range pH of 0.95 – 12.5. The amount of H^+ or OH^- adsorbed to soil samples at certain pH was the amount of me H^+ or me OH^- added to the suspension subtracted to me H^+ or me OH^- from the blank-curve at the pH corresponding to the same concentration of $CaCl_2$

Series I (0.1 *N* $CaCl_2$)	O	O	O	O	O	O	O	O	O	O	O
Series II (0.001 *N* $CaCl_2$)	O	O	O	O	O	O	O	O	O	O	O
Titration with (H^+ or OH^-)	---------- me H^+ ----------						---------- me OH^- ----------				
	2.5	2.0	1.5	1.0	0.5	0	0.5	1.0	1.5	2.0	2.5

O = beakers

Figure 1. Design for potentiometric titration method according to Raij and Peech (1972) and developed by Uehara and Gillman (1981).

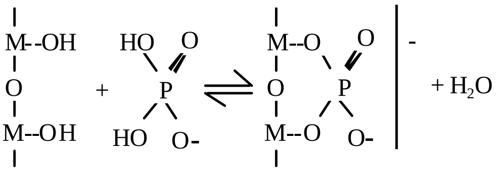
solution. A curve which shown the relationship between the amount of H^+ or OH^- adsorbed by soil and soil pH was called the potentiometric titration curve. Intersection of two line-curves from 0.1 *N* and 0.001 *N* $CaCl_2$ was called zero point of charge (zpc). The pH value at zpc was called pHo. The amount of me H^+ or OH^- adsorbed by soil equivalent to me negative or positive charge of soil.

RESULTS AND DISCUSSION

The magnitude of P applied to the soil was apparently very low P in soil solution (Figure 2) and vice versa P sorbed by soil P was very high (Figure 3). Figure 3 shows P sorption isotherm, describes the relationship between number of sorbed P (which includes absorbed P and adsorbed P) by soil and P in solution at equilibrium conditions. This experiment using 0.01 M $CaCl_2$ solution concentration and equilibrium temperature 26.5°C for incubation 6 days. Factors affecting the high P sorbed/fixation were among others: the high clay fractions (quantity and type, low soil pH and the presence of other ions (Al and Fe) high (Uribe 1988). The P adsorption on ferrihydrite contained soil under pHo 5.77 was higher (Rhoton and Bigham 2005).

This was supported by the physical and chemical properties of experimental soil in Table 1, where a high P adsorption was caused by a high clay content, a low soil pH and a high aluminum content. A high clay content which gave a large specific surface, enabling a high adsorption of phosphate ions as well. This was supported Al and Fe extracted with oxalate in the form of amorphous and organically complexes.

Soil pH condition was very acid promotes the higher concentration of $H_2PO_4^-$ ions and increased specifically P sorption by soil containing Al and Fe (M symbol) oxide surfaces as well as increased in negative charges of soil. Equation 2 shows reaction of $H_2PO_4^-$ ion sorption by oxide surfaces of soil (Ritchie 1989):



...... [2]

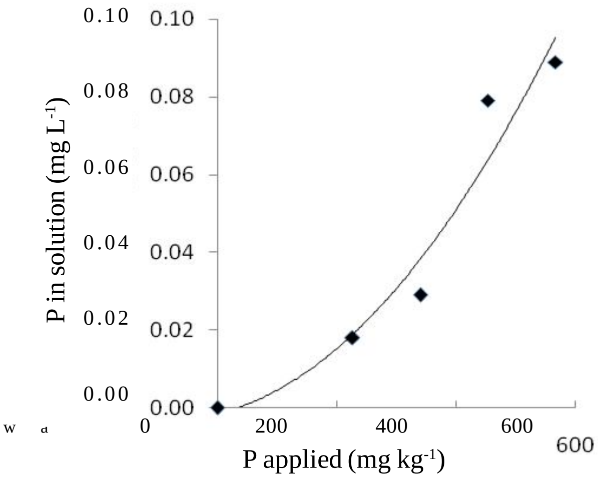


Figure 2. Relationship between P applied and P in solution at equilibrium condition.

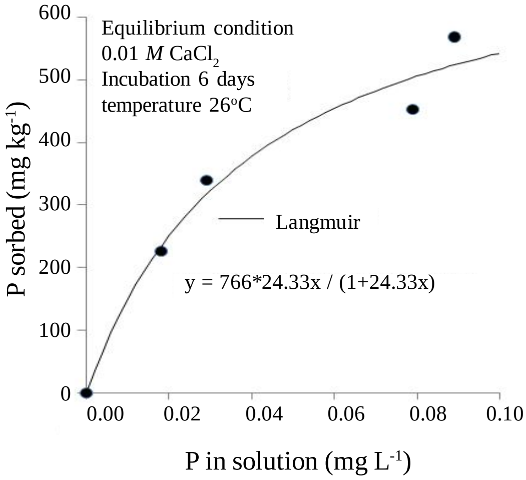


Figure 3. P sorption isotherm and curve of Langmuir equation at equilibrium condition.

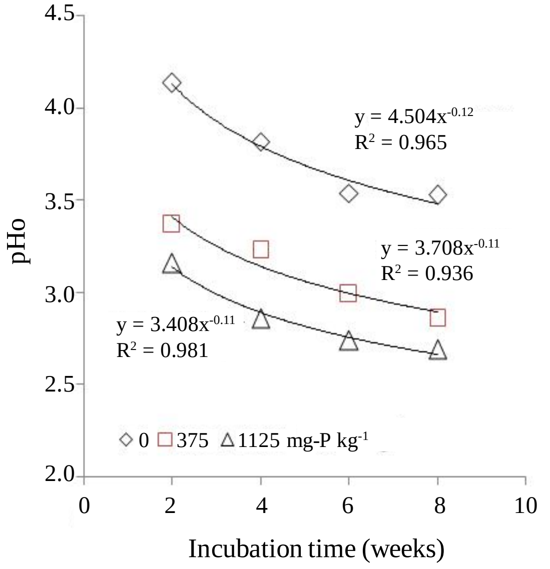


Figure 4. Relationship between value of pHo in various doses of P and the incubation time.

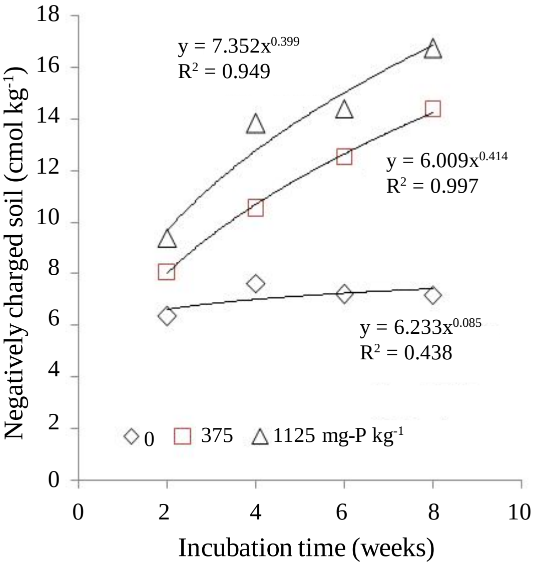


Figure 5. Relationship between the amount of negative charge in various doses of P and the incubation time.

Addition of higher P dose into the soil caused decreasing in pHo (Figure 4). Both P dose of 375 and 1,125 mg P kg^{-1} provided pHo significantly lower than 0 mg P kg^{-1} (control). Dose of 1,125 mg P kg^{-1} provided pHo value lower than the dose of 375 mg P kg^{-1}. The longer the incubation time, the lowering the pHo is. It was caused by the longer time, P adsorption was more slowly. Borggaard (1990) proposed that P adsorption by soil increased with the increasing reaction time, initially rapid and then more slowly.

The relationship of surface charge (δo) and pHo can be explained from the Nerst equation (Equation 3). If pHo was greater than pH, soil surface charge would be positive (δo+) and if pHo was less than pH, soil surface charge would be negative (δo-). The more negative the difference of pH (pHo - pH) or the lower pHo, the more negative charge created increased.

$$\delta o = \left[\frac{2\,n\,\varepsilon\,k\,T}{\pi}\right]^{1/2} \text{Sinh } 1.15z\,(\text{pHo} - \text{pH}) \text{ ....} \quad [3]$$

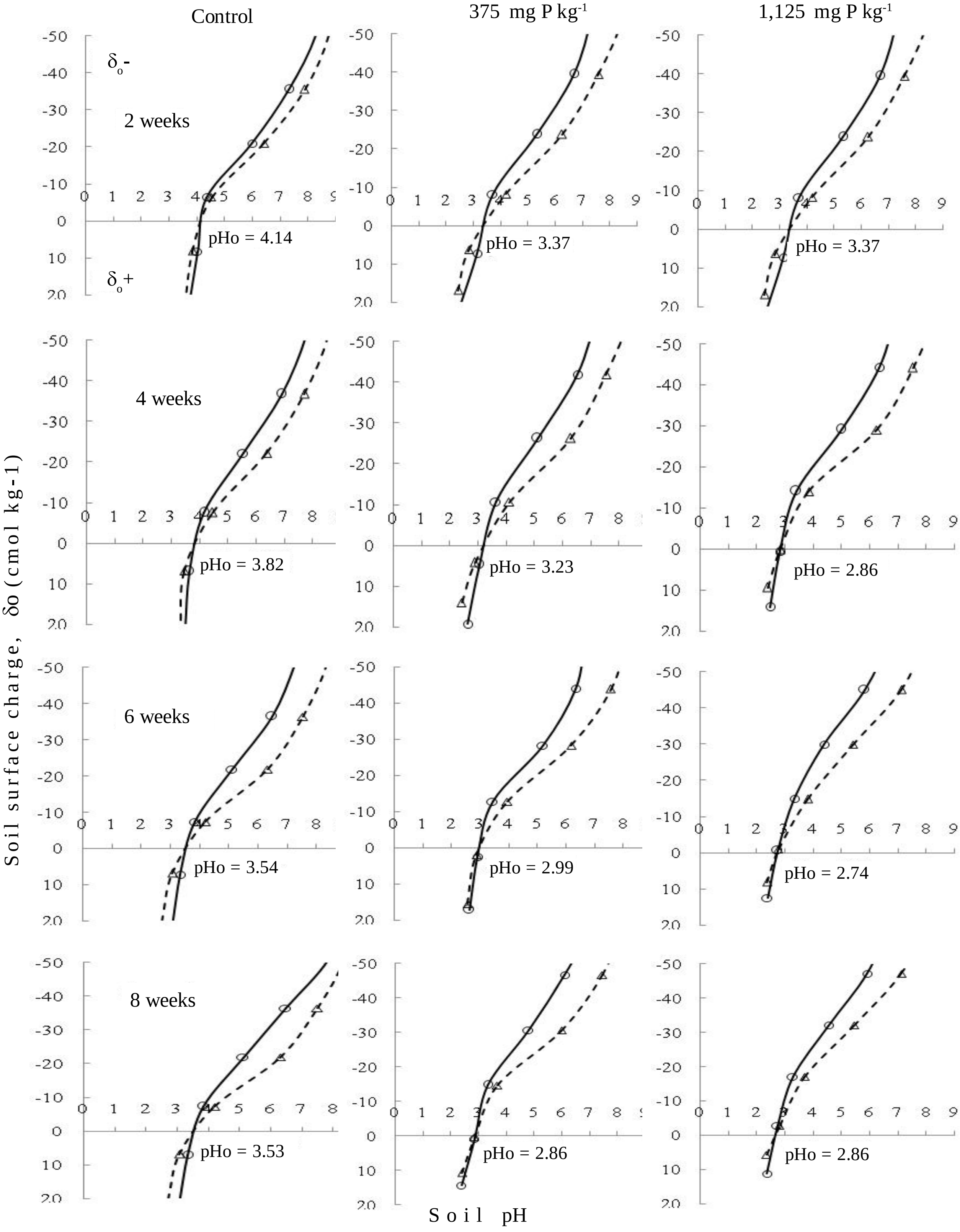
where: do = surface charge density (esu cm^{-2}); n = counter ion concentration in equilibrium condition (ion cm^{-2}); ε = dielectric constant (esu^2 dyne^{-1} cm^{-2}); k = Bolzman constant (ergs/degree); T = absolute temperature; z = counter ion valence; pHo = pH at the zero point of charge; pH = actual pH.

Increasing of P applied dosages and incubation time gave the effect on increasing the soil negative charge (measured at the point of zero titration, pzt) as shown in Figure 5. The charge at pzt was the charge which was measured without addition of acid (H^+) and base (OH^-), so raising the charge was only from P addition and salt concentration.

Figure 5 shows that both P dosages of 375 and 1,125 mg P kg^{-1} provided the negative charge significantly higher than those of 0 mg P kg^{-1} (control). The dose of 1,125 mg P kg^{-1} provided the negative charge higher than the dose of 375 mg P kg^{-1}. For the longer incubation time, the trendline curves of both P dosages of 375 and 1,125 mg P kg^{-1} were more steeper in increasing negative charge than dosages of 0 mg P kg^{-1} (control). The presence of more P in the soil can maintain the availability of soluble phosphate. Therefore, the longer time and the higher adsorbed P anion by the surface, the more negative charge was created. Barrow (1987) suggested that ion adsorption reaction was much influenced by ion concentration and time. The amount of ion adsorption increase proportionally to the magnitude of ion concentration and reaction duration .

Figure 6 shows the potentiometric titration curves for the relationship of variable charge (δo) and pHo due to P application and its incubation time as well as the difference of salt ($CaCl_2$) concentration.

Application P and its incubation time changed the position of intersection of two lines (called pHo) moved toward left of graph X-axis. This means that pHo was lower than pH. From the position of pH



Notations and legend: δ_o- = negatively charged soil; δ_o+ = positively charged soil; pHo = soil pH at the point of zero charge; –O– = electrolyte salt concentration 0.1 *N* $CaCl_2$; --Δ-- = electrolyte salt concentration 0.001 *N* $CaCl_2$.

Figure 6. Potentiometric titration curves for the relationship of soil surface charge (δo) and pHo due to P application and its incubation time (weeks).

towards the pHo, the curve can be split into two regions, namely: (1) negatively charged regions (δo-) and (2) positively charged regions (δo+). The soil will be negatively charged when the pH difference (ΔpH = pHo - pH) was negative (also see Equation 3) and positively charged when ΔpH was positive. The more negative of ΔpH, the higher negative charge of soil and vice versa. When pH = pHo or ΔpH = 0, the soil will zero charged. The salt concentration or counter ion also affected the variable charge of soil. At the negative ΔpH, 0.1 *N* $CaCl_2$ provided higher negative charge than 0.001 *N* $CaCl_2$. The difference of the amount of negative charge was greater when position of actual pH higher than pHo. The distance of two line-curve between 0.1 *N* $CaCl_2$ and 0.001 *N* $CaCl_2$ was likely to be wider. Increasing in salt concentration (ionic strength) will increase protonation (H^+ release) and to react with OH^-, consequently the pH was decreased (Bowden *et al*. 1980). Therefore, for the negatively charged soils (at pH > pHo), the pH using higher salt concentration (0.1 *N* $CaCl_2$) would be lower than pH using lower salt concentration (0.001 *N* $CaCl_2$).

The amount of negative charge on the variable charged soils was strongly influenced by the salt concentration and pH of soil solution. The higher salt concentration and soil pH caused the higher negative charge of soil. If we assume that the cation exchange capacity (CEC) of soil was explanation of the actual negative charge of soil, so the commonly determination of CEC in the laboratory became unsuitable. Recently, the determination of CEC using the salt concentration such as 1 *N* NH_4OAc and buffered at pH 7 or 0.5 *N* $BaCl_2$ and buffered at pH 8 would produce over estimate, because the concentration of salt (Na^+, K^+, Ca^{2+} and Mg^{2+}) in natural soil was likely to be much lower which is ranged between 0.0005 – 0.01 *M* (Bruggenwert *et al*. 1991) and soil pH generally below 6.5. Therefore the best method to approach the actual negative charge of soil was method of CEC determination using an unbuffered salt at a certain pH, such as NH_4Cl or KCl salt. These salts were likely to be working close to the real soil pH.

CONCLUSIONS

A high P adsorption decreased P availability in soil solution. However, in terms of its influence to increase the soil negative-charge because of the high P adsorption and the decrease in pHo was very beneficial especially for Ultisols having low CEC and exchangeable bases.

Determination of soil CEC, especially for soils dominated by the variable charge, had to be considered the factors that influence the variable charge. To obtain the best real value of the soil charge had to be adjusted the factors close to the field situation.

The position of the pHo towards soil pH was also be considered in the soil management, because many of the soil characteristics associated with the variable charge will affect the soil physical and chemical properties.

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