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Soil potassium status and adsorption characteristics of Thai lowland vertisols

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ABSTRACT: Lowland clayey soils dominated by 2:1 clay minerals are generally believed that application of K fertilizers are not necessary, particularly in Thailand. However, there is evidence that many of them contain only low levels of available K and thus K fertilizer application is required. This study aimed to investigate the distribution of K forms and K adsorption characteristics of Thai lowland Vertisols. Topsoil and subsoil samples of five representative soils were analyzed for various K forms and K adsorption characteristics. The results showed that available K content (water soluble K + exchangeable K) in Thai lowland Vertisols varied from low to high (64.3-120 mg/kg) in topsoils and very low (24.9-46.5 mg/kg) in subsoils. However, all soils had a very low K reserve (13.6-102 mg/kg). The K saturation values of these soils (0.06% – 0.95%) were far below critical value (1.5%), indicating that only a very small proportion of the CEC was occupied by K^+. Potassium adsorption was showed a good fit with the Freundlich isotherm only. The adsorption capacity (K_f) values of these soils were negatively correlated with the organic matter and extractable K contents in soils. Whereas the rate of K adsorption ($1/n$) was positively correlated with available K content and K:Mg ratio.

Keywords: non-exchangeable K, adsorption isotherms, smectitic soils, tropical soils.

INTRODUCTION

Potassium is a major element playing an important role in crop production. In general, soil K can be divided into four pools: water soluble K, exchangeable K, non-exchangeable K, and matrix K (Johnston and Goulding, 1990). These K pools are in equilibrium and transform by release, fixation, and sorption processes. Potassium transformation and behavior of added K fertilizer in the soil are dependent on soil properties, such as type of clay minerals, soil texture, charge density, and organic matter (OM) content (Wang and Huang, 2001; Havlin et al., 2005; Darunsontaya et al., 2010). These properties strongly influence the cation exchange capacity (CEC) of the soil. However, there is evidence suggesting that a high soil CEC value does not necessarily favor adsorption and release of K (Coulombe et al., 1996). In addition, other cation concentrations such as Ca^{2+} and Mg^{2+} also have a significant effect on K^+ activity in the soil (Feigenbaum et al., 1990).

Thai farmers and also Thai agricultural officers have long believed that lowland soils in the central plain of Thailand contain a sufficient level of available K for crops and that addition of K fertilizers are not necessary especially in clayey soils (Division of Rice Research Development, 2020). High K content in these soils is generally resulted from low soil weathering intensity and most soils are fine-textured. Lowland Vertisols in Thailand are mainly located in the central plain and central highland regions and are typically used for intensive rice cultivation. Their parent material is mainly local alluvium derived from limestone (Chittamart et al., 2010). Common characteristics of Vertisols are clayey, high CEC, and dominated by smectite silicate clays. In addition, Vertisols have calcium and magnesium saturating the cation exchange complexes and contain low OM content (Ahmad 1983; Coulombe et al., 1996). It is generally believed that the high exchangeable K levels of the soils are due to their high levels of clay and CEC (Finck and Venkateswarlu, 1982; Mengel, 2007).

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However, several studies have reported low exchangeable K content in lowland Vertisols (Kunze et al., 1963; Chittamart et al., 2010) and their low K reserve is the major constraint of these Thai soils (Laungta et al., 2015).

In general, soil clay content and soil organic matter content play an important role for improving CEC of the soil. Accordingly, Darunsontaya et al. (2018) reported that K sorption capacity of the studied soils was positively correlated with the soil clay content and soil organic matter content. Type of clay minerals also strongly affect the sorption process in the soil, for example; smectite have higher capacity to adsorb cations than kaolinite (Suttanukool et al., 2019). Nevertheless, many studies revealed that soil K dynamic does not only depend on both clay content and type of clay minerals, but also charge characteristics of the clay minerals. (Frost and Kloprogge, 2000; Pal et al., 2012). A high layer charges, especially the charges coming from the tetrahedral sheet, are very important factors to consider in potassium retention. Potassium are not freely exchangeable when the layer charge of smectite is above 0.45 electron per half unit cell (Coulombe et al., 1996). Furthermore, K adsorption also depends on the K concentration and competing cations such as calcium (Ca) and magnesium (Mg) in the soil solution (Feigenbaum et al., 1990; Moritsuka et al., 2004). However, there is limited information on the adsorption characteristics of added K in Thai lowland Vertisols. Therefore, the present study was conducted to gain a better understanding of the K status and K adsorption characteristics of representative lowland Vertisols in Thailand; this should provide useful information on K fertilizer management and maintaining K reserves for sustaining rice production.

Materials and Methods

Study sites and soils

Five representative lowland Vertisols, Ban Mi (Bm), Khok Krathiam (Kk), Wattana (Wa), Lop Buri (Lb) and Chong Khae (Ck) soil series were selected from the central plain regions of Thailand (Table 1). Topsoil (Ap horizon) and subsoil horizons (below the bottom of Ap horizon to 60 cm) of each soil were collected for investigation. All soils had been used for rice cultivation.

Table 1 Soil sampling sites

Soil series	Location	Coordination (UTM)
Ban Mi (Bm)	Nong Don subdistrict, Nong Don district, Saraburi province	47P 683187N 1624318E
Khok Krathiam (Kk)	Don Phut subdistrict, Don Phut district Saraburi province	47P 675582N 1614477E
Wattana (Wa)	Nong Don subdistrict, Nong Don district, Saraburi province	47P 684564N 1624258E
Lop Buri (Lb)	Ban Prong subdistrict, Nong Don district, Saraburi province	47P 683540N 1628633E
Chong Khae (Ck)	Roeng Rang subdistrict, Sao Hai district, Saraburi province	47P 693074N 1612330E

Physico-chemical and mineralogical analyses

The physico-chemical properties of soils were analyzed using standard methods (National Soil Survey Center, 1996). Soil pH was measured in 1:1 soil:water. Particle size distribution was determined by the pipette method. Organic matter content (OM) was determined by the Walkley and Black method. Cation exchange capacity (CEC) and extractable bases (Ca, Mg, Na, K) were measured with 1 M NH_4OAc at pH 7.0. Total nitrogen was determined by the Kjeldahl method (National Soil Survey Center, 1996). Available phosphorus was determined by the Bray II method (Bray and Kurtz, 1945). Clay mineral species were identified by scanning with a PANalytical X Pert^3 powder X-ray diffractometer from 2 to 30° 2θ angles after various pretreatments using CuKα radiation.

Forms of soil K

Sequential extraction of soil K was determined in triplicate using 3 g of soil in a 50 mL centrifuge tube. Thirty milliliters of deionized water was added and the sample was shaken for one hour.

The sample was then centrifuged and the suspension was collected to determine water-soluble K content. The tube containing the soil residue was then filled with 1 M NH_4OAc, shaken for one hour, and the suspension was collected to determine exchangeable K content. The readily available K content was calculated from water soluble K plus exchangeable K contents. Non-exchangeable K was determined using a solution made by boiling the soil residue in 20 mL of 1 M HNO_3 at 110 °C for one hour, followed by washing with 0.1 M HNO_3, and making up the final volume to 100 mL with 0.1 M HNO_3 (Pratt, 1965; Darunsontaya et al., 2018; Suttanukool et al., 2019). The solutions obtained from all steps were analyzed for K concentration using Atomic Adsorption Spectrophotometry (AAS). The K saturation percentage (% K sat) was calculated through using the value of extractable K content (in cmol unit) divided by cation exchange capacity (CEC) of the soil and then multiplied by 100 (Mutscher, 1995).

K adsorption

The adsorption of K was studied in duplicates by shaking 1 g of soil with 10 mL of KCl solutions of 0, 10, 30, 50, 100, 150, 200, and 300 mg K/L (equivalent to 0, 100, 300, 500, 1000, 1500, 2000, and 3000 mg K/ kg soil) for 72 hours at room temperature. The resulting suspension was centrifuged at 3500 rpm for 5 minutes and filtered. Potassium concentration was then determined and was expressed as Ce. The K concentration in suspension was subtracted from the initial concentration and the sorption of K per unit mass of soil (qe) was calculated from the following equation:

$$qe = \frac{(Ci-Ce)v}{m} \qquad (1)$$

where Ci and Ce are the initial and equilibrium K concentrations (mg/L), respectively; m is the mass of the soil (g); and V is the volume of K solution (mL). The obtained data was then fitted to Langmuir equation by plotting Ce against Ce/qe from the following equation (Ali et al., 2013):

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{q\mathrm{m}} \qquad (2)$$

The linear plot of specific adsorption (Ce/qe) against the equilibrium K concentration (Ce) provides constants b and qm that represent the energy of adsorption and maximum adsorption capacity, respectively. Their values were obtained from the intercept and slope of the plot. The same set of data was also fitted to a Freundlich isotherm by plotting log Ce and log qe from the following equation (Limousin et al., 2007):

$$Log\ (qe) = \frac{1}{n} log(Ce) + log\ (Kf) \qquad (3)$$

where qe represents the mass of K adsorbed per mass of soil at equilibrium (mg/g); Ce represents the equilibrium K concentration (mg/L); and K_f and $1/n$ are parameters determined by the K concentration and soil characteristics, respectively.

Results and Discussion

Physico-chemical properties of studied soils

The physico-chemical properties of Thai lowland Vertisols are summarized in **Table 2**. Soil pH ranged from moderately acid to slightly alkaline. According to Kanchanaprasert (1986), organic matter content was slightly high in topsoil and medium in subsoil horizons. The studied soils had very low to low total N content. Available P content varied from very low to medium. All soils had very high CEC values. Calcium was a dominant cation in these soils, ranging from 5.5 to 59.0 cmol/kg. All soils were clayey with clay content ranging from 590 to 733 g/kg.

Table 2 Some physico-chemical properties of studied soils

Soil series	Horizon	pH	OM	TN	Avai. P	CEC	Extr. Ca	Extr. Mg	Extr. Na	Extr. K	Sand	Silt	Clay	K_{sat}
			(g/kg)		mg/kg	(------------cmol$_+$/kg-------------)					(------g/kg------)			%
Bm	Top	6.4	30.8	1.25	10.0	64.4	37.0	7.9	1.0	0.25	33	239	728	0.39
	Sub	6.9	17.1	0.47	2.5	64.8	35.0	4.8	1.3	0.08	16	296	688	0.12
Kk	Top	5.8	30.1	1.02	4.7	42.5	11.0	8.2	2.5	0.17	41	369	590	0.40
	Sub	5.7	14.3	0.41	0.9	34.9	26.0	5.5	3.2	0.12	33	366	602	0.35
Wa	Top	6.0	30.4	1.17	18.2	54.7	49.0	6.2	1.0	0.32	45	256	699	0.58
	Sub	7.1	16.3	0.28	1.8	55.3	59.0	3.2	1.3	0.09	26	242	733	0.16
Lb	Top	7.2	21.5	0.49	7.2	53.5	59.0	5.7	0.7	0.20	88	294	618	0.38
	Sub	7.4	17.1	0.28	2.1	56.5	48.0	4.6	0.8	0.03	116	236	648	0.06
Ck	Top	5.9	30.0	1.36	1.7	32.2	7.7	7.3	1.3	2.5	48	346	605	0.79
	Sub	7.4	14.0	0.47	0.8	15.0	5.5	9.0	1.6	1.4	38	282	680	0.95

OM=organic matter; TN= total N; Avai.P = Available P; CEC=cation exchange capacity; Extr.= extractable; K_{sat}= K saturation

These soils were dominated by smectite in the clay fractions with trace to small amounts of kaolinite, illite, interstratified minerals, and quartz **(Table 3)**. Quartz was the dominant mineral in the silt fraction. The high CEC values in all soils correspond to their soil texture and clay type. However, slightly lower CEC levels in Ck and Kk were observed, as a result of higher kaolinite concentrations compared to other soils.

Table 3 Semi-quantitative minerals of clay and silt fractions for investigated soils

Soil series	Clay fraction[1/]					Silt fraction[1/]		
	Smec	Ill	Kao	Int 10-14 Å	Qtz	Qtz	Kao	Ill
Bm	xxxx	-	tr	-	tr	xxxx	-	-
Kk	xxx	-	x	tr	tr	xxxx	-	-
Wa	xxxx	-	tr	-	tr	xxxx	-	-
Lb	xxxx	-	tr	-	tr	xxxx	-	-
Ck	xxx	tr	x	-	tr	xxxx	tr	tr

[1/] Smec= Smectite; Ill = Illite; Kao = Kaolinite; Int = Interstratified; Qtz = Quartz
tr= trace (<5%), x= small (5-20%), xx= moderate (20-40%), xxx= large (40-60%), xxxx= dominant (>60%)

Soil K content in various forms

Water-soluble K in the studied soils ranged from 1.8 to 23.3 mg K/kg soil with the higher content being found in topsoil horizons **(Figure 1)**. The exchangeable K in topsoil horizons ranged from low to high (43.0–101.2 mg/kg) with a mean value of 73.8 mg/kg. The values of exchangeable K in the subsoil horizon ranged from very low to low levels (12.7–33.3 mg/kg). Higher available K content in topsoil horizons compared to that of subsoil horizons may have been a residual effect of K fertilizer application. Non-exchangeable K in these soils varied from 13.6 to 101.0 mg/kg with a mean value of 55 mg/kg. According to Rao et al. (2010), the studied soils contained low level of non-exchangeable K (<300 mg/kg). This result indicated depotassification of smectite minerals, which is the natural mechanism of K loss in the soil (Rezapour et al., 2010). As the environmental conditions required for smectite formation are surficial temperature to destabilize tetrahedral Al, low K concentration to promote depotassification of mica (and illite), high Ca^{2+} and Mg^{2+} activity to force the displacement of K^+ from the interlayer, and alkaline conditions (Essington, 2015). The higher content of non-exchangeable K in Kk and Ck soils was a result of their mineralogy, which included trace amounts of illite and interstratified minerals in the clay and silt fractions. Shadfan (1983) noted that the K status is influenced not only by micas but also by interstratified clay minerals. However, non-exchangeable K content of Thai lowland Vertisols was still lower than that of non-exchangeable K content in Vertisols from elsewhere reported by other studies. Taddesse (1999), Rao and Rao (2000) and Bahmani et al. (2013) reported that non-exchangeable K contents of their Vertisols ranged from 2,508-3,502 mg/kg (Ethiopia), 390-1,720 mg/kg (India) and 306-742 mg/kg (Iran), respectively. Furthermore, there was no significant correlation between contents of non-exchangeable K and exchangeable K in these soils (data not shown). This result indicated that the forms of K in these soils may not be in equilibrium. In other words, these soils could not meet the K requirements for prolonged rice production due to their lack of K reserve. There were no significant correlations between various forms of soil K content with clay content and CEC.

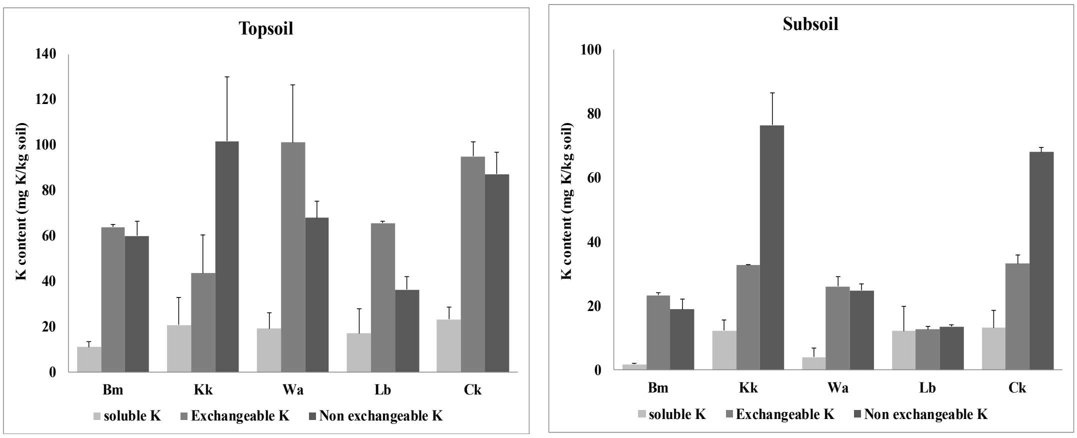

Figure 1 Content of various K forms in Thai lowland Vertisols. Bars indicate standard error

Potassium saturation (the percentage of CEC occupied by exchangeable K) is often a better indicator of soil K supply than the absolute amount of K extracted with 1 M ammonium acetate (Schneider and Villemin, 1992; Singh et al., 2004), because it takes into account the relationship between potassium and other exchangeable cations (Ca^{2+}, Mg^{2+}, and Fe^{2+}). The exchangeable K saturation of these soils ranged from 0.06% to 0.95% (Table 2). According to the range of K saturation required for rice growing as suggested by Dobermann and Fairhurst (2000), K saturation below 1.5% indicates low K status and that soil will benefit from potassium fertilization. The K saturation values of these soils were far below this critical value, indicating that only a very small proportion of the CEC was occupied by K^+. This result may indicate that these soils favored adsorption of other cations than K^+.

K adsorption characteristics

The amount of K adsorption at the highest concentration of added potassium solution (3000 mg K /kg soil) ranged from 63% to 73% for topsoil horizons, and from 66% to 75% for subsoil horizons. The added K in these soils showed a good fit with the Freundlich adsorption isotherm for both topsoil and subsoil horizons (R^2 = 0.909–0.985) **(Figure 2)**. In contrast, the added K was only well fitted by the Langmuir adsorption equation for subsoil horizons (R^2 = 0.005–0.558 for topsoil horizons and R^2 = 0.782–0.955 for subsoil horizons). This result suggested that K adsorption characteristics in these soils occurred on heterogeneous surfaces rather than through monolayer adsorption, because the Langmuir adsorption equation generally assumes homogeneity of sorption sites with complete monolayer adsorption of solutes (Ali et al., 2013). The good fit with the Freundlich adsorption isotherm for K adsorption characteristics in these soils was consistent with the existence of 2:1 clay which K could be adsorbed on both internal and external surfaces. This good fit of the Freundlich adsorption isotherm on K adsorption characteristics has been reported by many researchers (Pal et al., 1999; Hannan et al., 2007; Bangroo et al., 2012). However, the better fitted of added K to Langmuir adsorption equation in subsoil than in topsoil may attribute to the greater influences of both organic matter and clay minerals in topsoil (higher heterogeneity) in comparison to subsoil where only clay minerals could mainly be reacted to the added K (lower heterogeneity). (Spark, 2003; Darunsontaya et al., 2018).

In general, the Freundlich K*f* parameter indicates adsorption capacity. The current study found K*f* values of Thai lowland Vertisols ranging from 24.7 to 42.6 L/kg, and 52.8 to 83.5 L/kg for topsoil and subsoil horizons, respectively (Table 3). The K*f* value of these soils showed a strong negative correlation with soil OM content **(Figure 3a)**. This result was consistent with the lower K*f* values in topsoil horizons than that of subsoil horizons in all soils. The lower K adsorption capacity of topsoil horizons compared to that of subsoil horizons may be attributed to the affinity of organic ligands for the sorption sites (Hafiz et al., 2016). Sharma et al. (2006) suggested that the decrease in the adsorption capacity is due to the possible blockade of exchange sites in the soil by soluble humic substances, while removal of soil OM increases the adsorption maxima (Marzadori et al., 1991). Olk and Cassman (1995) reported that addition of nitrogen-rich soil organic matter fraction (mobile humic acid pool enriched with amino acid) reduced K fixation in calcareous vermiculitic soils. Such result was consistent to that reported by Jindaluang et al. (2013) who found that OM composition in fine-textured soils including Thai smectitic soils is dominated by amide ($-NH_2$) groups. This functional group might provide the positive charges in these soils and thus compete with K^+ on adsorption sites. Also, there is a negative correlation between K*f* values and extractable K content in the soil (R^2 = 0.68) **(Figure 3b)**. This result indicated that K adsorption capacity in these soils corresponded to their available exchange sites.

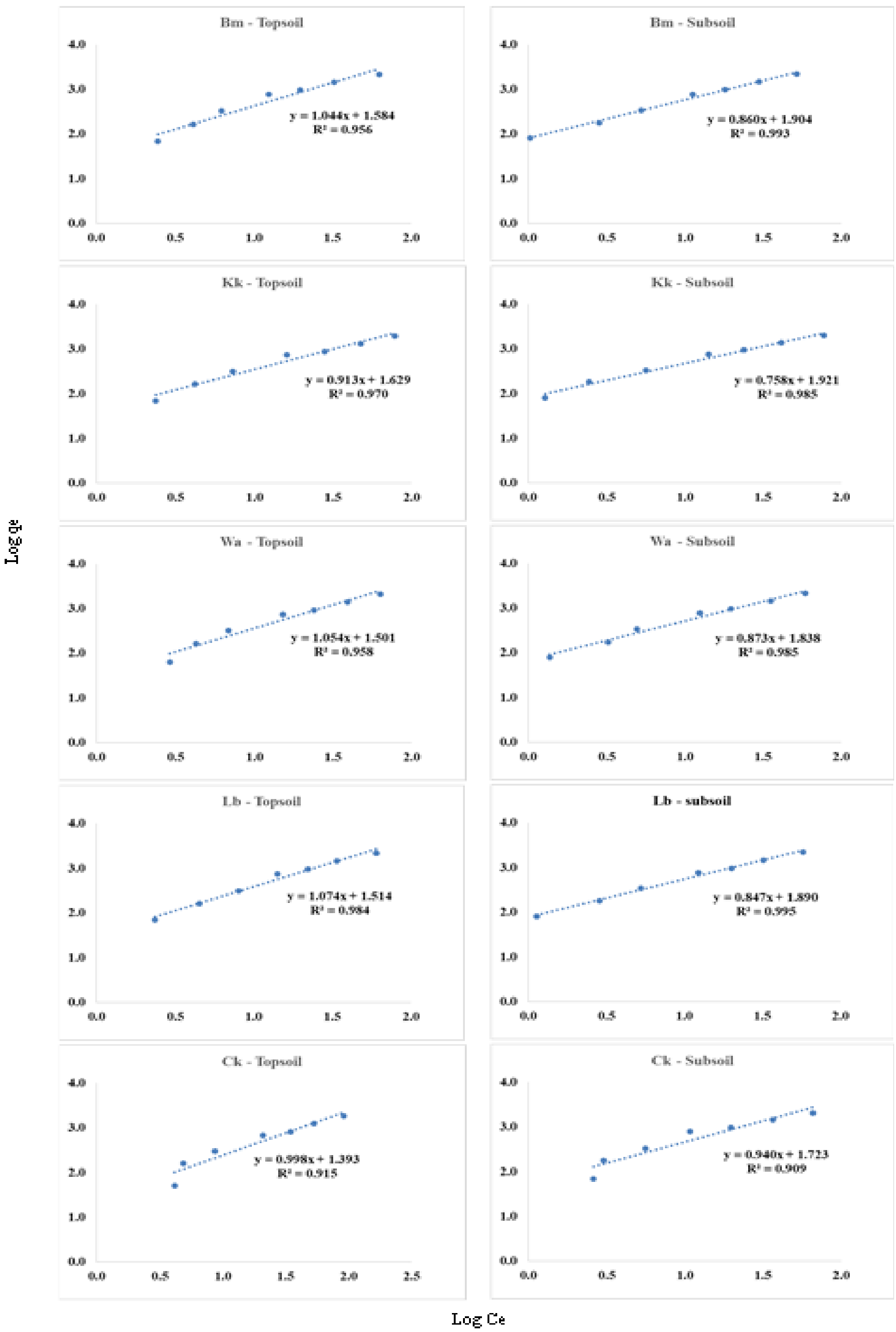

Figure 2 Linear fitting curves of K adsorption by Freundlich isotherm on Thai lowland Vertisols

Table 4 Estimated Freundlich isotherm constants of Thai lowland Vertisols

Soil series	Horizon	Freundlich isotherm			Extr.K/Extr.Mg[1/]
		K*f* (L/kg)	1/*n*	R^2	
Bm	Top	38.4	1.04	0.956	0.031
	Sub	80.2	0.86	0.993	0.016
Kk	Top	42.6	0.91	0.970	0.021
	Sub	83.5	0.76	0.985	0.022
Wa	Top	31.7	1.05	0.958	0.052
	Sub	68.9	0.87	0.985	0.028
Lb	Top	32.7	1.07	0.984	0.036
	Sub	77.6	0.85	0.995	0.007
Ck	Top	24.7	0.99	0.915	0.035
	Sub	52.8	0.94	0.909	0.016

Extr.= extractable

The Freundlich 1/*n* parameter is the slope of straight line when data has fitted to the Freundlich model. This constant describe the linearity of adsorption across the concentration range tested. Typically, value of 1/*n* value equal to 1 indicates that the rate of K adsorption is constant across the whole range of added K in the experiment. Whereas value of 1/*n* less than 1 signified that when the concentration of K under investigation increases, the relative adsorption decreases. In other words, high rate of K adsorption occurs at low K concentrations, and vice-versa for value of 1/*n* higher than 1. (Bangroo et al., 2012, Ali et al., 2013). The results of this study showed that the rate of K adsorption in these soils ranged from 0.76 to 1.07 with a mean value of 0.936 **(Table 4)**. In general, the rate of K adsorption in these soils mainly approached unity (nearly 1.00) in topsoil horizons. This result suggested that the rate of K adsorption was not affected by increasing of K concentration. However, values of 1/*n* in subsoil horizons were less than 1.00. This result indicated that the rate of K adsorption decreased with increasing K concentration in subsoil horizons. The decrease in relative adsorption may imply that adsorption sites in subsoil horizons tend to be saturated with K^+ when solution K concentration increases, resulting in lower K adsorption.

There was a positive relationship between the rate of K adsorption and available K content in these soils **(Figure 3c)**. When the available K content increased, the rate of K adsorption increased. This result suggested that the rate of K adsorption in these soils was partially dependent on available K content. Furthermore, the rate of K adsorption in these soils showed a positive relationship with the ratio of K:Mg in soils **(Figure 3d)**. The result highlighted that when the concentration of Mg in the soil system increased, the rate of K adsorption decreased. Feigenbaum et al. (1990) noted that with increasing concentration of competing cations (e.g. Ca^{2+}, Mg^{2+}), K^+ may be more easily leached from root zone. Therefore, the findings of this study showed that due to the dominant basic cations, Ca and Mg in these soils, long-term stability of K levels in these soils may not be promoted as shown by the decrease in the rate of K adsorption or energy of K adsorption in these Thai lowland Vertisols as the K:Mg ratio decreased.

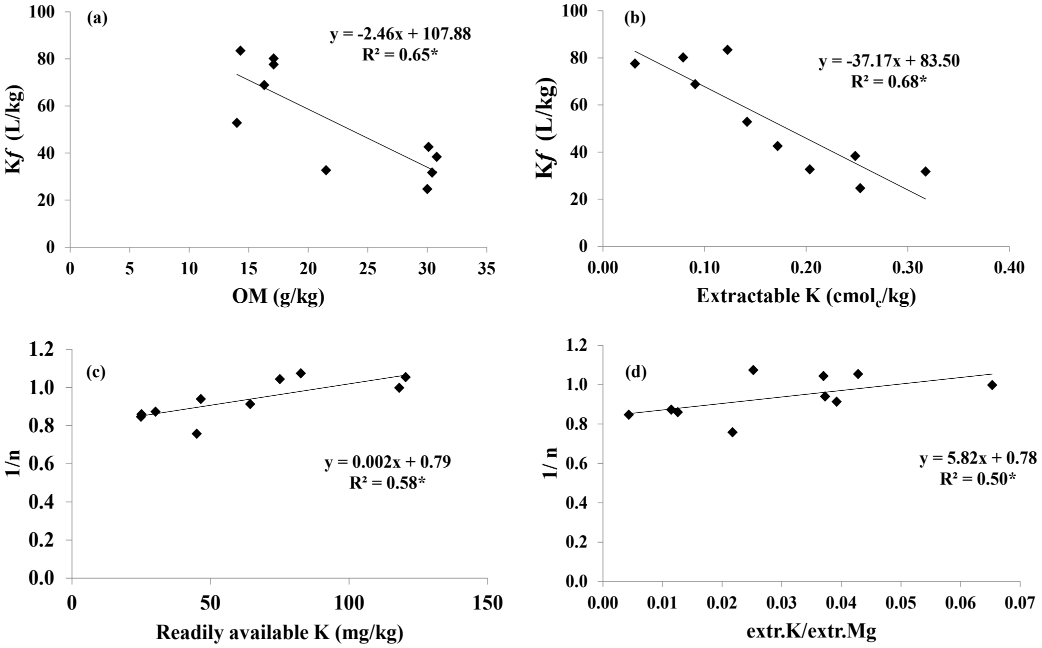

Figure 3 Relationships between Freundlich isotherm constants and some soil properties. $*P \leq 0.05$

Conclusions

Results of this study showed that most Thai lowland Vertisols contained low level of available K (except in topsoil horizons of Wa and Ck) and all soils have low K reserve. The results also revealed that various forms of K contents and K adsorption characteristics of selected Thai lowland Vertisols were not directly dependent on clay content and CEC. Instead, soil OM and other basic cations such as Ca and Mg strongly affected various forms of K contents and their activities in soils. Although these soils had high K adsorption capacity, competition between K^+, organic substances, and other basic cations may reduce the retention of K in this soil system. Moreover, the low soil K saturation values found in the present study contradict the current belief that these Thai soils do not require addition of K fertilizers. Therefore, application of fertilizers formulated with K would potentially affects short-and long-term crop yield in these clayey soils. Furthermore, application of K fertilizers will be more effective, if K fertilizers are applied in periodic small doses during rice growing to reduce K losses.

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