## Relationship between K release from clay fraction to NaTPB solution and properties of clay for Thai upland soils

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#### Introduction

Thai upland soils normally have low exchangeable and non-exchangeable K levels because the high weathering and leaching promoted by high rainfall and high temperatures have removed much K. A measurement of buffer power that takes into account the contribution of exchangeable and non-exchangeable K and clay mineralogy is important for the proper management of K in crop production as non-exchangeable K contributes a significantly proportions of K to plant nutrition (Huang, 2005). There are few studies of the K status or the relationships between K release and clay properties for these soils. In particular it is necessary to identify the mineral species containing K (feldspar, micas, etc) and the availability of these forms of K.

## **Materials and Methods**

Surface and subsurface samples of 18 upland Oxisols and Ultisols from the Southeast Coast and Peninsular Thailand were used for this study. Clay samples were separated and the amount of K release, the chemical composition and the mineralogical properties of the clay were determined. Exchangeable K was determined by extraction in 1M NH<sub>4</sub>OAc. Non-exchangeable K release was determined by shaking clay samples with 0.3M sodium tetraphenylboron (NaTPB) solution for 168 hours and subtracted the exchangeable K value. XRD of the K-depleted clay was used to identify the mineral sources of this K. Total chemical composition of the clay was determined using X-ray fluorescence spectrometry.

#### Results

#### Properties of clay

All clay fractions contain much kaolinite, and various amounts of minor accessory clay minerals including illite (K containing), smectite and hydroxyl Al interlayered vermiculite together with quartz, feldspar (K containing), goethite, hematite, maghemite, gibbsite, boehmite and anatase. Minor amounts of illite (5-20%) are present in Sh, Tim1 and Cp clays and trace amounts of illite occur in Nb1, Pk, Pga and Tim2 clays.

The CSD size of kaolinite calculated from the 001 reflection of the kaolinite ranges from 8.9 to 41 nm but is not systematically different between the two soil groups (Table 1). The kaolinite in Ti and Nb

which is derived from basalt has smaller crystal sizes than for soils derived from clastic rocks. The CEC of the clays range from 5.6 to 44.4 cmol/kg and specific surface area (SSA) from 1.6 to 81.6  $m^2/g$ . The Oxisols clays have higher values of CEC and SSA than the Ultisols clay due to the smaller crystal size of kaolinite and iron oxide minerals in Oxisols. Values of the surface charge density (CD) of the clay fraction calculated from CEC and SSA range from 0.12 to 3.0 C/m<sup>2</sup>. The greater values of CD for Ultisols clays are likely to reflect the more common presence of small amounts of illite, vermiculite and/or smectite which may have higher values of surface charge density than kaolinite.

	Oxisols	(n=14)	Ultisols (n=22)			
Clay property and K release	range	mean	range	mean		
CSD 001-kaolinite (nm)	9.2-32	19	8.9-41	18		
CEC (cmol/kg)	19-44	35	5.7-39	21		
SSA $(m^2/g)$	15-81	48	8.6-51	30		
$CD(C/m^2)$	0.20-2.1	0.91	0.12-3.0	1.1		
Exch. K (mg/kg)	44-200	105	41-226	99		
Exch. Mg (mg/kg)	2.0-187	41	3.8-214	73		
Total K (mg/kg)	276-2581	919	243-25115	6370		
Total Mg (mg/kg)	1180-2234	1823	893-5848	1841		
Total Rb (mg/kg)	2.0-31.0	17.1	5.0-398	111		
K released at 168 hour (mg/kg)	39-135	86	26-548	149		

Table 1. Range and mean value of some properties of clay for Thai upland Oxisols and Ultisols.

## The amount of K release in relation to clay properties

The amount of non-exchangeable K release to NaTPB solution ranged from 39 to 135 mg/kg for Oxisols and from 26 to 548 mg/kg for Ultisols. The amounts of K released from illite-containing clays were much higher than from soils containing only kaolinite and inhibited vermiculite. The K released values have been statistically related to clay properties (Table 2) and the results show that the amount of K released has significant positive relationships with K, Mg and the ratio of illite to kaolinite of the clay. These properties are associated with illite content in these clays. The release of non-exchangeable K is not related with either CEC and SSA. This is probably due to non-exchangeble K being mostly from interlayer sites in illite and not from the external surface or interlayer cation exchange sites of kaolin which is the dominant clay mineral in these soils and provides most of the SSA and CEC.

Total Rb is strongly correlated with total K content in all parent rock (Fig. 1). Total Rb was also related to the release of K from these clays. The higher Rb in clays are for soils derived from sediment and granitic rock in which Rb is probably present in K-feldspar, mica grain and clay minerals.

	К	CEC	551	CD	CSD 001	111/1/200	Exchangeable		Total content			
	Released	CEC	33A	CD	kaolinite	III/Ka0	Κ	Mg	K	Mg	Rb	Ca
K Released	1.00											
CEC	0.04	1.00										
SSA	-0.22	0.06	1.00									
CD	0.29	0.56	-0.71	1.00								
CSD 001	-0.32	0.04	-0.40	0.19	1.00							
Ill/kao	0.81	0.11	-0.36	0.47	-0.39	1.00						
Ex.K	0.55	0.28	-0.19	0.26	-0.32	0.57	1.00					
Ex.Mg	0.35	-0.27	-0.14	-0.04	-0.23	0.20	0.11	1.00				
Total K	0.73	0.03	-0.37	0.49	-0.46	0.71	0.32	0.44	1.00			
Total Mg	0.81	0.09	-0.05	0.17	-0.39	0.55	0.50	0.21	0.57	1.00		
Total Rb	0.69	-0.16	-0.27	0.26	-0.39	0.56	0.17	0.55	0.90	0.46	1.00	
Total Ca	0.11	0.36	-0.19	0.44	-0.31	0.22	0.26	0.42	0.45	0.10	0.38	1.00

Table 2. Correlation coefficients (r) for relationships between the K release from clay and clay properties



.Fig. 1. Relationship between K and Rb contents in the clays from various parent rocks.

# Mineralogical changes as affected by extraction of K by NaTPB

XRD patterns were modified by dividing intensities by the Lorentz-polarisation (LP) factor to provide greater clarity in the low 2 $\Theta$  region (Brown and Brindley, 1980). The three XRD patterns for Mg saturated clay, namely before extraction, after 16 hours and after 168 hours of extraction by NaTPB were identical for most soils. In particular the basal reflection of kaolinite did not change. However for Sh, Tim1 and Cp soils, extraction of K led to a substantial decrease in illite content and to an increase in vermiculite (Fig. 2). This is evidence for the release of K from the interlayer site of illite in these clays.



Fig. 2. Diffraction patterns of basally oriented, Mg-saturated clay of Cp soil modified using the LP factor showing changes in the relative peak intensity of vermiculite and illite for 16 and 168 hours of shaking with 0.3M NaTPB. (V=vermiculite, I= illite, K= kaolinite). The reflection at 11° 20 is due to KTPB

## Conclusion

Clay mineralogy is the major factor controlling the release potassium to NaTPB solution from these soil clays. The amounts of K released from illite-containing clay are much higher than for clay containing only kaolinite with or without inhibited vermiculite. For these Thai soil clays in which kaolinite is the dominant clay mineral, the release to NaTPB of significant amounts of K is indicative of the presence of long-term available K in the soil. The possibility that kaolinite contains minor amount of interlayer K requires investigation. Values of exchangeable K indicate that most soils have low K reserves but this interpretation may need to be revised on the basis of the presence of significant amounts NaTPB extractable-K.

#### Acknowledgments

The authors are grateful to The Royal Golden Jubilee Ph.D. Program under the Thailand Research Fund for financial support and to the laboratory staff at the School of Earth and Environment, UWA.

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