A comparison of extraction methods to assess potassium availability for Thai upland soils

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Abstract
The effectiveness of several extraction procedures for K in predicting K uptake by Guinea grass in the glasshouse was determined for 18 upland soils from Thailand. NH_4OAc solution extracted exchangeable K that is closely related (R^2=0.97) to plant K uptake at 168 days, by which time most plants had died from K deficiency. This linear relationship has near unit slope so that plant uptake of K is quantitatively determined as exchangeable K. HNO_3-K and NaTPB-K determine different forms of non-exchangeable K in these soils that were relatively weakly related to the plant K uptake (R^2=0.62 for HNO_3-K and R^2=0.45 for NaTPB–K). These relationships indicate that exchangeable K is the K available to plants and non-exchangeable K was not readily available for plant growth over the time scale of the experiment. The XRD patterns of clay from the soils after cropping mostly show no change from that of the initial soil confirming that plant growth did not affect mineral forms of K. XRD patterns for samples extracted with NaTPB show a decrease in illite (001) peak-intensity with a concomitant increase in vermiculite (001) peak-intensity due to K removal from interlayer site in illite by NaTPB.

Key Words
Non-exchangeable K, HNO_3-K, NaTPB-K, NH_4OAc-K, highly weathered soils

Introduction
In Thailand, potassium deficiency is widespread under a tropical monsoonal climate in crops on highly weathered upland soils which are deficient in K bearing minerals. Critical assessment of the ability of soils to release K for plant uptake is important for the proper management of K in crop production. Exhaustive cropping techniques in a glasshouse study combined with chemical analyses of soils are useful for relating plant uptake of K to the various forms of soil K (Martin and Sparks 1985). For particular soil–plant systems, the suitability of a soil test extractant for predicting K supply depends on how closely the extracted K indicates the actual uptake of K by plants. Most extractants determine readily available K, which is generally assumed to be solution K plus exchangeable K. Replenishment of plant available K will depend on the release of mineral forms of K. For effective K management of Thai upland soils it is necessary to identify forms of K including mineral species containing K in these soils and establish which forms of K are released to plants.

Methods
Site sampling and physico-chemical analyses
Surface and subsurface samples of 18 upland agricultural soils from the Southeast Coast and Peninsular Thailand were used for this study. The physico-chemical properties were analyzed using standard methods (National Soil Survey Center 1996). Bulk soil samples were air–dried and crushed to pass through a 2 mm sieve before laboratory analysis. Soil pH was determined in water and in 1M KCl using 1:1 soil:liquid. Organic carbon (OC) was determined by the Walkley and Black wet oxidation procedure (Nelson and Sommers 1996) and calculation of organic matter content (OM) used the relationship OM = OC × 1.724. Cation exchange capacity (CEC) was determined by saturating the exchange sites with an index cation (NH_4^+) using 1M NH_4OAc at pH 7.0. Extractable acidity was measured by barium chloride-triethanolamine ($BaCl_2$-TEA) buffered at pH 8.2. Available phosphorus was determined by the Bray II method. Particle size distribution was determined by the pipette method.

X–ray diffraction (XRD) analysis of the clay fraction used CuKα radiation with a Philips PW–3020 diffractometer equipped with a graphite diffracted beam monochromator. Oriented clay was prepared on ceramic plates and XRD patterns were obtained from 4–35° 2θ with a step size of 0.02° 2θ and a scan speed of 0.04°/second after various pretreatments to aid the identification of clay minerals (Brindley and Brown 1980).

Potassium study
Exchangeable K was determined by extraction in 1M NH_4OAc at pH 7.0. Non-exchangeable K was determined using two chemical extractants. One molar HNO_3-extractable K (HNO_3-K) was determined by boiling 2 g of soil in 20 mL 1M HNO_3 at 113°C for 25 minutes (Pratt, 1965). NaTPB-K was extracted by shaking 1g of clay in 10 mL of 0.3M NaTPB for 168 hours. One milliliter of 1M NH_4OAc was immediately added to the suspension to prevent continuing K exchange from the suspended clay and to block subsequent fixation of dissolved K. The KTPB precipitate was then dissolved in 50 mL of 70% acetone. The acetone was then collected from the sample by filtration and acidified with 5 mL 6M H_2SO_4. The resulting solution was heated on a hot plate for 2 hours at 60°C to concentrate the H_2SO_4 which was then made up to a final volume of 100 mL with deionized water. Potassium in this solution was determined with a flame photometer (Schulte and Corey 1963, 1965). The values of K released from the clays to NaTPB solution were converted to a whole soil basis by multiplying by the clay proportion. HNO_3-K and NaTPB-K also included NH_4OAc-K. Total K in soils was determined using X-ray fluorescence spectrometry.

An exhaustive K depletion glasshouse experiment was conducted on these soils using Guinea grass (*Panicum maximum*) to assess their K supply capacities. One kilogram of air-dry soil per pot was used for cropping and basal nutrients were applied initially and after each harvest to ensure that general nutrient supply did not limit plant growth. Thirty grass seeds were sown in each pot and thinned to 4 uniform plants after emergence. Soils were watered daily to field capacity with deionised water. The grass was harvested every 30 days and the K content of plants was determined after acid digestion.

Results
Classification and general properties
These Thai upland soils are highly weathered and highly developed. They are classified as Oxisols and Ultisols and all soils experience a udic soil moisture regime. They exhibit a wide range of general properties (Table 1). The pH in water and in 1M KCl ranges from 3.7 to 6.5 and from 3.4 to 5.6 respectively. The CEC of these soils ranges from 1.4 to 28 cmol/kg, OM ranges from 0.3 to 30 g/kg, EA ranges from 1.1 to 27 cmol/kg and available P ranges from 0.3 to 176 mg/kg. Soil texture ranges from sand to clay. Most of soil samples have low values of pH, CEC and organic matter because of their advanced weathering due to the high rainfall and elevated temperatures in this region.

Table 1. Range and mean value of some properties of Thai upland soils.

Property	min	max	mean
pH (1:1 H_2O)	3.7	6.5	5.0
pH (1:1 KCl)	3.4	5.6	4.1
CEC (cmol/kg)	1.4	28	6.9
EA (cmol/kg)	1.1	27	7.6
OM (g/kg)	0.3	30	5.6
Available P (mg/kg)	0.3	176	25
Sand (g/kg)	43	811	471
Silt (g/kg)	35	453	160
Clay (g/kg)	76	872	369
NH_4OAc-K (mg/kg)	8.0	212	37
HNO_3-K (mg/kg)	25	248	79
NaTPB-K (mg/kg)	7.5	189	57
Total K (mg/kg)	67	29931	3366

Soil potassium determined by various extraction methods
NH_4OAc extractable K in these soils ranges from 8.0 to 212 mg/kg (mean 37 mg/kg) and includes water soluble and exchangeable K. The Oxisols have higher values of this K form than the Ultisols due presumably to the higher clay content of Oxisols. HNO_3-K ranges from 25 to 248 mg/kg (mean 79 mg/kg) and NaTPB-K ranges from 7.5 to 189 mg/kg (mean 57 mg/kg). The mean value of NaTPB extractable K is less than HNO_3-K because nitric acid extractable K includes non-exchangeable K from the destructive

dissolution of silicate minerals, whereas NaTPB extraction is less severe and only extracts structural K from interlayer sites in micaceous minerals. However, K removed by all three extractants represents only a small proportion of total soil K, as has commonly been reported for other highly weathered soils (Markewitz and Richter, 2000)

Relationships between K removed by the extraction procedures and plant K uptake

The values of K removed by the three extractants have been compared with the K taken up by plants during 180 days of growth in a glasshouse experiment, by which time most plants had died from K deficiency (Figure 1). The results show that cumulative K uptake by plants has weak exponential relationships with NaTPB-K (R^2=0.45) and HNO_3-K (R^2=0.62). There is a much closer linear relationship between plant K content and NH_4OAc-K (R^2=0.97) with the plant K content being numerically equal to the exchangeable K content of the soil (*i.e.* slope of regression line is nearly unity) (Figure 1c). This relationship indicates that exchangeable K is practically the only form of K available to plants and that non-exchangeable K is not readily available for plant growth over a period of 180 days.

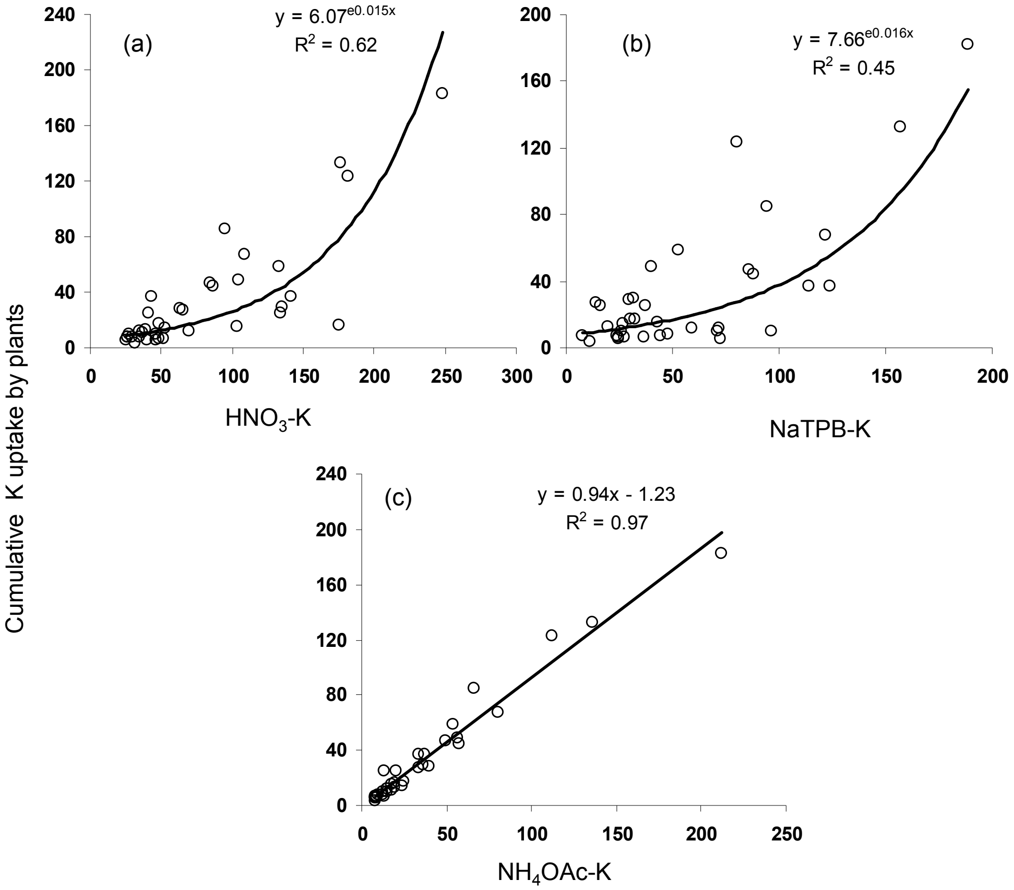

Figure 1. Relationships between soil K removed by extractants and cumulative K uptake by Guinea grass in 180 days.

Availability of K to plants in relation to clay mineralogy

The clay fractions of these soils contain much kaolin and various amounts of minor accessory minerals including illite, gibbsite, anatase, quartz, maghemite, hematite, goethite and hydroxyl Al interlayered vermiculite. XRD patterns of clays shows that there was no change in clay mineralogy due to plant growth indicating that the structure of the clay minerals was not affected by K depletion due to plant growth. This is consistent with K being provided to plants from the exchange sites and not from the structural sites in layer silicates. However, the XRD pattern from a sample extracted with NaTPB for 168 hours and that contains illite shows a decrease in illite (001) peak-intensity with a concomitant increase in vermiculite (001) peak-intensity due to K removal from illite by NaTPB (Figure 2).

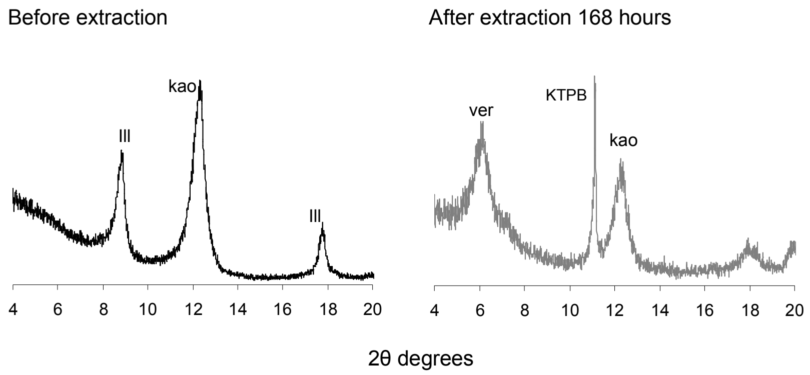

Figure 2. Diffraction patterns of basally oriented, Mg-saturated clay from Chumphon (Cp) surface soil showing changes in the relative peak intensities of vermiculite and illite resulting from 168 hours of shaking with NaTPB. (Ver=vermiculite, Ill= illite, Kao= kaolinite). The reflection at 11° 2Θ is due to KTPB.

Conclusions

This study has identified NH_4OAc-K as being a highly predictive indicator of the availability of K to plants grown in the glasshouse for these highly weathered upland soils whereas NaTPB-K and HNO_3-K are not readily available to plants. The K-exhaustion glasshouse experiment involved small volumes of soil that were intensively exploited by roots and the removal of plant tops ensured that there was limited recycling of K. Under field conditions plant roots can exploit a much larger volume of soil and recycling of K from foliage can occur. Furthermore, under a humid tropical climate the weathering process can promote the release of K from K-minerals. Consequently, K exhaustion of soils will occur at a slower rate in the field. However these soils clearly contain little exchangeable K and the non-exchangeable K is not readily available to plants so that soil K will eventually become too low to support annual field crops if K fertilizers are not provided.

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