PREDICTING PLANT AVAILABLE POTASSIUM USING A MODIFIED SODIUM TETRAPHENYLBORON METHOD[1]

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ABSTRACT

Current potassium (K) fertilizer recommendations in the midwest are based primarily on the ammonium acetate exchangeable K (NH_4OAc) soil test. In soils where nonexchangeable K comprises a major portion of plant available K, the ammonium acetate soil test is unreliable. Soil K extraction by sodium tetraphenylboron (Na-TPB) accesses both exchangeable and nonexchangeable K and mimics the action of K uptake by plant roots. A Na-TPB method utilizing a 5-minute extraction period is described, and the potential of the method to predict plant available K in 11 midwestern soils was evaluated. The extraction procedure is fairly rapid and the additional reagent cost over the NH_4OAc method is approximately $0.10 per sample. Results of exhaustive cropping in the greenhouse showed that in all soils, the Na-TPB procedure gave good prediction of K uptake by wheat before plants became deficient ($r^2 = 0.94$), but the 1 *M* NH_4OAc method failed to predict plant available K in soils in which nonexchangeable K contributed significantly to plant nutrition. At every period of soil sampling during the cropping period K removed by wheat uptake was well reflected in the change in Na-TPB K (ΔNa-TPB K = -61 + 1.0 x K removed, $r^2 = 0.95$), but not NH_4OAc K (ΔNH_4OAc K = 15 + 0.39 x K removed, $r^2 = 0.40$). This study shows that the Na-TPB procedure can probably be used as a K soil test method. Field correlation and calibration studies are needed to further evaluate the utility of the method.

INTRODUCTION

The primary goal of soil testing for potassium (K) and other plant nutrients is to estimate the potential of an economic return on fertilizer investment. Our inability to predict plant nutrient availability at small scales in the field is a major limitation in precision farming. In the midwest, the ammonium acetate (NH_4OAc) exchangeable soil test procedure is used to estimate plant available K and establish guidelines for K fertilization. Exchangeable K determinations may be adequate for predicting K availability in soils where nonexchangeable pools do not constitute a substantial portion of plant available K. However, in some soils in this region, crop response to K fertilizer recommendations can be erratic because the NH_4OAc extraction procedure does not estimate the amount of nonexchangeable K that can become available to a crop during the growing season. Soil test methods that can estimate the availability of both exchangeable and nonexchangeable K over a wide range of soil types will help delineate the variability of K status in fields and improve our ability to predict the likelihood plant response to fertilizer K. This will greatly enhance the economic potential of variable rate technology.

The sodium tetraphenylboron (Na-TPB) extraction procedure was developed by Smith and Scott (1966) to release nonexchangeable K held in the interlayer of soil micas. We chose this reagent to estimate K availability because it mimics the action of plant roots by lowering the concentration of K in solution to facilitate the release of nonexchangeable K. This procedure

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was modified by Cox et al. (1996) to make it more adaptable for routine work. Since then, additional modifications have been made to refine its potential as a soil test method for K. In this paper we present, (i) a description of the procedure, and (ii) results from a greenhouse study conducted to evaluate the potential of the procedure to estimate plant available K in some midwestern soils.

METHODS

Soils

Eleven surface soils (0-30 cm) representing a wide range of textural classes were collected from five Midwestern states (Indiana, Iowa, Ohio, Kentucky, and Wisconsin). Selected soil properties are presented elsewhere (Cox et al., 1996). Soil texture ranged from sand to clay loam and cation exchange capacity ranged from 4.4 to 36 $\mathrm{cmol_c\ kg^{-1}}$. Potassium status of the soils was determined by 1M NH_4OAc and by 3 Na-TPB extraction times (5 minutes, 15 minutes, and 7 days).

Sodium Tetraphenylboron Extraction Procedure

The Na-TPB extraction method is a three step procedure. In the first step the TPB^- anion combines with K in solution and precipitates as potassium tetraphenylboron (K-TPB), while Na acts as an exchanger for K. The rate of K release increases as the Na concentration in the extracting solution increases to a maximum of about 1.9 *M* Na. In the second step the extraction is quenched by adding NH_4Cl. Ammonium in the quenching solution serves to stop further release of K from nonexchangeable sites and precipitate the excess TPB^- as NH_4-TPB. Finally, in the recovery step Cu breaks down the TPB^- anion after K-TPB is dissolved on boiling.

Subsamples of 0.5 g soil were weighed into Folin wu tubes and 3 mL of extracting solution (1.7 *M* NaCl-0.01 *M* EDTA-0.2 *M* Na-TPB) added. After each incubation period (5 minutes, 15 minutes, or 7 days), 25 mL of quenching solution (0.5 *M* NH_4Cl-0.11 *M* $CuCl_2$) was added to the tube to stop the reaction. The tube was placed in a heating block on a hot plate at approx. 150 degrees C and left until the precipitate dissolved completely (30 to 45 minutes). The suspension in the tubes was made to 50 mL, mixed, then left to sit for 30 minutes to allow most of the soil to settle down. A 20-mL aliquot of the clear solution was poured into 50 mL centrifuge tubes containing three drops of 6 *M* HCl then spun at 2,000 rpm for 5 minutes. Acidification of the extract helps to prevent precipitation of Cu and the break-down products of Na-TPB. Aliquots of the clear supernatant were diluted ten times with dionized water and K determined by flame emission spectrophotometry. The matrix of all standards used for calibration were prepared similar to that of the sample.

Plant K Uptake in the Greenhouse

The experiment was conducted using a randomized complete block design with eleven soils and three replications. One-kilogram portions of each soil were blended with a minus K-nutrient mixture and left to equilibrate moist on the greenhouse bench for 1 week. Winter wheat (*Triticum aestivum* L. 'Abe') was sown at fifteen seeds per pot, then thinned to twelve plants per pot after emergence. Pots were watered daily with reverse osmosis water and all drainage collected in a base container and returned to the pots to minimize nutrient loss by leaching. Nitrogen was supplied weekly at 40 mg N kg $\mathrm{soil^{-1}}$ as calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$). Plant tops were harvested every 28 days for a total of three harvests. After the third harvest, the soil in the pots was sieved moist and a sample obtained for analysis. The soil sample was weighed to determine the mass of soil remaining in the pots. The remaining soil was blended with the minus K-nutrient mixture and returned to the pots for another cropping cycle as described previously. The sequence of cropping and soil sampling was done three times (nine crops) for soils in which K was depleted relatively quickly and five times (fifteen crops) for soils needing more extensive cropping for K depletion. The number of plants per pot and addition of nutrients was reduced for each additional cropping sequence to minimize variation in the plant density and soil fertility throughout the experiment.

Plant tissue was digested in a mixture of sulfuric acid and hydrogen peroxide for K determination. Potassium in the soil samples collected at the end of each cropping sequence was determined using both the 1M NH_4OAc and 5-minute Na-TPB extraction methods.

RESULTS AND DISCUSSION

Sodium Tetraphenylboron Method

The precision of the 5-minute Na-TPB extraction procedure was tested by two operators using replicated analysis of five soils having a wide range of textures, exchangeable K and total Na-TPB-extractable K (7-day incubation) (Table 1). The results obtained by operator 1 showed relatively high variability (CV = 8 to 10). Operator 2 obtained good precision (CV = 1 to 5%) except in the Bloomfield soil. There was essentially no difference in the means obtained by each operator. These results show that the procedure outlined has good potential for routine work, but some effort is needed to improve its precision. Using a larger samples for analysis (for example 1 or 2 g) may help to increase the repeatability.

The potential utility of the extraction procedure must be based on both analytical and economic considerations. The amount of Na-TPB used should not limit the amount of K that is potentially extractable for any specified incubation time (5 minutes in this case). The total moles of Na-TPB used per sample should be at least 2x as much as the K that is potentially extractable in the sample. Using this '2x rule', the 0.6 *mM* Na-TPB used in this procedure can effectively extract 12 mg K or 24,000 ppm K in a 0.5 g sample. In the approach outlined, for either unfertilized or fertilized soils, samples as large as 2 g can be used to effectively extract K. Whenever the Na-TPB method is used to extract large quantities of K, selection of sample size and total moles of Na-TPB in the extracting solution should be dealt with accordingly.

The Na-TPB reagent is relatively expensive and represents about 75% of reagent cost for the procedure outlined. Using current retail prices (Fisher Scientific), total reagent cost for the Na-TPB procedure is about $0.38 per sample compared to $0.28 per sample for the conventional NH_4OAc method. Because additional reagent cost for the analysis is relatively minor, the utility of the method for routine soil testing may be based mainly on its ability to estimate plant available K. The extraction procedure outlined can be conducted fairly rapidly (approx. two hundred samples per 8 man hr.). Further modifications and automation can also help to increase the speed of extraction.

If the procedure is adapted for routine work, disposal of analytical waste is an important consideration. The extraction procedure produces 175 mg Cu and 205 mg of break down products of Na-TPB per sample as waste. This amount of Cu is the lower limit for effective recovery of K precipitated by Na-TPB. Proper guidelines of waste disposal should be followed.

Potassium Status of Soils

There were considerable differences in the K status of the soils used in this study (Table 2). Based on the fertilizer recomendations used in Indiana, Ohio, and Michigan (Vitosh et al., 1995), for all the soils except the Chalmers and Milford, exchangeable K was above the critical level (K status at which alfalfa, corn, soybeans, and wheat will likely respond to K fertilization). The Na-TPB extracted at each time period represents all the solution and exchangeable K, and a portion of the nonexchangeable K held in the interlayer of soil clays. The 7-day extraction period releases almost all interlayer K, and is an estimate of the total reserve that can potentially replenish more readily available K pools. Potassium that is extractable in the shorter incubation periods (5 and 15 minutes) should be much more available. There is little relationship between NH_4OAc- and Na-TPB-extractable K. Because Na-TPB can access both exchangeable and interlayer K, the amount of K that can be extracted depends largely on soil mineralogy. The Hoytville and Pewamo soils have micaceous mineralogy, therefore they have relatively large reserves of nonexchangeable K (Table 2). Exchangeable K determination may indicate only the immediate K supply, but Na-TPB extraction can probably better estimate the long-term K-supplying power of soils.

Potassium Uptake in Relation to Soil Test K

Optimum potassium content of wheat grown under the conditions outlined in the greenhouse was established by growing wheat in a K deficient Chalmers silt loam at various K fertilization rates. The relationship between relative dry matter yield and K concentration in plant tissue indicated a critical K level of 1.9 % K (data not shown). This K concentration is within the sufficiency range (1.5-3%) reported for field-grown wheat (Ward et al., 1973). For the entire greenhouse study K content below this critical level was used as evidence of K deficiency. The cumulative amount of K taken up by wheat through the crop cycle where tissue K concentrations fell below the critical level (Table 3) was used as an estimate of plant available soil K. The first wheat crop in the Chalmers and Milford soils were below the critical level. Therefore, these two soils were rated as K-deficient according to the conditions outlined in this experiment. The data in Figure 1 show the relationship between wheat K concentrations for the first harvest within each of the five cropping sequences and soil K determined by both the NH_4OAc and Na-TPB methods in soil samples analyzed immediately prior to planting each of the five crops. Above 150 mg K kg $soil^{-1}$ using the NH_4OAc method and 400 mg K kg $soil^{-1}$ using the Na-TPB method, wheat tissue K concentrations were generally above the critical level. Although these data cannot be used to make reliable estimates of critical soil test K, it is evident that critical levels for Na-TPB may be higher than those for NH_4OAc.

The amount of K removed by wheat prior to becoming K deficient varied widely among soils (Table 3). This cumulative uptake was greater than the initial 1 *M* NH_4OAc-exchangeable K (Table 2). This indicates that nonexchangeable K can contribute a significant portion (up to 75% of uptake) of available K. The inability of the NH_4OAc method to estimate available K was most obvious in the Bloomfield and Hoytville soils. Exchangeable K levels in these soils were relatively low (Table 2), but substantial amounts of nonexchangeable K were available for plant uptake. Wheat K concentrations remained above the critical level for all fifteen wheat harvests in the Pewamo soil. Although not all plant available K was removed by exhaustive cropping in this soil, nonexchangeable K still contributed nearly 50% of total plant K. The data in Figure 2 show that exchangeable K is a poor predictor of available K in the Hoytville and Pewamo soils, but it may be good ($r^2 = 0.92$) for soils in which nonexchangeable K is not a significant source of plant available K. The inability of the NH_4OAc method to predict available K in the Bloomfield soil is not well exemplified in Figure 2 because of the relatively low cumulative uptake (Table 3) in this soil. The Na-TPB method gave good prediction for all soils, except the Pewamo soil (r^2 = 0.94). However the predictive ability of the Na-TPB method in the Pewamo soil is superior to the NH_4OAc method (Fig. 2).

If a soil test can reflect the change in soil K status associated with removal or addition of K, it will be useful for maintaining more reliable soil K inventories. The data presented for five soils in Figure 3 show that in soils where nonexchangeable K constitutes a significant portion of K uptake, reductions in NH_4OAc-K with crop removal follow no consistent pattern among soils or among the magnitude K removal within the same soil. This is well illustrated in the Hoytville and Okoboji soils. However, soil test K by the Na-TPB procedure declined almost linearly with crop uptake for all soils. Figure 4 shows cumulative K uptake versus cumulative change in soil K for the 5 cropping sequence used in the greenhouse study. There was almost a 1:1 relationship between K uptake and change in Na-TPB-extractable K. This relationship shows that following periods of cropping, soil sampling and K determination using the 5-minute extraction with Na-TPB can estimate crop K removal. This approach can be also used in conjunction with plant analysis to estimate other losses of soil K. This type of nutrient balancing in terms of crop removal and soil reserves is also an integral part of variable rate technology.

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Table 1. Precision of sodium tetraphenylboron extraction method (5 minutes) potassium determined by two operators.

Soil	Operator 1				Operater 2			
	Range	mean†	SD‡	CV§	Range	mean	SD	CV
	-------- mg K kg soil^{-1} --------			%	-------- mg K kg soil^{-1} --------			%
Bloomfield s	221 -273	243	23	9	240 - 291	262	25	10
Chalmers sil	123 - 150	138	12	9	124 - 126	125	1	1
Hoytville sicl	905 - 1100	1047	95	9	1013 - 1154	1111	57	5
Okoboji sicl	924 - 1119	1026	83	8	976 - 1124	1053	57	5
Withee sil	689 - 845	784	67	9	846 - 905	872	24	3

† mean of 5 analyses.

‡ standard deviation.

§ coefficient of variation.

Table 2. Potassium status of 11 midwestern soils determined by 1 *M* ammonium acetate and 3 extraction periods by sodium tetraphenylboron.

	1 *M* NH_4OAc-exchangeable K		Na-TPB-extractable K		
Soil	measured†	critical level‡	5 min	15 min	7 days
	---------------------- mg K kg $soil^{-1}$ ------------------------------				
Bloomfield s	92	86	265	305	1,531
Chalmers sil	56	103	138	141	2,037
Crider sil					
(1)	145	104	308	426	2,420
(2)	238	95	502	624	3,074
Hoytville cl	199	154	1,239	1,692	9,901
Milford sil	75	103	162	166	1,440
Okoboji cl	448	166	1,060	1,147	3,025
Pewamo cl	823	162	1,877	2,533	10,402
Raub sil	279	101	580	607	2,386
Withee sil	545	106	812	942	2,522
Zanesville sil	391	102	568	587	1,910

† Critical level = 75 + 2.5 x CEC; (Vitosh et al., 1995).

‡ 1:10 soil:solution; 1 h shaking.

Table 3. Total and nonexchangeable K uptake by wheat before plant K status indicates deficiency.

Soil	Uptake mg K kg soil^{-1}	Nonexchangeable Uptake mg K kg soil^{-1}	 % of uptake
Bloomfield s	218	126	57.7
Chalmers sil	0	---	---
Crider sil			
(1)	198	53	26.9
(2)	250	12	4.8
Hoytville cl	801	602	75.2
Milford sil	0	---	---
Okoboji cl	662	214	32.4
Pewamo cl‡	1610	787	48.9
Raub sil	366	87	23.7
Withee sil	628	83	13.2
Zanesville sil	472	81	17.1

† total K uptake minus 1 *M* NH_4OAc exchangeable.

‡ wheat K in Pewamo soil was not depleted below critical level.

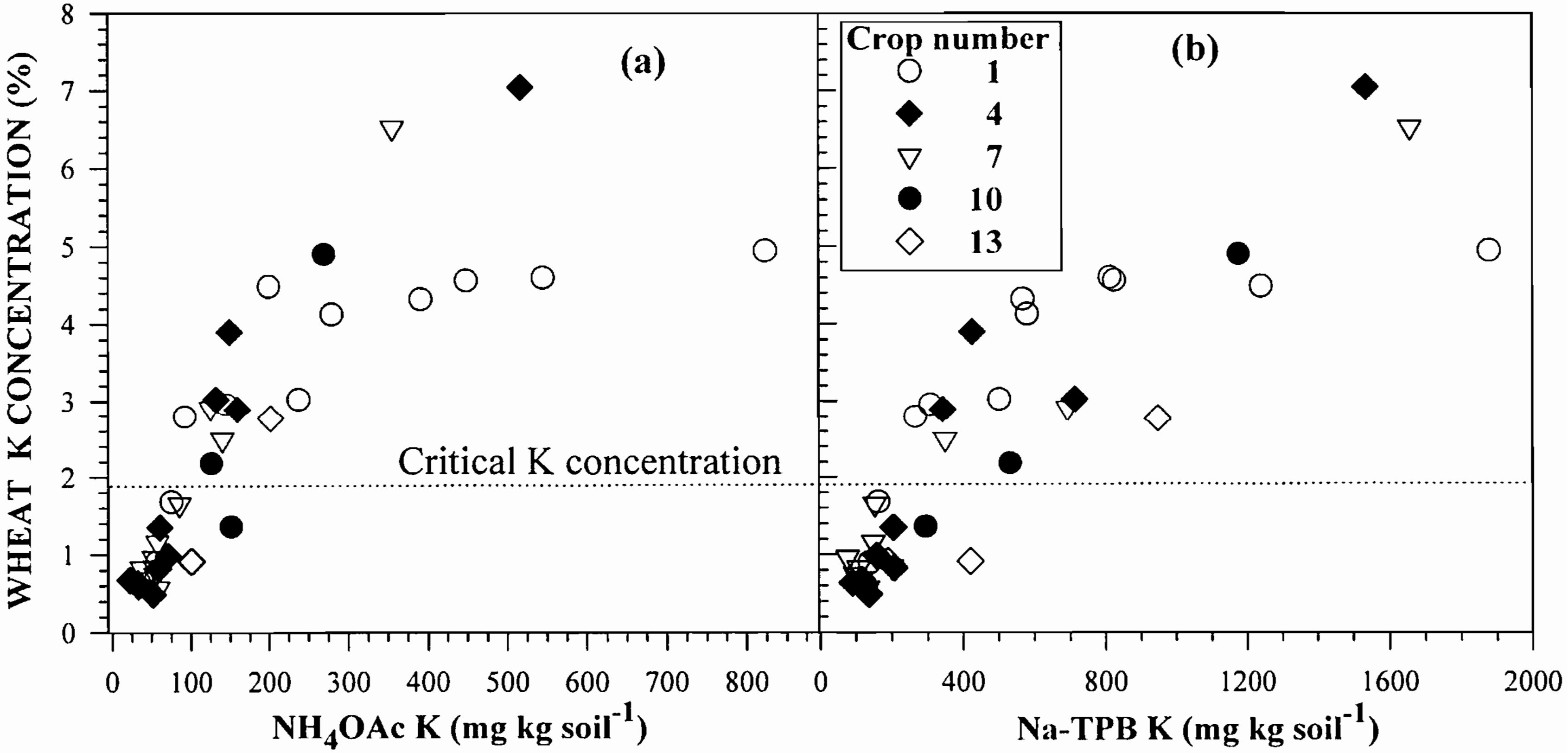

Figure 1. Soil test K by (a) NH$_4$OAc and (b) Na-TPB methods determined before each of five wheat crops and K concentration in wheat tissue.

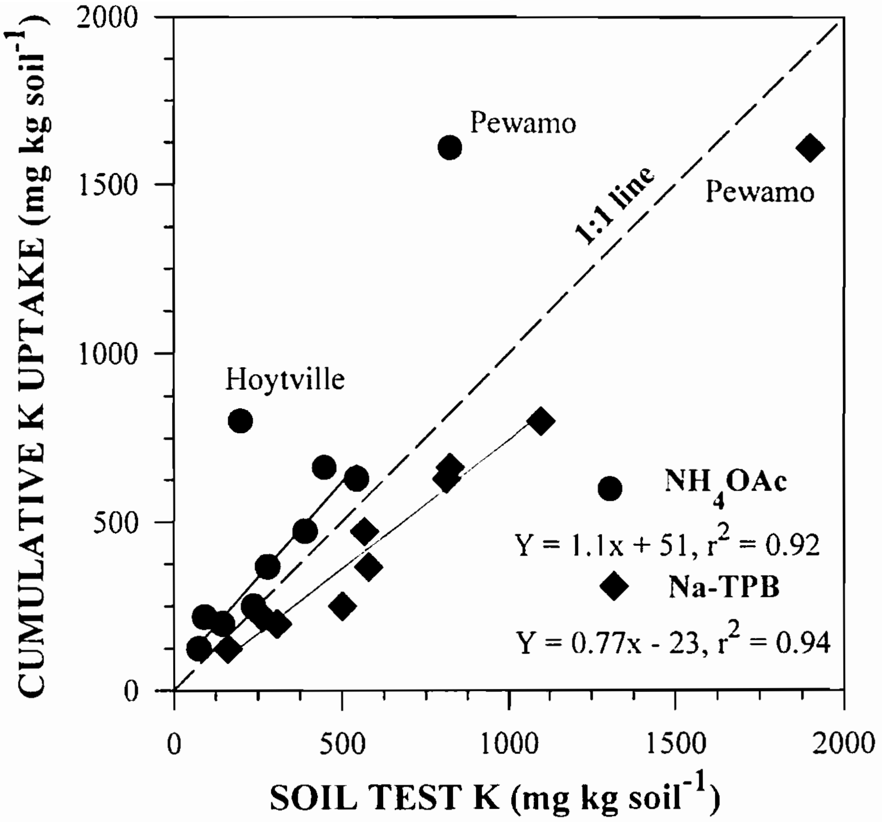

Figure 2. Relationship between soil test K and cumulative K uptake by wheat at deficiency. Regression lines do not include Hoytville and Pewamo soils for NH_4OAc and Pewamo soil for Na-TPB.

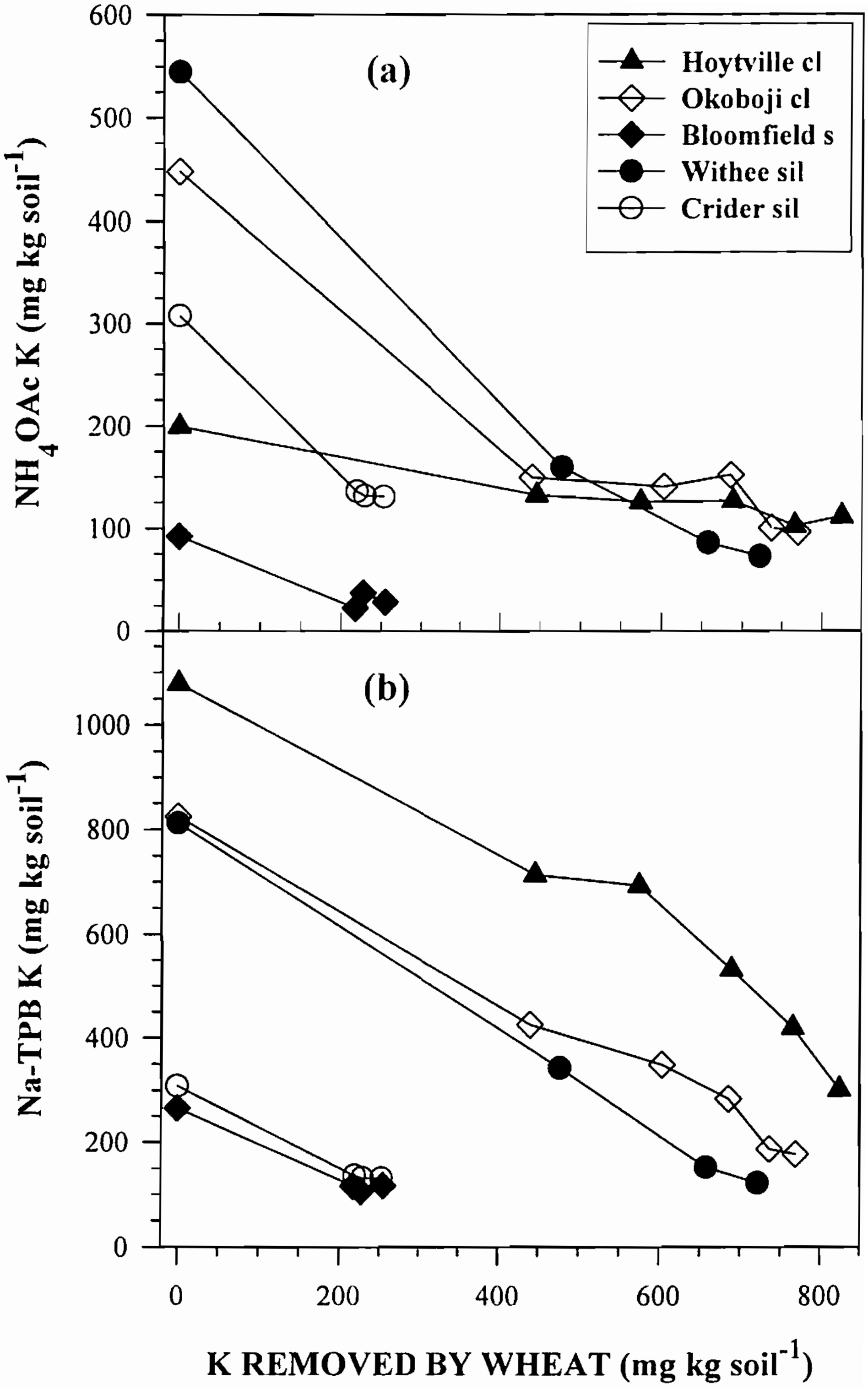

Figure 3. Relationship between removal of soil K by wheat uptake and depletion of K extractable by (a) NH_4OAc and (b) Na-TPB.

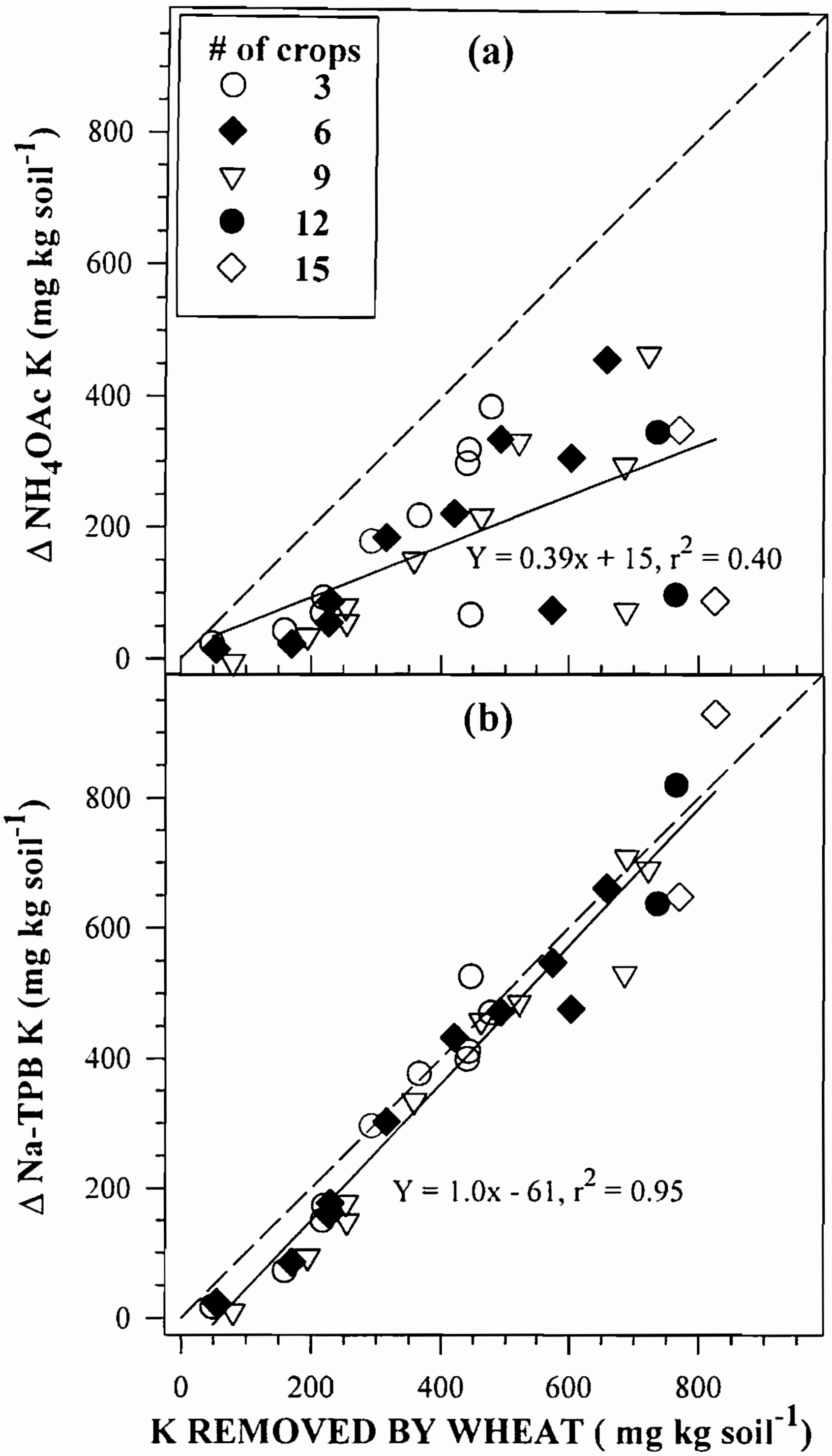

Figure 4. Cumulative K uptake by wheat vs change in soil K determined by (a) NH_4OAc and (b) Na-TPB after every three crops for the entire cropping period in the greenhouse.

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