Evaluation of Cation Exchange Resin Method for Determination of Exchangeable Bases, Manganese and Zinc in Soils of the Low Country of Sri Lanka

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ABSTRACT. Exchangeable cations including zinc and manganese were determined by cation exchange resin method in twenty two soil series collected from the low country region of Sri Lanka. The values were compared with calcium, magnesium, potassium and sodium determined by the standard 1 M ammonium acetate extraction, DTPA extractable manganese and zinc, EDTA! extractable Zn and 0.05 M HCl extractable Zn. The relative yield (RY) of Panicum maximum grown on each of the twenty two soils in pots in a green house with and without K fertilizer application was taken as the plant index for soil potassium.

Exchangeable cations determined by cation exchange resin were highly significantly correlated (r > 0.97, P < 0.001) with results obtained by standard 1 M ammonium acetate method. Manganese and zinc determined by resin method did not significantly correlate with other standard methods except for HCl extractable Zn (r = 0.75, p < 0.05). Relative yields of <u>Panicum</u> and exchangeable K by both methods significantly fitted to two population models as suggested by Cate and Nelson (1971). The relationships were used to determine threshold values for soil exchangeable K in respect to each method.

The overall results indicated that cation exchange resin was suitable for the determination of exchangeable cations but it has to be calibrated by green house and field experiments with respect to each exchangeable cation before employing for routine laboratory soil analysis. Further improvement of the resin technique is needed for determination of trace elements. Correlation between RY and exchangeable K of soils provided a guideline for threshold values for potassium with respect to each method.

INTRODUCTION

The plant availability of any nutrient in a soil is assessed either by biological or chemical methods. Chemical methods are less costly, and quicker compared to biological methods and therefore much attention is given to improve chemical methods. Among many chemical methods available for plant nutrient estimations in the soil, multi-element extractions are more attractive because simultaneous determination of a range of nutrients is economical in routine analysis for advisory work.

Cation exchange resins can be used for simultaneous multi-element extraction of cationic soil nutrients. This method is performed without addition of any acid, base or any precipitating or complexing reagents commonly employed in other chemical extraction procedures. Cation exchange resins in NH₄⁺ form do not exert any destructive influence to the lattice structure of clay minerals (Arnold, 1958; Bolton, 1973). Wimaladasa and Sinclair (1988) found that the crop response to K fertilizer and K removed by crops were better related with soil K determined by the mixed ion exchange resin method, than that by 1M NH₄OAc and 2.5% HAc.

In most cases, the cation exchange resin method has been evaluated for temperate soils (Arnold, 1958; Barber and Matthews, 1962; Waddy and Vimpany, 1970 and Bolton, 1973), but few studies have been done with tropical soils (Van Raij et al., 1986; Wimaladasa and Sinclair, 1988). There are major mineralogical differences in the clay fraction between temperate (montmorillonite and vermiculite dominant) and tropical (Kaolinite dominant) soils (Millot, 1979). Therefore the method should be thoroughly evaluated for tropical soils as well using a range of crops before adopting it for such soils.

Hence the objective of this study was to evaluate the suitability of the cation exchange resin method as a multi-element extraction method for the determination of exchangeable bases, manganese and zinc in Sri Lankan soils.

MATERIALS AND METHODS

Soil samples were collected from A horizon (including A1 and Ap) of twenty two soil series from the low country of Sri Lanka. These include three from the wet zone, fourteen from the intermediate zone and five from the dry zone. Five great soil groups were included in this. The pH, organic matter and textural separates of each soil is given in Table 1. Air dried 2mm sieved soils were used for a green house pot experiment and analysis in the laboratory.

Table 1. The pH, organic matter and textural separates of soils.

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Soil Series	pH 1:1 Soil:H₂O	% Organic matter	% Sand	% Silt	% Clay
		Wet Zone Soils			
1. Boralu	4.89	1.34	54.45	10.06	35.49
2.Warakapola	4.93	1.47	64.49	13.08	22.43
3. Pallama	4.85	0.92	77.54	6.03	16.43
	Inter	mediate Zone So	oils		
4. Kuliyapitiya	4.74	1.06	77.45	3.05	19.50
5. Melsiripura	6.18	1.12	49.34	11.23	39.43
6. Wariyapola	5.99	0.93	45.32	8.05	46.63
7. Maho	6.31	0.181	66.32	4.05	29.63
8. Kurunegala	6.81	0.91	75.18	6.38	18.44
9. Kiriwana	5.20	0.82	67.58	6.03	26.39
10. Welipalassa	5.55	0.56	88.55	3.98	7.47
11. Ambekelle	5.36	0.19	84.62	2.01	13.37
12. Rajakadaluwa	5.33	0.12	81.59	3.02	15.39
13. Palugaswewa	5.46	0.29	88.51	3.95	7.54
14. Ratupasa	5.76	0.27	93.95	3.80	2.25
15. Madampae	5.43	0.08	88.63	4.56	6.81
16. Andigama	5.48	0.99	63.16	9.32	27.52
17. Wilattawa	5.85	0.17	81.62	2.01	16.37
]	Dry Zone Soils			
18. Gambura	6.19	0.39	66.36	4.05	29.59
19. Aluthwewa	6.29	1.10	71.62	6.01	22.37
20. Ranorawa	5.74	0.99	78.38	3.05	18.57
21. Mavillu	6.78	0.72	78.59	2.92	18.49
22. Weliketiya	6.26	0.37	95.62	1.79	2.59

Each pot was filled upto a constant volume of 2.5 L after compacting soils by tapping the pot three times against a firm surface. Constant soil volume in pots were preferred to constant weight because the amounts of

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nutrients available to a plant depends on available soil volume rather than available soil weight. Each soil was treated with three levels of K, *i.e.*, K0 (No potassium), K1 (0.3 g KCl/pot), K2 (0.45 g KCl/pot). All the treatments were duplicated.

Each pot was treated with a basal dose of 0.33 g of ammonium sulphate (20.6% N), 0.2 g of magnesium sulphate (16% MgO), and 2 g of triple super phosphate (46% P_2O_5). The micro nutrients were added using salts such as 0.1 g of ferrous sulphate (FeSO₄. 7H₂O, 19%Fe), 0.1 g of manganese sulphate (MnSO₄. 1H₂O, 32.5% Mn), 0.02 g of zinc sulphate (ZnSO₄. 7H₂O, 22% Zn), 0.04 g of copper sulphate (CuSO₄. 5H₂O, 25% Cu), 0.0001 g of ammonium molybdate ((NH₄)₆Mo₇O₂₄. 4H₂O, 54% Mo) and 0.05 g of sodium borate (Na₂B₄O₇. 10H₂O, 11%B).

After application of treatments, pots were kept in the green house for a period of one week. The pots were watered daily with sufficient distilled water until it just started to drain from the soil. Five uniform size *Panicum maximum* cuttings were planted in each pot and after one week, the weakest one was removed to retain four cuttings in each pot. Pots were arranged in two blocks (one block for one replicate) in the green house and different soils receiving three potassium levels were randomized within the block.

Plant biomass was harvested at one month intervals over five months. At each harvest, fresh and dry weight of biomass were recorded. The same dose of fertilizer as the basal N, P and Mg was applied after each harvest upto the fourth harvest. Pots were dismantled after the last cutting and fresh and dry weights of stubble and roots were recorded separately. Samples of air dried 2mm sieved soils taken prior to treatment application were used for chemical analysis. The following analysis were performed.

Determination of exchangeable bases

- (a) 1M ammonium acetate method (NH₄OAc 1)
 - I) By shaking

A sample of 5 g of soil was shaken with 100 ml of 1M ammonium acetate solution on a mechanical shaker for 2 h and filtered through Whatman No. 42 filter paper (Schollenberger and Simon, 1945). The filtrate was analyzed for Na, K, Ca, and Mg by Atomic Absorption Spectrophotometer (AAS).

ii) By centrifuging (NH₄OAc -2)

A sample of 5 g of soil was taken into a centrifuge tube and 33 ml of 1 M ammonium acetate was added and shaken for 5 min. Then the content was centrifuged and decanted. This was repeated three times and the sample volume was adjusted in a 100 ml volumetric flask upto the mark and filtered. The filtrate was analyzed for Na, K, Ca and Mg by AAS (Thomas, 1982).

(b) Cation exchange resin (CER) method

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A sample of 5 g of soil was taken into a 250 ml bottle and 100 ml of distilled water and a mesh bag containing 2.88 g of Duolite 255 - NH₄⁺ cation exchange resin were added to it. The contents were shaken for 16 h in a reciprocal shaker. The resin bags were then recovered, washed with distilled water to make them free of soil residues. To elute cations, adsorbed to the resin, the resin bag was shaken in 50 ml of 1M NH₄Cl solution for 30 minutes. The elute was analyzed for cations (Somasiri and Edwards, 1992).

Determination of micro nutrients

(a) Diethylene triamine penta acetic acid (DTPA) - extractable copper, zinc, manganese and iron

A sample of 25 g air dried 2 mm sieved soils was taken into a 250 ml polyethylene bottle and 50 ml of DTPA extraction solution was added. It was then stoppered and shaken for 2 h on a mechanical shaker. The extracts were filtered. The concentrations of Zn and Mn in the filtrate were determined by Atomic Absorption Spectrophotometry (Soltanpour and Schwab, 1977).

(b) Ammonium bicarbonate/EDTA - extractable Cu and Zn

A sample of 10 g of soil was taken into a polyethylene extracting container and 20 ml of ammonium bicarbonate/EDTA extraction solution was added. The contents were shaken for 30 min at room temperature and filtered. The concentrations of Cu and Zn in the filtrate were determined by AAS (Best et al., 1985).

0.05M HCl - extractable Zn

A sample of 20 g of soil was taken into a 100 ml of glass bottle and 50 ml of 0.05M HCl solution was added. Then the content was shaken for 5 min and filtered through Whatman no. 42 filter paper. The concentration of Zn was determined by AAS.

Relative yield (RY %)

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The crop yield on a soil would depend on the combined effect of biological properties. Therefore, yield without K application (K0 treatment) does not reflect the K status of soils particularly when different kinds of soils are compared. When the ratio of yields from -K and +K treatments (relative yields) is taken, the influence of soil properties would be cancelled off except for the effect of K. Therefore, the RY was taken here as the plant index.

Relative Yield of the Panicum maximum grass in each soil was calculated as:

$$RY(\%) = \frac{Yield\ treatment-KO}{Yield\ treatment-K2} \times 100$$

The cumulative total dry weight including shoot, stubble and roots were taken as the yield of plant.

RESULTS AND DISCUSSION

Cation exchange resin and other standard methods

Linear regression performed on values of exchangeable bases (K, Mg, Ca and Na) by the two methods (1M ammonium acetate and cation exchange resin) showed that correlations were highly significant (p < 0.001). The best correlation was obtained for K followed by Mg, Ca and Na respectively (Table 2).

The linear regression values for each exchangeable base between $NH_4OAc - 1$ and $NH_4OAc - 2$ methods showed highly significant correlations (r > 0.949, P < 0.001). The regression coefficient (b) was also greater than 0.87 for all the elements which indicate that values were also of the same order. The results indicated that there was no significant difference between the values of

Table 2. Parameters obtained from linear regression of exchangeable bases between ammonium acetate and cation exchange resin methods.

Element	Methods	a	b	r
K	NH4OAc -1 Vs NH4OAc -2	2.593	0.874	0.99
	NH ₄ OAc -1 Vs Resin	12.860	1.321	0.98
	NH₄OAc -2 Vs Resin	- 10.175	1.164	0.98
Mg	NH4OAc -1 Vs NH4OAc -2	9.523	0.888	0.99
	NH ₄ OAc -1 Vs Resin	3.306	0.504	0.97
	NH₄OAc -2 Vs Resin	7.818	0.404	0.97
Ca	NH4OAc -I Vs NH4OAc -2	24.142	0.894	0.99
	NH ₄ OAc -1 Vs Resin	- 11.522	0.623	0.97
	NH₄OAc -2 Vs Resin	2.312	0.561	0.97
Na	NH4OAc -1 Vs NH4OAc -2	2.429	0.976	0.94
	NH ₄ OAc -1 Vs Resin	2.929	0.735	0.88
	NH ₄ OAc -2 Vs Resin	2.593	0.722	0.84

exchangeable bases by both methods. NH₄OAc -1 method is much simple and more suitable for routine laboratory purposes compared to NH₄OAc -2 method which involves three consecutive extractions and centrifuging.

Regression coefficients between Resin - Mg and NH₄OAc 1 - Mg as well as Resin - Ca and NH₄OAc 1 - Ca ranged from 0.4 to 0.6 indicating that resin values for exchangeable Mg and Ca were lower than NH₄OAc values. Resin values for exchangeable Na were also lower than NH₄OAc values. But regression coefficient of 1.164 between exchangeable potassium by resin and NH₄OAc indicates that values by both methods are of similar magnitude.

Linear regression of Mn and Zn values by DTPA and cation exchange resin showed a very poor correlation (Table 3). But Zn determined by EDTA and resin as well as that by HCl and resin showed correlation coefficients of 0.534 and 0.740 respectively. The latter correlation is significant at 5% level.

Table 3. Parameters obtained from linear regression of Zn and Mn by different methods.

Element	Methods	a	b	r
Zn	DTPA Vs Resin	0.914	0.0001	0.002
	EDTA Vs Resin	0.2636	1.2726	0.534
	0.05M HCl Vs Resin	0.0594	1.0599	0.741
Mn	DTPA Vs Resin	1.8764	0.0006	0.013

a = intercept b = regression coefficient r=correlation coefficient

As seen from Table 4, total exchangeable bases determined by cation exchange resin and NH₄OAc showed highly significant correlation (r = 0.975, p < 0.001). Similarly total exchangeable bases (TEB) determined by NH₄OAc - 1 and NH₄OAc -2 correlated highly significantly with a regression coefficient of 0.89.

The regression coefficient between Resin and NH₄OAc values for TEB ranged from 1.58 to 1.77 which indicates that resin values for TEB are lower than NH₄OAc values. The results indicated that although exchangeable bases determined by cation exchange resin and ammonium acetate are proportionate, the magnitude of the values are different. The reason for the under estimation of exchangeable bases by the resin method could be due to incomplete release of resin sorbed cations at the elution step (Somasiri, 1991).

Somasiri and Edwards (1992) showed that K, Mg, and Ca cannot be completely recovered at the elution step but a well defined fraction of the adsorbed quantity of each cation could be recovered. Therefore it is apparent

Table 4. Parameters obtained by linear regression of total exchangeable bases by different methods.

Methods	a	b	r
NH ₄ OAc -1 Vs NH ₄ OAc -2	0.209	0.890	0.995
Resin Vs NH ₄ OAc -1	0.161	1.586	0.975
Resin Vs NH₄OAc - 2	-0.050	1.769	0.975

that a correction factor for the recovery of resin sorbed cations should be used to workout the exact exchangeable quantity by the resin.

Correlation between relative yield and soil potassium values

Correlation between relative yields of Panicum maximum obtained by the pot experiment and K extracted by resin and NH₄OAc data fitted to a two population model rather than continuous functions as shown by Cate and Nelson model (Cate and Nelson, 1971). The relationships were used to determine the threshold level of soil K in respect of each extraction method. The relative yields determined by total shoot dry weight showed a better relationship with exchangeable K values than total dry weights of grass. It implies that the response to K is more related to the weight of shoots than the other parts of the plant.

To determine the threshold levels, the graph between relative yields and exchangeable K was divided into four quadrants in such a way that the lowest number of points fall into the upper left quadrant and the lower right quadrant. The threshold level is then shown by the line which intersect the X axis (Figures 1, 2 and 3). The threshold levels determined for ammonium acetate (centrifuge method), ammonium acetate (shaking method) and cation exchange resin method were 18.33 mg of extractable K/kg of soil, 30.0 mg of extractable K/kg of soil and 17.9 mg of extractable K/kg of soil respectively.

Relative Yield (%)

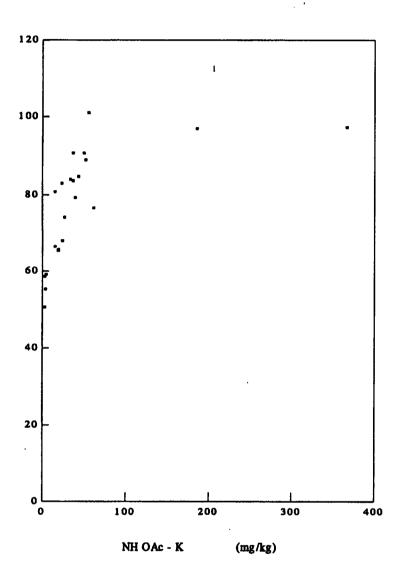


Figure 1. NH₄OAc (cen) - K Vs Relative Yield of Panicum maximum.

Relative Yield (%)

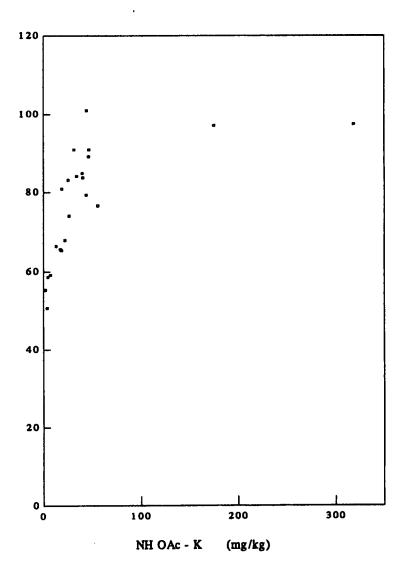


Figure 2. NH₄OAc (shake) - K Vs Relative Yield of *Panicum maximum*.

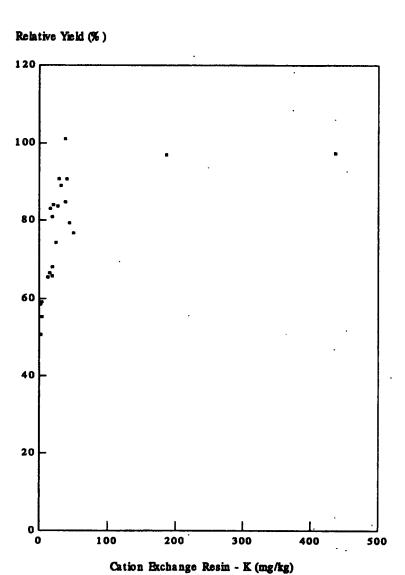


Figure 3. Cation Exchange Resin - K Vs Relative Yield of *Panicum maximum*.

Table 5. Relative yields and exchangeable K values obtained from three methods.

Soil Series	Relative Yield (%)	Exchangeable K values (ppm)			
		CER method	NH₄OAc - I	NH₄OAc - 2	
Boralu	76.70	49.81	55.55	61.22	
Warakapola	66.56	14.91	12.85	15.09	
Pallama	59.17	3.51	7.05	4.53	
Kuliyapitiya	74.22	24.12	26.17	25.34	
Melsiripura	84.79	37.86	39.71	43.09	
Wariyapola	90.85	28.72	31.08	36.54	
Maho	68.09	18.85	21.93	23.94	
Kurunegala	101.04	37.65	44.21	54.97	
Kiriwana	90.80	40.01	46.50	49.62	
Welipalassa	83.08	15.90	25.18	23.22	
Ambekelle	65.46	12.52	18.33	18.91	
Rajakadaluwa	58.91	2.05	4.34	3.05	
Palugaswewa	50.67	2.15	3.69	3.05	
Ratupasa	89.07	31.66	46.22	51.62	
Madampae .	55.33	37.78	2.09	3.65	
Andigama	79.36	20.55	43.79	39.38	
Wilattawa	80.87	13.32	18.83	15.14	
Gambura	65.76	18.80	17.14	19.27	
Aluthwewa	97.05	186.19	174.77	185.45	
Ranorawa	97.40	436.42	318.48	366.67	
Mavillu	84.06	20.37	33.85	33.42	
Weliketiya	83.71	26.92	40.35	36.80	

Since relative yields and exchangeable K values (Table 5) showed good correlations for a range of soils (22 soil series), both NH₄OAc and cation exchange resin methods are suitable for the determination of soil K. Both methods could be successfully calibrated for the assessment of K status in soils. As the threshold value is subjected to variable factors in the field and crop types, the values obtained by the present experiments are not directly applicable to field conditions. But, those values give a guideline on the possible range of threshold level by each method. Further, each method has to be properly calibrated by data obtained in field experiments prior to employing them for routine soil analysis.

CONCLUSION

Correlation between relative yields of *Panicum maximum* and exchangeable K determined by 1M NH₄OAc and cation exchange resin showed that both methods are suitable and applicable for a wide range of soils. Cation exchange resin method is equally good as the standard 1M NH₄OAc method for the determination of total exchangeable bases. Applicability of ion exchange resin for the determination of more trace elements has to be investigated further.

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