

An Evaluation of Cation Exchange Capacity Methods for Acid Tropical Soils

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Keywords: CEC, acid tropical soils, variable-charge soils, correlation study

ABSTRAK

Keupayaan pertukaran kation (KPK) adalah kriteria penting bagi menilaikan kesuburan tanah selain daripada digunakan untuk pengelasan tanah. Tujuh kaedah telah dikaji untuk penentuan dan perbandingan nilai KPK tanah berasid tropika, iaitu, (1) $BaCl_2$ - triethanolamine atau $BaCl_2$ - TEA (pH 8.2), (2) NH_4OAc (pH 7.0) - larutlesap, (3) NH_4OAc (pH 7.0) - digoncang, (4) kaedah pertukaran mendadak oleh Gillman, 1979 (KPK_{PM}), (5) kaedah pertukaran mendadak diubahsuaikan oleh Gillman, 1986 (KPK_B), (6) kaedah pencampuran Ca dari kaedah 5 dengan Al tukarganti menggunakan larutan 1M NH_4NO_3 (KPK_{jumlah}), dan, (7) kaedah pencampuran bes tukarganti dari NH_4OAc (pH 7.0) dengan Al tukarganti dari 1M KCl (KPK_{campur}). Semua kaedah memberikan nilai KPK yang berbeza, iaitu, $BaCl_2$ - TEA > NH_4OAc digoncang - NH_4OAc dilarutlesap > $KPK_{campur} = KPK_{jumlah} > KPK_{PM} = KPK_B$. Kaedah yang hampir serupa dengan keadaan pH di ladang memberikan nilai KPK yang lebih rendah dari kaedah menggunakan larutan penampapan. Ini adalah disebabkan oleh pertambahan cas pada koloid cas berubah oleh larutan penampapan. Oleh itu, kaedah larutan penampapan memberikan nilai KPK yang tidak benar. Korelasi yang tinggi diperolehi di antara kaedah $BaCl_2$ - TEA dan NH_4OAc larutlesap; KPK_{PM} dan KPK_{campur} ; dan, KPK_B dan KPK_{jumlah} . Daripada kaedah-kaedah yang dinilai, kaedah NH_4OAc (pH 7.0) ialah kaedah yang disyorkan sebagai kaedah rutin untuk tujuan pengelasan tanah manakala KPK_{campur} disyorkan untuk penilaian agronomi.

ABSTRACT

The cation exchange capacity (CEC) of soil is an important criteria for assessing soil fertility beside its use in soil classification. Seven methods, namely, (1) $BaCl_2$ - triethanolamine or $BaCl_2$ - TEA (pH 8.2), (2) NH_4OAc (pH 7.0) - leaching, (3) NH_4OAc (pH 7.0) - shaking, (4) compulsive exchange method of Gillman (1979) (CEC_{CE}), (5) modified compulsive exchange method of Gillman (1986) (CEC_B), (6) Summation of Ca from method 5 with 1 M NH_4NO_3 exchangeable Al (CEC_{total}) and (7) summation of NH_4OAc (pH 7.0) exchangeable bases with 1 M KCl exchangeable Al (CEC_{sum}), were used to determine and compare the CEC values of five acid tropical soils. All methods gave different CEC values which followed the order $BaCl_2$ - TEA > NH_4OAc shaking = NH_4OAc leaching > $CEC_{sum} = CEC_{total} > CEC_{CE} = CEC_B$. Methods with pH conditions close to field situations gave much lower CEC values than the buffered methods. The buffered methods generate charge on the variable-charge colloids, thus resulting in inflated CEC values, while the unbuffered methods do not. There is a high correlation between $BaCl_2$ - TEA and NH_4OAc (pH 7.0) leaching method; CEC_{CE} and CEC_{sum} ; and, CEC_B and CEC_{total} . Amongst the methods evaluated, the NH_4OAc (pH 7.0) leaching is recommended in routine soil analyses for classification purposes while CEC_{sum} is recommended for agronomic evaluation.

INTRODUCTION

Cation exchange capacity (CEC) is used in characterizing soils for soil classification as well as in assessing their fertility status. Several proce-

dures have been established, modified and officially accepted as standard methods for CEC determination. Some methods determine CEC under conditions of pH and ionic strength close

to the natural state of the soil while others do not (Bache 1976). The CEC values obtained are highly dependent on methods used and therefore it is essential to evaluate these methods. It is also desirable that the methods selected should measure exchangeable bases as well as the anion exchange capacity (AEC) in the complete characterization of the charge properties of soils.

The humid tropical climate with high rainfall and temperatures favours rapid dissolution and leaching of weatherable minerals. As such, resultant soils are rich in kaolinitic clays and sesquioxides, which possess pH-dependent charges. Therefore, CEC of most Malaysian soils depends largely on the pH at which CEC of the soil is determined, the ionic strength, dielectric constant and the counter ion valency of the solutions used (Tessens and Shamsuddin 1982). If the objective of the CEC determination is to assess the ability of the soil to retain cation nutrients for plant use or to study other reactions that may be affected by CEC, then the measurement should be made on the soil at its natural acidity. If, on the other hand, the objective is to use CEC as an aid to soil classification, then there are strong grounds to determine it at a standard pH. An example of such a method is NH_4OAc method buffered at pH 7.0. This method has some very definite advantages: (i) the method is used worldwide, thus the CEC values obtained can be compared with those measured elsewhere, and (ii) in soil survey and classification work, soils of the same series, which have different pH values as a result of liming or fertilizer application, will have the same CEC in a buffered system (Bache 1976).

The objective of this study was to compare the CEC values determined by various methods and to suggest a suitable method for use in soil classification and fertility status evaluation. For soil classification purposes, a method which is widely practised as well as easy to perform and does not require sophisticated instrumentation will be recommended, whereas a method which closely reflect CEC at field condition will be recommended for fertility evaluation.

MATERIALS AND METHODS

Six soils commonly found in Peninsular Malaysia, that is, Bungor, Holyrood, Munchong, Rengam and Serdang, were used in this study. The soils were air-dried, ground and sieved through a 2.0-mm sieve before use. Seven meth-

ods of CEC determination were studied. The first three determinations (methods 1 - 3) were at the buffered soil pH, whereas the last four (methods 4 - 7) were determined close to the soil natural pH. The summary of procedures for all the methods is given in Table 1.

RESULTS AND DISCUSSION

The classification and relevant characteristics of the soils used are shown in Table 2. The CEC depends not only on clay content but also on clay types, that is, on specific surface and charge density. All the soils, except Munchong, have kaolinite as the dominant clay type. The dominant clay type for Munchong series soil is oxides of Fe and Al. Both these type of clays are variable charge colloids. Therefore, the charges of these clays will be affected by pH changes. This is exhibited in the increase in CEC values where the pH of determination has been increased, that is, using BaCl_2 - TEA (pH 8.2) and NH_4OAc (pH 7.0) methods (Table 3). Also, soils with a high percentage of clay, such as the Bungor, Munchong and Rengam series soils have higher CEC values than the Holyrood and Serdang series soils. Besides clay type and content, the pH dependence of soil CEC is also a function of organic matter. However, in this case, the amounts of organic C among these 5 soils are low and relatively similar; thus, the charge contribution from organic matter can be considered minimal.

The average values of CEC obtained by the different methods are given in Table 3. Generally, the CEC values of all five soils are rather low. This can be expected of soils dominant in kaolinitic clay (Birrell and Gradwell 1956). The CEC values determined under conditions close to natural soil pH, that is, CEC_{CE} , CEC_{B} , $\text{CEC}_{\text{total}}$ and CEC_{sum} are much lower than those obtained by the BaCl_2 - TEA (pH 8.2) and NH_4OAc (pH 7.0) methods.

The BaCl_2 - TEA (pH 8.2) method gave the highest CEC values for all the soils. The buffering of the BaCl_2 - triethanolamine solution to pH 8.2 causes further dissociation of weakly acidic groups comprising the pH-dependent charges in soils (Peech 1965). Therefore, this procedure results in inflated CEC values for acid soils. The inflated CEC values can also be explained in terms of the valency of the displacing cation. Tan (1970) showed that CEC values determined by leaching with monovalent cation

TABLE 1
CEC methods used in the evaluation study

Method	Solution used for saturated	Method of displacement	Solution used for displacement	Reference
Buffered				
1	BaCl ₂ -TEA (pH 8.2)	0.5 M BaCl ₂ (pH 7.0)	0.025M MgSO ₄	Bascomb (1964)
2	NH ₄ OAc (pH 7.0)	1M NH ₄ OAc (PH 7.0)	0.05M K ₂ SO ₄	Soil Survey Staff (1972)
3	NH ₄ OAc (pH7.0) shaking for 10 minutes	1M NH ₄ OAc (pH 7.0)	0.05M K ₂ SO ₄	
Unbuffered				
4	Compulsive exchange of Gillman (1979) (CEC _{CE})	0.1M BaCl ₂ and 0.1M NH ₄ Cl	0.005M MgSO ₄	Gillman(1979)
5	Modified compulsive exch. of Gillman (1986) (CEC _B)	0.1M CaCl ₂	1M NH ₄ NO ₃	Gillman and Sumpter (1986)
6	Summation method of Gillman (1986) (CEC _{total})	0.1M CaCl ₂ for bases and 1M NH ₄ NO ₃ for Al	-	Gillman and Sumpter (1986)
7	Summation of NH ₄ OAc exch. bases and KCl exch. Al (CEC _{sum})	1M NH ₄ OAc (pH 7.0) for bases and 1M KCl for Al	-	Coleman and Thomas (1967) Kamprath (1970)

TABLE 2
Some characteristics of the soils studied

Soil	Depth (cm)	Classification*	pH _{H₂O} (1:2.5)	pH _{KCl} (1:2.5)	Org. C (%)	Exch Al (cmol(+)kg ⁻¹)	Clay (%)
Bungor	0-20	Fine clayey, kaolinitic, isohyperthermic, Typic Paleudult	5.1	4.1	0.92	1.02	50
Holyrood	0-20	Fine loamy, kaolinitic, isohyperthermic, Typic Dystropept	4.7	3.8	0.97	0.96	15
Munchong	0-20	Clayey, oxidic, isohyperthermic, Tropeptic, Hapludox	5.0	4.0	1.00	0.60	71
Rengam	0-15	Clayey, kaolinitic, isohyperthermic	4.4	3.8	1.28	2.31	69
	15-30	Typic Paleudult	4.4	4.0	0.53	1.34	72
Serdang	0-20	Fine loamy, kaolinitic, isohyperthermic, Typic Paleudult	4.8	3.8	0.94	0.77	25

*Soil Taxonomy USA (Soil Survey Staff 1975)

TABLE 3
CEC values of soils determined by the seven methods (cmol (+)kg⁻¹)

Soil series	*BaCl-TEA	NH ₄ OAc *Leaching	(pH 7.0) *Shaking	*CEC _{CE}	**CEC _B	**CEC _{total}	**CEC _{sum}
Bungor	14.10	7.32	7.48	2.93	2.45	2.92	4.65
Holyrood	10.04	4.65	3.97	0.61	1.26	2.18	1.28
Munchong	13.35	6.35	8.40	1.26	1.56	2.23	1.55
Rengam							
- top soil	15.74	7.58	9.80	1.72	1.94	2.82	2.78
- subsoil	11.58	5.65	7.87	1.53	1.60	2.06	1.64
Serdang	12.90	5.70	6.57	2.22	3.25	4.21	3.21

*CEC values are average of 6 replicates

#CEC values are average of 3 replicates

**No replicates

ons such as NH_4^+ , is lower than that obtained with divalent cations such as Ba^{2+} . According to the lyotropic series, the higher the valency of the cations, the more difficult it is for these cations to be replaced from the exchange sites colloids by cations of lower valency (Bohn *et al.* 1985).

The NH_4OAc (pH 7.0) leaching method has been widely accepted for the determination of CEC for soil classification purposes. The shaking procedure as compared with leaching will help to minimize the analysis time and hence large numbers of samples can be determined. From Table 3, it can be seen that the CEC values for the shaking are greater than for the leaching method. The shaking method results in the rupturing of some clay surfaces and hence produces greater CEC values. A correlation study between these two techniques showed quite a significant correlation, $r = 0.83$ (Table 4).

The CEC values obtained by the CEC_{CE} method are on the average about 27% of the NH_4OAc (leaching) CEC values and this demonstrates the need for caution in CEC determination at a pH value higher than the soil pH, using solutions of relatively high ionic strength. The BaCl_2 - TEA (pH 8.2) and NH_4OAc (pH 7.0) methods produce higher CEC values due to an increase in the adsorption of Ba^{2+} and NH_4^+ as a result of the increase in the negative charge on variable charge colloids. Soils extracted with unbuffered soil solutions as in CEC_{CE} , depict the true CEC values (Bache 1976; Gillman 1979). Since the solutions have little effect on soil pH values, the pH-dependent

charge will remain unchanged. However, the CEC_{CE} method is laborious and unsuitable for large-scale routine work, where only 64 samples per week can be determined (Gillman 1979).

The CEC_{B} and $\text{CEC}_{\text{total}}$ is a modification of the CEC_{CE} method. CEC_{B} measures only the Ca^{2+} adsorbed after saturating the soil with CaCl_2 . Below pH 5.0, Al^{3+} is measured in the 1M NH_4NO_3 solution which was used to extract the Ca^{2+} . $\text{CEC}_{\text{total}}$ is a measure of the amount of Ca^{2+} and Al^{3+} adsorbed. This modified technique is less tedious than the CEC_{CE} method. The CEC_{B} is not significantly correlated to CEC_{CE} and $\text{CEC}_{\text{total}}$ with $r = 0.77$ and 0.60 , respectively (Table 4). According to Gillman and Sumpter, 1986, CEC_{B} will give the true CEC value of soils under natural condition even if free lime is present. This method could also be used for calcareous and saline soils.

CEC_{sum} is an easy way to obtain CEC values. With this sum method, it is assumed that all the cations extracted with NH_4OAc are exchangeable, and this might not always be so. Apparently, the size of NH_4^+ allows more complete displacement of K^+ from the micaceous clay mineral wedge zone (Rich and Black 1964). The K^+ released from highly specific sites by the NH_4^+ ions are generally considered as fixed or unavailable to plants (Donahue *et al.* 1983; Mengel 1985; Sawhney 1972). Therefore, it is incorrect to include this K^+ as part of the exchangeable cations at the colloidal surfaces. In general, this will not be a problem to the mineral soils of the tropics since micaceous clay is not abundant in these soils. In the CEC_{sum} method, it is further assumed that all of

TABLE 4
Correlation study between different CEC methods

	BaCl_2 -TEA	NH_4OAc (Leaching)	NH_4OAc (Shaking)	CEC_{CE}	CEC_{B}	$\text{CEC}_{\text{total}}$	CEC_{sum}
1) BaCl_2 -TEA		0.96**	0.85*	0.59 ^{ns}	0.39 ^{ns}	0.34 ^{ns}	0.59 ^{ns}
2) NH_4OAc (Leaching)			0.83*	0.65 ^{ns}	0.27 ^{ns}	0.17 ^{ns}	0.65 ^{ns}
3) NH_4OAc (Shaking)				0.37 ^{ns}	0.11 ^{ns}	0.01 ^{ns}	0.24 ^{ns}
4) CEC_{CE}					0.77 ^{ns}	0.60 ^{ns}	0.95**
5) CEC_{B}						0.96**	0.74 ^{ns}
6) $\text{CEC}_{\text{total}}$							0.62 ^{ns}
7) CEC_{sum}							

The r values labelled*, **, are significant at the 5% and 1% levels, respectively, ns = non-significant

the acidic cations extracted with 1M KCl are exchangeable. However, Amedee and Peech (1976) showed that this is not true for some highly weathered tropical soils. An increase in solution electrolyte concentration induces a greater negative charge on variable charge surfaces by the release of surface protons, which then cause dissolution of amorphous oxide coatings. Hence, not all of the aluminium extracted is truly exchangeable (Gillman and Sumpter 1985). The values of CEC_{CE} and CEC_{sum} differ (Table 3), that is, $CEC_{CE} < CEC_{sum}$ although it can be predicted well from the CEC_{CE} , $r = 0.95$ (Table 4). The difference in CEC value could be because CEC_{total} also measures aluminium that are not truly exchangeable. Thus CEC_{sum} and CEC_{total} slightly overestimate the true CEC values of the soils. However, the limitation of CEC_{sum} is that it does not measure the AEC of the soil and might not be accurate if used for freshly fertilized or limed soils, unless the non-exchangeable cations can be separated from the basic exchangeable cations.

CONCLUSION

The nature of the soil and the purpose of determination are two main factors to consider when selecting a method for CEC determination. The $BaCl_2$ - TEA (pH 8.2) and NH_4OAc (pH 7.0) methods overestimate the ability of variable charge soils to retain cations under field conditions. It is recommended that methods which represent the maximum amount of basic cations that the soil can retain, such as CEC_{CE} and CEC_{sum} may be used for agronomic evaluation. However, the CEC_{CE} method is tedious and therefore not feasible for routine advisory purposes where speed and simplicity of operations are important. The CEC_{sum} method appears to be a suitable choice for fertility evaluation because it is easier to perform and can be carried out on a routine basis. However, for soil classification purposes, the NH_4OAc (pH 7.0) leaching is still the method of preference.

ACKNOWLEDGEMENT

The authors would like to record their gratitude and appreciation to Universiti Putra Malaysia for the financial and technical support of this study.

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(Received 13 June 1996)

(Accepted 20 December 1997)