

Examination into the accuracy of exchangeable cation measurement in saline soils

H. B. So¹, N. W. Menzies¹, R. Bigwood^{1,2}, P. M. Kopittke^{1,*}

¹*School of Land and Food Sciences, The University of Queensland, St. Lucia, Qld, Australia, 4072. Ph: +61 7 3365 2079, Fax: +61 7 3365 1177, Email: p.kopittke@uq.edu.au*

²*Present address: Department of Natural Resources and Mines, 80 Meiers Rd, Indooroopilly, Qld, Australia, 4068.*

ABSTRACT

Despite the increasing prevalence of salinity world-wide, the measurement of exchangeable cation concentrations in saline soils remains problematic. Two soil types (Mollisol and Vertisol) were equilibrated with a range of sodium adsorption ratio (SAR) solutions at various ionic strengths. The concentrations of exchangeable cations were then determined using several different types of methods, and the measured exchangeable cation concentrations compared to reference values. At low ionic strength (low salinity), the concentration of exchangeable cations can be accurately estimated from the total soil extractable cations. In saline soils, however, the presence of soluble salts in the soil solution precludes the use of this method. Leaching of the soil with a pre-wash solution (such as alcohol) was found to effectively remove the soluble salts from the soil, thus allowing the accurate measurement of the effective cation exchange capacity (ECEC). However, the dilution associated with this pre-washing increased the exchangeable Ca concentrations while simultaneously decreasing exchangeable Na. In contrast, when calculated as the difference between the total extractable cations and the soil solution cations, good correlations were found between the calculated exchangeable cation concentrations and the reference values for both Na (Mollisol: $y=0.873x$ and Vertisol: $y=0.960x$) and Ca (Mollisol: $y=0.901x$ and Vertisol: $y=1.05x$). Therefore, for soils with a soil solution ionic strength greater than 50 mM (electrical conductivity of 4 dS/m) (in which exchangeable cation concentrations are overestimated by the assumption they can be

estimated as the total extractable cations), concentrations can be calculated as the difference between total extractable cations and soluble cations.

Key words: effective cation exchange capacity; exchangeable cations; exchangeable sodium percentage; pretreatment for salts; salinity; soil solution

INTRODUCTION

Saline soils are commonly found throughout the world, but are of particular importance in countries such as Australia, India, and the USA. In addition to dry-land salinity, the soil application of saline irrigation water may result in an increase in salinity. Where the salinity consists largely of NaCl, the soil sodicity (exchangeable sodium percentage (ESP)) will increase, thereby increasing the tendency of the soil to disperse, resulting in decreased percolation rates. Despite the practical importance of salinity and sodicity, little attention has been directed to the accurate characterisation of these soils. This is particularly true for the assessment of exchangeable cations where the most widely used methods have long been known to yield inaccurate results (Black, 1968), but few researchers have considered the magnitude of the error in their measurements or its influence on their interpretation of the data.

In Handbook 60 from the US Salinity Laboratory, Richards (1954) suggested that the concentration of exchangeable cations in saline soils should be calculated as the concentration of extractable cations, minus the concentration of soluble cations determined from the saturated extract. However, this method (originally suggested by Bower (1952)), has not been validated against soils with a known distribution of soluble and exchangeable cations, and has not been widely adopted, with other quicker and simpler methods used in preference.

Methods used for the routine measurement of exchangeable cations in saline soils are generally of two types. The first type assumes all cations extracted from the soil are exchangeable, making no correction for soluble salts. This failure to adequately account for soluble cations prior to measurement results in an overestimation of exchangeable cations. For non-saline soils, however, this error, resulting from the presence of soluble salts, is typically small (see Menzies and Bell (1988)). The second type of method is that in which soluble cations are removed from the soil prior to the extraction of the remaining (exchangeable) cations. The removal of soluble cations from the soil solution can be achieved through leaching with water or alcohol mixtures (Levy and Hillel, 1968; Shainberg et al., 1987; Tucker, 1985; Nadler and Magaritz, 1981), or by dialysis. However, for variable charge soils, the decrease in ionic strength associated with this pretreatment process results in a decrease in CEC (Uehara and Gillman, 1981), a release (and loss) of exchangeable cations, and hence an underestimation of ECEC. In addition, for soils containing sparingly soluble salts (such as gypsiferous or calcareous soils) incomplete removal of these salts during pretreatment will result in an overestimation of ECEC due to dissolution of these salts (and release of cations) into the extractant. Further, dilution of the soil during pretreatment may result in a redistribution of cations amongst soluble and exchangeable pools, with Ca replacing Na on the exchange (Sposito, 1981).

The objective of the work presented here was to measure exchangeable cation concentrations using these two types of commonly used methods (exchangeable cations estimated as the extractable cations, and the use of a pre-extraction washing step), and to compare these results with known values. In addition, exchangeable cation concentrations were determined as described by Richards (1954) (based on Bower (1952)); total extractable cations minus soluble cations, and the results compared to reference values.

MATERIALS AND METHODS

Soil preparation

Two soils, a Mollisol and Vertisol (Soil Survey Staff, 2003) (a Dermosol and a Vertosol (Isbell, 2002)), were collected from the Beaudesert area in Queensland, Australia, air-dried, and sieved (2 mm) (Table 1). The dominant clay minerals present were determined for both soils using X-ray diffraction (XRD) analysis of the <2 µm fraction (Philips PW1800, 0.05° 2 theta steps with 3.0 s counting per step, quantitative analysis using SIROQUANT). Soil solutions were extracted at field capacity after 48 h equilibration by centrifuge drainage (Gillman, 1976), and analysed for pH (TPS 901-CP), electrical conductivity (EC) (Radiometer CDM210), and major cations (by inductively coupled plasma atomic emission spectroscopy (ICPAES) (Spectro Analytical Instruments)).

Using NaCl and CaCl₂·2H₂O at predetermined rates, 15 solutions were prepared (comprising five SAR treatments (3, 6, 12, 18, and 24 (mmol_(c)/L)^{0.5}) at three ionic strengths (10, 50, and 150 mM)). Leaching columns were prepared to allow the equilibration of the two soil types with the 15 solutions, each treatment with two replicates (yielding a total of 60 soils). Solution was leached through each of the soils (approximately 300 g air-dry) until the EC of the leachate was similar to that of the initial equilibrating solution (approximately 10 pore volumes).

Determining actual exchangeable cation concentrations (Reference method)

In order to allow comparison of the accuracy of the various methods, the actual soil exchangeable cation concentrations were determined following equilibration with various SAR solutions, as described by Marsi and Evangelou (1991). A sub-sample (approximately 10 g) was removed from each of the soils following leaching, and oven-dried to determine water content. On the basis of this value, an air-dry equivalent of 4.0 g soil was removed from each column and placed in a 50 mL tube, with the volume of entrained equilibrating SAR solution in each tube calculated by mass. Total cation concentrations (exchangeable plus entrained cations) were determined by ICPAES following extraction with 40 mL 0.1 M BaCl₂/0.1 M NH₄Cl (Gillman et al., 1982). The

concentration of cations in the entrained solution was measured, and the exchangeable cations determined by the subtraction of entrained cations from total extractable cations.

Removal of soluble cations (Pre-wash method)

The effect of pretreatment for soluble salts (as described by Tucker (1985)) on soil exchangeable cations was investigated. All remaining soil was removed from the leaching columns and air-dried, 4.0 g (air-dry) sub-sample of this was placed in a 50 mL tube. Using 60 % ethanol (60:40 ethanol:water) and 20 % glycerol (20:80 glycerol:water) mixtures, each sample was pretreated for soluble salts as described by Tucker (1985). A 1:5 soil:ethanol suspension was prepared using the 60 % ethanol mixture, shaken for 30 min, centrifuged, and the supernatant discarded. The process was repeated one further time with the 60 % ethanol, and finally with the 20 % glycerol. The quantity of entrained solution in the soil was determined by mass and used to correct extractant volume, and the exchangeable cation concentrations determined using 40 mL 0.1 M BaCl₂/0.1 M NH₄Cl as before.

Extraction of total soil cations (Total cations method)

A method was examined in which soluble salts are not removed from the soil, and all extracted cations are assumed to be exchangeable. Exchangeable cation concentrations were determined as described by Sumner and Miller (1996), with 0.1 M BaCl₂/0.1 M NH₄Cl used as the extractant rather than 0.2 M CaCl₂/0.125 M CaSO₄ in order to allow the determination of exchangeable Ca²⁺ in addition to Mg²⁺, K⁺ and Na⁺.

A 4.00 g sub-sample of air-dry soil was placed in a 50 mL tube and cations extracted using 40 mL 0.1 M BaCl₂/0.1 M NH₄Cl. Cation concentrations were determined using ICPAES and exchangeable cations calculated as the total extractant concentration.

Correction of total extractable cations for soluble cations (Difference method)

The Difference method was examined to allow more accurate exchangeable cation determinations for saline soils. A 4.0 g air-dry sub-sample of each soil was placed in a 50 mL tube, and total extractable cation concentrations extracted using 40 mL 0.1 M BaCl₂/0.1 M NH₄Cl and determined by ICPAES. Approximately 125 g of the air-dry soil was wet to field capacity using triple de-ionised water and allowed to equilibrate for 48 h in a closed box lined with wet paper towelling to minimise evaporative loss (Menzies and Bell, 1988). The soil solution was extracted using centrifuge drainage (Gillman, 1976), filtered to 0.22 µm (Millipore GSWP) and cation concentrations determined using ICPAES. The soil exchangeable cations were then calculated as the difference in concentration between total extractable and soil solution cations.

Using GenStat 6 (GenStat, 2002), a two-way analysis of variance (completely randomised design) of the ECEC as calculated from each of the methods was performed for both soils. Comparisons between means were made using Fisher's protected least significant difference (LSD) test. A grouped linear regression was used to examine the relationship between ionic strength, and the measured and actual exchangeable Na and Ca concentrations for the three methods. Where a significant interaction was found between ionic strength and the actual exchangeable cation concentration (indicating a significant difference in the regression slopes for the various ionic strengths), a regression was fitted through each of the three ionic strengths. However, where there was no significant interaction between ionic strength and the actual exchangeable cation concentration, a single regression was fitted through the combined data of the three ionic strengths. A linear regression was performed to examine the relationship between actual ESP and the measured ESP for the various methods.

RESULTS AND DISCUSSION

Using the results obtained from each of the various methods, ECEC was calculated as the sum of exchangeable cations and presented as a function of ionic strength (Figure 1). Significant interactions were found between ionic strength and the method of ECEC measurement for both the Mollisol (LSD (5 %) = 0.428, $p < 0.001$) and the Vertisol (LSD (5 %) = 1.53, $p = 0.012$), indicating different patterns of response across ionic strength by the measurement methods examined.

Reference method

As expected for pH neutral, predominantly constant charge soils (Table 1), ionic strength did not affect the actual ECEC (Reference method), with no significant differences between values at any ionic strength for either the Mollisol or the Vertisol (Figure 1). However, it is possible that the ECEC values (and exchangeable cation concentrations) established using this Reference method are slight underestimates of the true values. Anion exclusion (negative adsorption) has previously been found to effect the measurement of exchangeable cations, although this effect tends to be substantive only at ionic strengths of approximately 120 mM and greater ($EC > 10$ dS/m) (Bower and Hatcher, 1962; Amrhein and Suarez, 1990). As ionic strength (salinity) increases, the degree of anion exclusion tends to increase, resulting in an overestimation of soluble (or entrained) cations, and hence an underestimation of the exchangeable cation concentrations (Amrhein and Suarez, 1990). Anion exclusion is therefore problematic in methods where exchangeable cations are calculated as the difference between extractable and soluble (entrained) cations (i.e. both the Reference and Difference methods of the current study). Although anion exclusion in 'pure' clay minerals may result in substantial ECEC calculation errors (observed to be up to 28 % of the CEC at an ionic strength of 1 M), it appears that in many soils anion exclusion is negligible as anion exclusion is balanced by anion adsorption (Amrhein and Suarez, 1990). In addition, although anion exclusion can be accurately accounted for in soils which have been deliberately equilibrated with Cl^- salts (Amrhein and Suarez, 1990), for normal field soils (which contain many anions – Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , etc.), the accurate calculation of anion exclusion is difficult (if not impossible).

Therefore, in the current study, calculations of exchangeable cations did not include anion exclusion corrections.

Total cation method

At low ionic strength (10 mM, approximate EC of 1 dS/m), no significant differences were found between the actual ECEC (Reference method) and that calculated from the Total cation method for either the Mollisol or the Vertisol (Figure 1). At these low ionic strengths, the contribution of soluble cations in the soil solution to the total overall soil cations was low. In addition, at these low ionic strengths, concentrations of exchangeable Na and Ca determined by the Total cations method generally corresponded well to actual concentrations; at 10 mM, exchangeable Na concentrations were 1.3 times that of the actual concentrations for the Mollisol and 1.1 times in the Vertisol, and exchangeable Ca concentrations 0.96 times in the Mollisol, and 1.1 times in the Vertisol (Figure 2 and Figure 3).

As ionic strength increased, the ECEC calculated from the Total cations method was found to increase significantly with each increase in ionic strength for both soils (Figure 1). This overestimation of ECEC at the higher ionic strengths is due to a failure to account for the presence of soluble cations in the soil solution. At 150 mM, exchangeable Na concentrations determined using the Total cations method were 2.4 times higher than actual concentrations in the Mollisol and 1.4 times higher in the Vertisol, and exchangeable Ca concentrations 1.3 times higher in the Mollisol and 1.1 times higher in the Vertisol (for the Vertisol, measured exchangeable Ca concentrations did not increase significantly with increasing ionic strength ($p=0.485$)) (Figure 2 and Figure 3).

Although the accuracy of the Total cations method decreases with increasing ionic strength, the percentage error is dependent upon the soil properties. The degree to which ECEC (and

exchangeable Na and Ca) is overestimated at a given ionic strength is not constant, but dependent upon the actual ECEC (CEC) of the soil. The percentage contribution of soluble cations to the measured 'exchangeable' (extractable) cations will decrease as the soils actual ECEC increases. For example, from Figure 1 it can be seen that at the highest ionic strength (150 mM), although the measured ECEC is approximately 4 $\text{cmol}_{(c)}/\text{kg}$ greater than the actual value for both the Mollisol and the Vertisol, the relative overestimation using this method is greater in the Mollisol (68 % greater) than the Vertisol (12 % greater) due to the comparatively low ECEC of the Mollisol.

From the data presented (Figure 1), the measurement of exchangeable cations from the total soil cations is considered generally suitable only for soils with soil solution ionic strengths less than approximately 50 mM (EC of approximately 4 dS/m), with errors increasing with increasing ionic strength (increasing soluble salts).

Pre-wash method

Values of ECEC obtained from soil pretreated for soluble salts (Pre-wash method) were generally similar to actual ECEC values (Reference method), with a small but significant difference observed between the two methods only at 10 mM in the Mollisol (Figure 1). In addition, for the Pre-wash method, ECEC tended to remain constant across all ionic strengths, although a small but significant difference was found for the Mollisol between ECEC values at 10 and 150 mM (Figure 1). Pretreatment for soluble salts using ethanol and glycerol is therefore considered an effective method for the removal of soluble salts from the soil solution, with measured values of ECEC similar to actual ECEC values even in high ionic strength (saline) soils. However, although the ECEC can be relatively accurately measured using the Pre-wash method, the distribution of exchangeable cations comprising this ECEC was found to be different from the actual composition; the degree of change tending to be greater at higher ionic strengths (Figure 2 and Figure 3). For the 150 mM treatment, the exchangeable Na concentrations measured using the Pre-wash method were approximately half

that measured by the Reference method for both the Mollisol ($y=0.421x$) and the Vertisol ($y=0.568x$), while exchangeable Ca concentrations increased slightly in the Mollisol ($y=1.26x$) and in the Vertisol ($y=1.13x$) (although measured exchangeable Ca concentrations did not change significantly with increasing ionic strength for the Vertisol ($p=0.736$)) (Figure 2 and Figure 3). This shift in exchangeable cation composition is due to the effect of dilution on the exchange isotherm. Sposito (1981) showed that for uni-bivalent exchange, even assuming a non-preference isotherm (in which the exchanger shows no preference for either ion), a reduction in ionic strength increases the percentage of the exchange occupied by the bivalent ion. Therefore, in the current uni-bivalent ($\text{Na}^+ - \text{Ca}^{2+}$) exchange system, dilution of the soil during the pre-wash step increased exchangeable Ca concentrations while decreasing exchangeable Na concentrations.

Pretreatment of a soil for soluble salts prior to the extraction of exchangeable cations is recommended if the EC (1:5 soil:water suspension) exceeds 0.3 dS/m (soil solution EC of approximately 3-4 dS/m (Shaw, 1999)). Tucker (1985) reported that pretreatment using ethanol and glycerol effectively removed soluble salts with “minimum disturbance of the exchangeable cations”. However, Gupta et al. (1985) observed that alcohol solutions may alter the degree of solvation of exchangeable cations and the dielectric constant of the solution, thus affecting the double-layer environment of the exchange. The data from this study suggest that while ECEC can be determined from soils pretreated for soluble salts (Figure 1), dilutional effects preclude the use of this method for the accurate measurement of concentrations of the individual exchangeable cations irrespective of the ionic strength of the soil solution (Figure 2 and Figure 3).

Difference method

Ionic strength did not affect ECEC values calculated by the Difference method, with no significant differences in ECEC between ionic strengths for either soil (Figure 1). However, at the higher ionic strengths (50 and 150 mM) in the Mollisol, the ECEC calculated by the Difference method was

found to be significantly lower than that calculated by the Reference method (Figure 1). Similarly for the Vertisol, as ionic strength increased, ECEC calculated by the Difference method tended to underestimate (but not significantly) that calculated by the Reference method (Figure 1). It is thought that this decrease in the Difference method ECEC compared to the Reference method ECEC at higher ionic strengths is due, at least in part, to anion exclusion effects. As discussed previously, anion exclusion results in an underestimation of the ECEC, the magnitude of this effect increasing with increasing ionic strength. Therefore, it is considered that due to the higher moisture content (and hence lower ionic strength) of the soils following centrifugation in the Reference method (Mollisol – 45 %, Vertisol – 63 %) compared to the field capacity soils in the Difference method (Mollisol – 30 %, Vertisol – 43 %), underestimation of ECEC was greater in the Difference method; the magnitude of this difference greater at an ionic strength of 150 mM than at 10 mM.

The low ECEC values measured by the Difference method in the Mollisol are due to an underestimation of both exchangeable Na ($y=0.873x$) and Ca ($y=0.901x$) (Figure 2). For the Vertisol, measured concentrations of exchangeable cations correlated well with actual values for both Na ($y=0.960x$) and Ca ($y=1.05x$) (Figure 3). No significant interactions were found between ionic strength and actual exchangeable concentrations (Na or Ca) for either the Mollisol (Figure 2) or the Vertisol (Figure 3); indicating that there were no significant differences in the regression slopes for the various ionic strengths, and hence, that ionic strength did not effect the measured concentrations of exchangeable cations.

From the above discussion, it can be seen that the method used to determine exchangeable cations in saline soils can substantially affect the concentrations of the individual cations measured. Particularly in saline soils, these exchangeable cation concentrations are often used for the calculation of other soil properties, such as the soil ESP. The effect of measured exchangeable cation concentrations on ESP was calculated for both soils (Figure 4). When calculated from the

Pre-wash method, measured ESP was found to be approximately half that determined by the Reference method for both the Mollisol ($y=0.534x$) and the Vertisol ($y=0.621x$). This underestimation is due to the movement of Ca onto (and Na off) the soil exchange (Figure 2 and Figure 3). In contrast, soil ESP values calculated from the Total cation method tended to be greater than that calculated by the Reference method ($y=1.44x$ for the Mollisol, and $y=1.12x$ for the Vertisol). However, when calculated from the Difference method, ESP values corresponded well with those of the Reference method for the Mollisol ($y=0.960x$) and Vertisol ($y=0.932x$).

CONCLUSIONS

While many methods have been proposed for the measurement of exchangeable cations in saline soil, the results presented here demonstrate that in low ionic strength soils ($EC < 4$ dS/m) exchangeable cation concentrations can be estimated from the total soil concentrations (as described by Sumner and Miller (1996)) due to the relatively low concentrations of soluble cations. However, as ionic strength increases, failure to account for soluble salts results in an overestimation of both exchangeable Ca and Na, the magnitude of the error increasing with ionic strength. Pretreatment of a soil using alcohol (such as described by Tucker (1985)) was found to be effective in removing soluble salts, with measured ECECs generally not significantly different to actual values. However, although the ECEC can be accurately measured following pretreatment, the dilution associated with this method resulted in an increase in exchangeable Ca and a decrease in exchangeable Na. Concentrations of exchangeable cations calculated as the total extractable cations minus soil solution (soluble) cations were generally observed to correspond well to actual concentrations, even in high ionic strength soils. For soils with a soil solution ionic strength greater than 50 mM (approximately > 4 dS/m), in which exchangeable cations cannot be accurately calculated from the total cations, it is therefore proposed that exchangeable cations should be calculated according to the method proposed by Richards (1954); as the difference between total extractable cations and soil solution cations.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of David Bowen and David Appleton with the chemical analyses and soil preparation. The statistical advice of Rosemary Kopittke was also gratefully received.

REFERENCES

- Amrhein, C., and D. L. Suarez. 1990. Procedure for determining sodium-calcium selectivity in calcareous and gypsiferous soils. *Soil Science Society of America Journal* 54:999-1007.
- Black, C. A. 1968. *Soil-Plant Relationships*. New York: John Wiley & Sons, Inc.
- Bower, C.A., and J.T. Hatcher. 1962. Characterization of salt-affected soils with respect to sodium. *Soil Science* 93:275-280.
- Bower, C.A., R.F. Reitemeier, and M. Fireman. 1952. Exchangeable cation analysis of saline and alkali soils. *Soil Science* 73:251-261.
- GenStat for Windows. Release 6.1. Sixth Edition. VSN International Ltd, Oxford.
- Gillman, G.P. 1976. A Centrifuge Method for Obtaining Soil Solution. Division of Soils Technical Paper No. 16. Brisbane, Australia: CSIRO Publishing.
- Gillman, G.P., J.O. Skjemstad, and R.C. Bruce. 1982. A Comparison of Methods Used in Queensland for Determining Cation Exchange Properties. Division of Soils Technical Paper No. 44. Brisbane, Queensland: CSIRO Publishing.
- Gupta, R. K., C. P. Singh, and I. P. Abrol. 1985. Determining cation exchange capacity and exchangeable sodium in alkali soils. *Soil Science* 139:326-332.
- Isbell, R. F. 2002. *The Australian Soil Classification*. Collingwood, Victoria: CSIRO Australia.
- Levy, R., and D. Hillel. 1968. Thermodynamic equilibrium constants of sodium-calcium exchange in some Israeli soils. *Soil Science* 106:393-398.
- Marsi, M., and V P Evangelou. 1991. Chemical and physical behavior of two Kentucky soils: I. Sodium-calcium exchange. *Journal of Environmental Science and*

So, H.B., N.W. Menzies, R. Bigwood, and P.M. Kopittke. 2006. *Commun. Soil Sci. Plant Anal.* 37:1819-1832.

Health, Part A: Toxic-Hazardous Substances & Environmental Engineering 267:1147-1176.

Menzies, N. W., and L. C. Bell. 1988. Evaluation of the influence of sample preparation and extraction technique on soil solution composition. *Australian Journal of Soil Research* 26:451-464.

Nadler, A., and M. Magaritz. 1981. Expected deviations from the ESP-SAR empirical relationships in calcium- and sodium-carbonate-containing arid soils: field evidence. *Soil Science* 131:220-225.

Richards, L.A. 1954. *Diagnosis and Improvement of Saline and Alkali Soils. Report No. 60.* Washington: United States Department of Agriculture.

Shainberg, I., N. I. Alperovitch, and R. Keren. 1987. Charge-density and Na-K-Ca exchange on smectites. *Clays and Clay Minerals* 35:68-73.

Shaw, R.J. 1999. Soil salinity, electrical conductivity and chloride. In *Soil Analysis: An Interpretation Manual*, eds. K. I. Peverill, L. A. Sparrow and D. J. Reuter, 129-145. Melbourne, Victoria: CSIRO Publishing.

Soil Survey Staff. 2003. *Keys to Soil Taxonomy.* Washington, D.C.: United States Department of Agriculture.

Sposito, G. 1981. *The Thermodynamics of Soil Solutions.* New York: Oxford University Press.

Sumner, M.E., and W P Miller. 1996. Cation exchange capacity and exchange coefficients. In *Methods of Soil Analysis. Part 3. Chemical Methods*, ed. J. M. Bartels. Madison, WI: SSSA and ASA.

Tucker, B. M. 1985. Active and exchangeable cations in soils. *Australian Journal of Soil Research* 23:195-209.

So, H.B., N.W. Menzies, R. Bigwood, and P.M. Kopittke. 2006. Commun. Soil Sci. Plant Anal.

37:1819-1832.

Uehara, Goro, and Gavin Gillman. 1981. *The Mineralogy, Chemistry, and Physics of Tropical Soils with Variable Charge Clays*. Boulder, Colorado: Westview Press.

Table 1. Selected properties of the soil solutions of the Mollisol and Vertisol (extracted using centrifuge drainage at field capacity) and their major clay minerals (as determined by quantitative X-ray diffraction analysis of the < 2 μm fraction)

	pH	EC	Na	Ca	Mg	K	Major clay minerals
		dS/m	-----	mM	-----		
Mollisol	5.95	7.79	39.8	16.9	0.16	0.57	Smectite (58 %), kaolinite (33%)
Vertisol	7.56	3.22	18.0	3.17	4.20	0.33	Smectite (78 %), kaolinite (20 %)

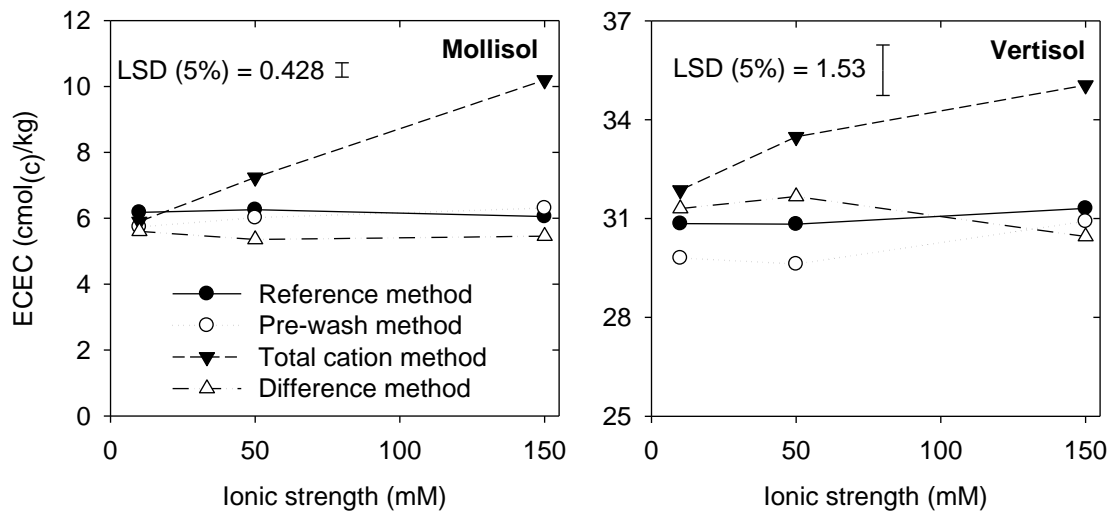


Figure 1. Effect of equilibrating solution ionic strength on the effective cation exchange capacity (ECEC) of the Mollisol (left), and the Vertisol (right), measured as the actual ECEC (Reference method), ECEC following pretreatment for soluble salts (Pre-wash method), ECEC of air-dry soil calculated using total (soluble and exchangeable) soil cations (Total cation method), and ECEC of air-dry soil calculated as total minus soluble cations (Difference method) (results are the arithmetic mean of five sodium adsorption ratio (SAR) solutions and two replicates)

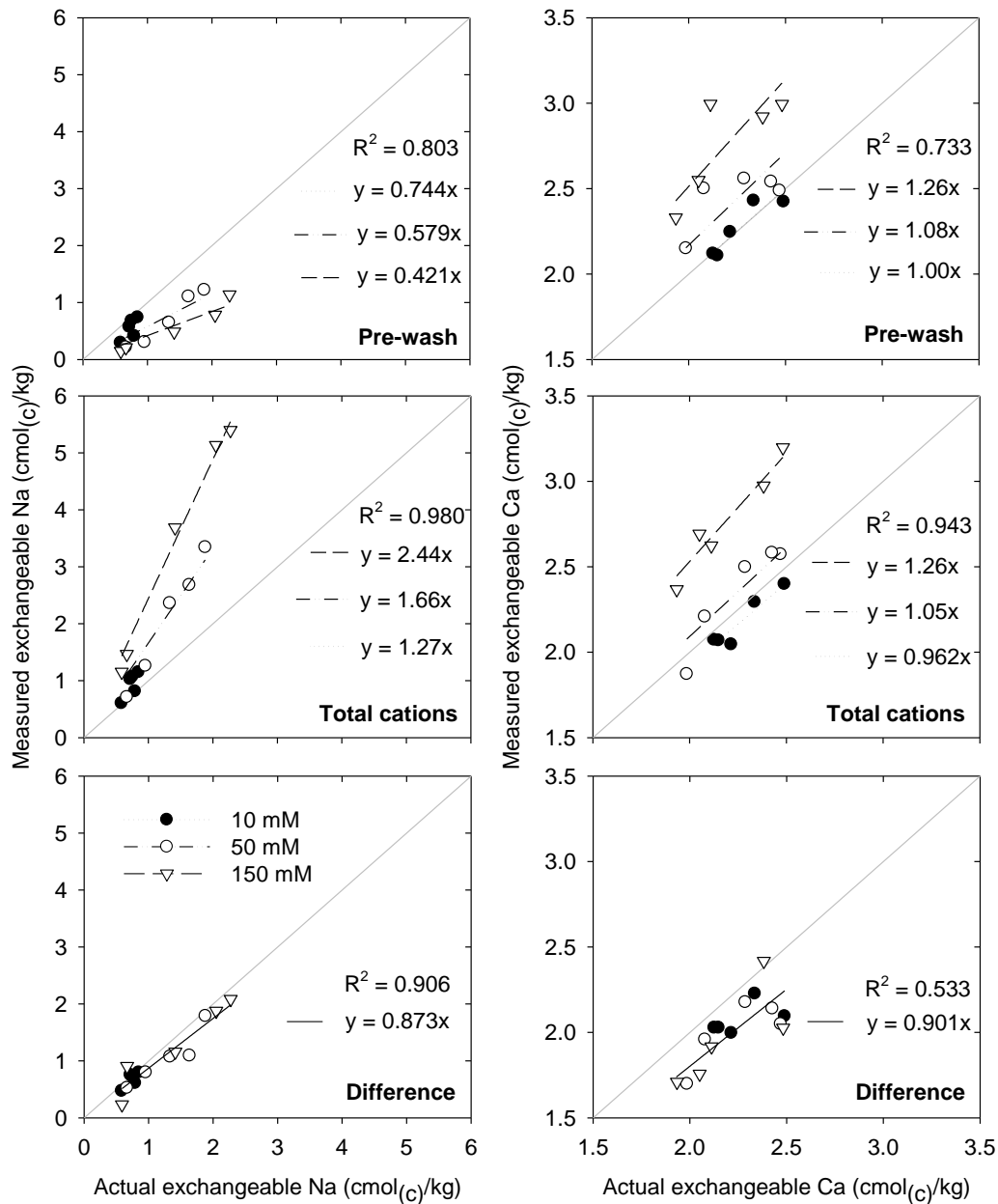


Figure 2. Exchangeable concentrations of Na (left) and Ca (right) for the Mollisol at ionic strengths of 10 mM, 50 mM, and 150 mM (measured following pretreatment for soluble salts (Pre-wash method) (top), measured as the total (soluble and exchangeable) soil cations (Total cation method) (middle), and measured as the total minus soluble cations (Difference method) (bottom)) in comparison to actual exchangeable concentrations (Reference method). A single regression was fitted through all three ionic strengths where there was no significant interaction between ionic strength and the actual exchangeable cation concentration (i.e. no significant difference in slope for the various ionic strengths) ($P > 0.05$). (Results are the arithmetic mean of two replicates) (solid grey line represents $y = x$).

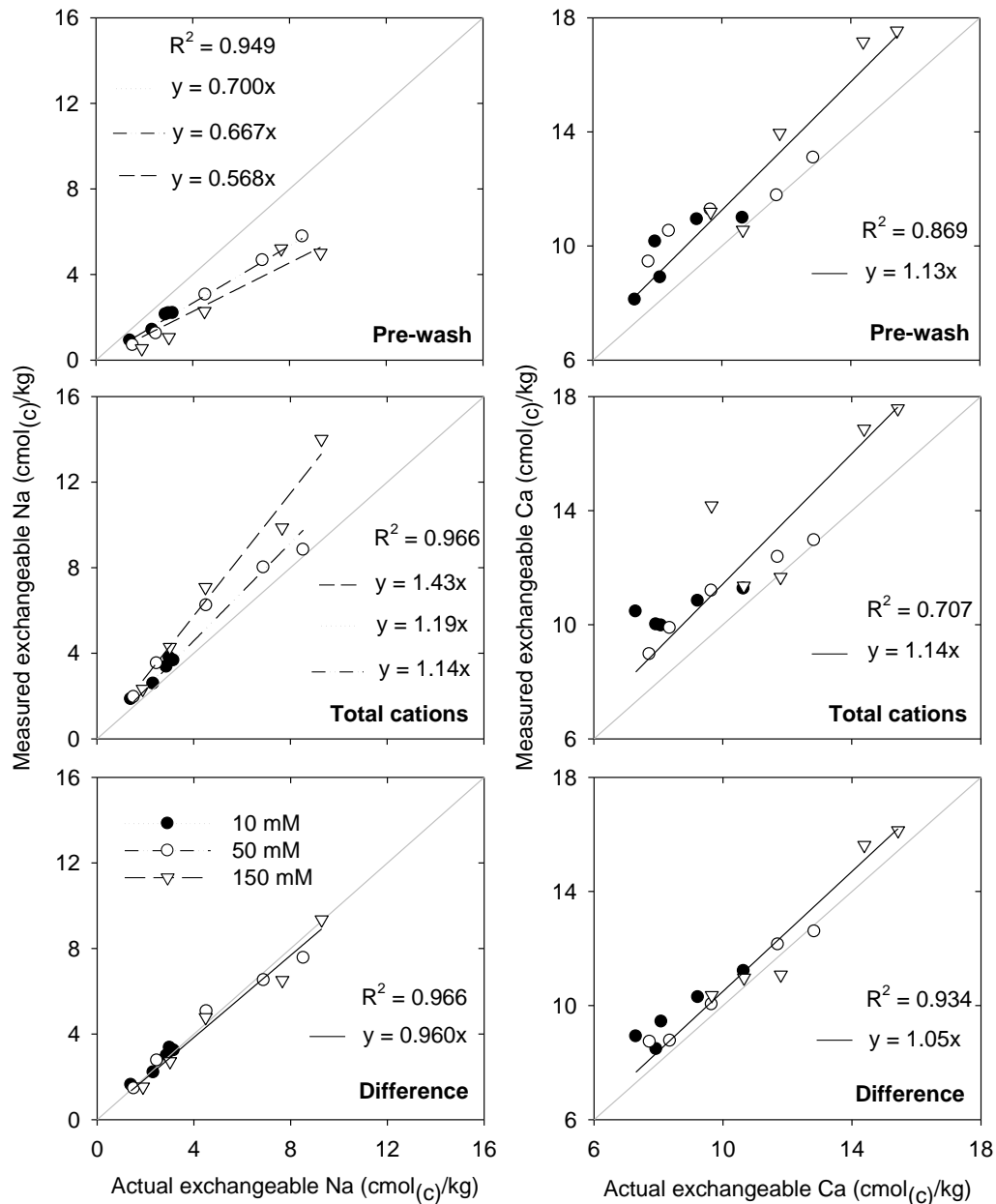


Figure 3. Exchangeable concentrations of Na (left) and Ca (right) for the Vertisol at ionic strengths of 10 mM, 50 mM, and 150 mM (measured following pretreatment for soluble salts (Pre-wash method) (top), measured as the total (soluble and exchangeable) soil cations (Total cation method) (middle), and measured as the total minus soluble cations (Difference method) (bottom)) in comparison to actual exchangeable concentrations (Reference method). A single regression was fitted through all three ionic strengths where there was no significant interaction between ionic strength and the actual exchangeable cation concentration (i.e. no significant difference in slope for the various ionic strengths) ($P > 0.05$). (Results are the arithmetic mean of two replicates) (solid grey line represents $y = x$).

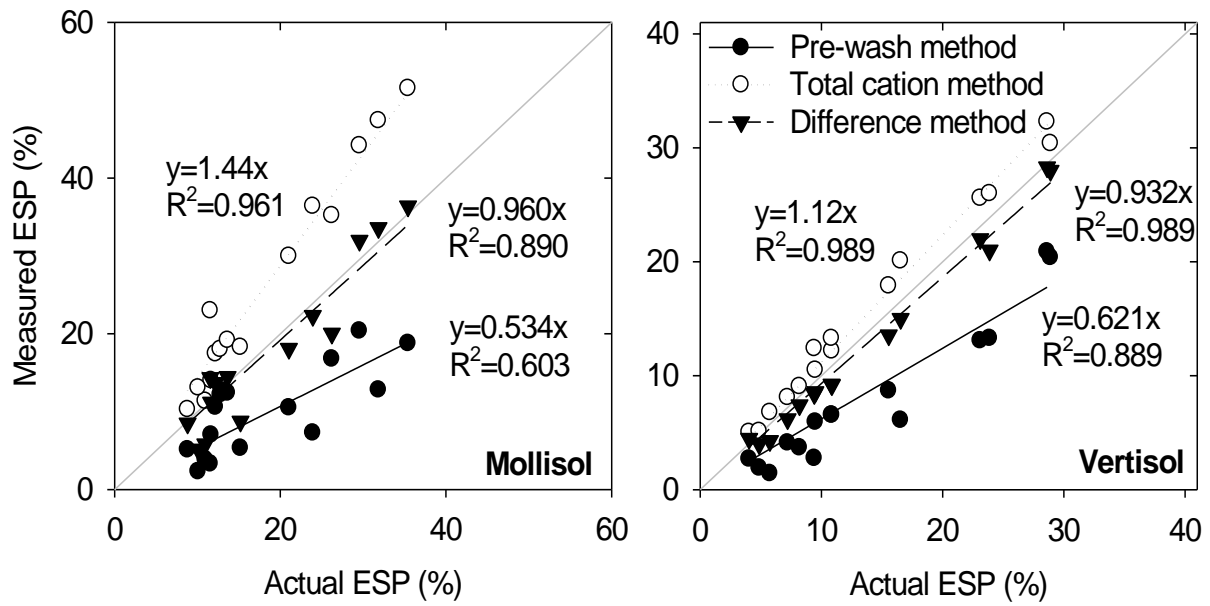


Figure 4. Exchangeable sodium percentages (ESPs) calculated from exchangeable cation concentrations measured using the Pre-wash method, Total cation method, and Difference method compared to the actual ESP as calculated from the Reference method, for the Mollisol (left) and Vertisol (right).