

Chapter 6.

**A simple method for predicting cation exchange capacity, with special respect to
sand rootzones**

Abstract

The cation exchange capacity (CEC) of soil samples submitted to commercial soil testing laboratories is often estimated by summation of the nonacid cations (CEC_{sum}) extracted in a routine soil nutrient analysis. These CEC estimates can predict measured CEC in non-calcareous soil samples but are inappropriate for use in calcareous soils and have not been evaluated in anthropogenic sand rootzones of turfgrass sites. In a dataset of 37 sand and 17 soil samples varying in pH, calcium carbonate equivalent (CCE), and organic matter (OM) content, we evaluated the ability of the summation method to predict measured CEC_{CE} (by compulsive exchange) using 5 extraction methods: 1 M NH_4OAC , Mehlich 3, Morgan, 0.01 M $SrCl_2$, and 1:5 H_2O . The CEC_{sum} estimates based on 1 M NH_4OAC , Mehlich 3, and Morgan extractions were inaccurate for the calcareous samples and overestimated CEC_{CE} in sands with $CCE < 10 \text{ g kg}^{-1}$. The CEC_{sum} based on the 1:5 H_2O extraction underestimated CEC_{CE} in all soil types. Estimates based on the 0.01 M $SrCl_2$ extraction were accurate in all sands and in soils with $CEC_{CE} < 60 \text{ mmol}_c \text{ kg}^{-1}$. In soils with $CEC_{CE} > 60 \text{ mmol}_c \text{ kg}^{-1}$, two consecutive extractions with 0.01 M $SrCl_2$ and summation of nonacid cations extracted provided an accurate estimate of CEC_{CE} .

Introduction

Most commercial soil testing laboratories estimate CEC from the quantity of nonacid cations extracted in an agronomic soil test (Ross, 1995; Sumner and Miller, 1996). Exchangeable acidity is also included in these estimates if the laboratory concludes that acidity is appreciable; in general, the exchangeable acidity can be considered negligible if soil pH in water is > 5.5 .

In anthropogenic sand rootzones, extracting solutions such as Mehlich 3, Morgan, or 1 M NH₄OAc are commonly used for extraction of nonacid cations, but the CEC estimates derived from nonacid cations extracted in these sand rootzones are of unknown accuracy. These sand rootzones are usually established with a minimum sand content of 920 g kg⁻¹ and maximum silt and clay content of 50 g kg⁻¹ and 30 g kg⁻¹, respectively (USGA, 2004). Common extracting solutions such as Mehlich 3, Morgan, and 1 M NH₄OAc have higher ionic strength (*I*) and a different pH than are found in soil solution, and these differences may influence the quantity of nonacid cations extracted from the organic matter which provides the majority of cation exchange sites in sand rootzones. Because sand rootzones are inherently low in exchangeable nonacid cations, any error in the measurement of exchangeable nonacid cations could have a relatively large influence on the estimated CEC. Furthermore, calcareous sands are geographically ubiquitous (Christians, 1990), but the usual method of estimating CEC based on the nonacid cations extracted with an agronomic extractant is clearly inappropriate for calcareous materials (Sumner and Miller, 1996).

There are numerous methods which make a more direct measurement of CEC (Bache, 1976; Gillman and Sumpter, 1986; Gillman et al., 1983; Matsue and Wada, 1985; Sumner and Miller, 1996), but they suffer from a common drawback that precludes their regular use: most methods are very time-consuming. For example, the BaCl₂ compulsive exchange method (CEC_{CE}) of Gillman and Sumpter (1986), which determines the exchange of Mg²⁺ for Ba²⁺ at a known solution pH and *I*, requires multiple rinsing and equilibration steps that extend the procedure to 24 hours. Avila-Segura (1999) and Sumner et al. (1994) have suggested simplifications to the CEC_{CE} method, but the method is in infrequent use at commercial soil testing laboratories, despite its accuracy, due to the length and complexity of the procedure.

Matsue and Wada (1985) found that specific adsorption of SO_4^{2-} on andisols resulted in overestimation of CEC_{CE} , and recommended an alternative method involving sample equilibration with 0.01 M SrCl_2 in five consecutive centrifuge washings, after which adsorbed Sr^{2+} is removed by 0.5 M HCl and the removed Sr^{2+} measured as the CEC. This method requires 48 hours of equilibration and exchange, and therefore has not been widely used in commercial laboratories.

A single extraction with 0.01 M SrCl_2 has been used to measure exchangeable K (Woods et al., 2005a) and Ca and Mg (Woods et al., 2005b) of a calcareous sand rootzone. This rapid extraction adjusts to soil pH and has an I similar to that of soil solution.

For 37 sand and 17 soil samples, we compared the CEC_{CE} with CEC estimates derived from soil OM and pH and with CEC estimates calculated from summation of nonacid cations extracted by different extracting solutions: 1 M NH_4OAC , Mehlich 3, Morgan, 0.01 M SrCl_2 , and 1:5 H_2O . Our objective was to determine which of the CEC estimates could accurately predict CEC_{CE} across a range of calcareous and non-calcareous sands and soils.

Materials and Methods

Fifty-four sand (Table 6.1) and soil (Table 6.2) samples were obtained. Sands represented a range of pH, CCE, and OM typical of many turfgrass rootzones. Each sand sample was collected to a depth of 10 cm. The soils represented a range of pH, CCE, and OM; additionally, soil samples represented 5 of the 6 soil management groups (Bergstrom et al., 1987) in New York. Each soil sample was collected to a depth of 20 cm.

Table 6.1. List of sands analyzed with associated data including pH, calcium carbonate equivalent (CCE), cation exchange capacity by compulsive exchange (CEC_{CE}), and organic matter (OM).

Sample Description	Location	pH (H ₂ O)	Al	OM	CCE	CEC_{CE}
			mmol _c kg ⁻¹	g kg ⁻¹	g kg ⁻¹	mmol _c kg ⁻¹
Sand - golf green	Philippines	4.4	11	17	3	16
Sand - golf green	Philippines	4.6	14	20	5	34
Sand - golf fairway	New York	5.0	4	7	2	6
Sand - golf green	Thailand	5.5	1	20	4	23
Sand - golf green	Japan	5.7	1	17	5	11
Sand - golf green	Japan	6.1		14	4	19
Sand - golf fairway	Oregon	6.2		18	3	10
Sand - golf green	New York	6.2		41	6	59
Sand - golf green	Japan	6.4		20	7	7
Sand - golf green	New York	6.5		37	7	45
Sand - quarry	Unknown	6.5		0	2	0
Sand - quarry	Unknown	6.6		4	2	0
Sand - golf green	Oregon	6.7		14	6	30
Sand - golf green	Oregon	6.8		10	3	19
Sand - golf fairway	China	6.9		4	2	8
Sand - golf green	Georgia	6.9		13	2	10
Sand - golf tee	Thailand	7.0		11	4	27
Sand - golf green	Japan	7.0		23	8	33
Sand - golf green	Oregon	7.0		24	3	37
Sand - golf green	Oregon	7.0		25	4	41

Table 6.1 (Continued)

Sand - golf green	California	7.2	15	7	40
Sand - golf green	New York	7.2	52	13	101
Sand - quarry	Unknown	7.3	2	2	0
Sand - golf green	Thailand	7.3	16	5	27
Sand - golf green	China	7.4	3	3	8
Sand - golf green	Spain	7.4	30	206	55
Sand - golf green	California	7.5	9	9	26
Sand - golf green	Japan	7.7	16	12	18
Sand - golf green	California	7.8	9	4	27
Sand - golf green	Japan	7.9	13	8	20
Sand - golf green	New York	8.2	8	241	14
Sand - golf green	New York	8.3	10	249	13
Sand - golf green	New York	8.3	11	233	13
Sand - golf rough	Hawaii	8.4	12	438	30
Sand - golf green	Arizona	8.5	5	18	30
Sand - golf green	Hawaii	8.8	6	740	9
Sand - quarry	New York	9.0	3	91	6

Table 6.2. List of soils analyzed with associated data including pH, calcium carbonate equivalent (CCE), cation exchange capacity by compulsive exchange (CEC_{CE}), and organic matter (OM).

Soil Description	Location	pH	Al	OM	CCE	CEC_{CE}
			(H_2O)	$mmol_c$	$g\ kg^{-1}$	$g\ kg^{-1}$
			kg^{-1}			
Fluventic Dystrudepts	New York	5.4	2	32	5	52
Typic Fragiudepts	New York	5.7	1	61	6	94
Typic Dystrudepts	New York	5.8	1	37	5	72
Typic Eutrudepts	New York	6.1		38	6	74
Typic Dystrudepts	New York	6.2		17	3	34
Fluventic Dystrudepts	New York	6.3		29	7	89
Aeric Endoaquepts	New York	6.4		37	6	71
Aeric Endoaqualfs	New York	6.7		47	8	191
Hudson clay loam	New York	6.7		53	7	79
Glossic Hapludalfs	New York	6.9		20	6	77
Glossic Hapludalfs	New York	7.0		36	10	109
Glossic Hapludalfs	New York	7.1		66	12	166
Glossic Hapludalfs	New York	7.1		106	19	172
Lamellic Hapludalfs	New York	7.2		28	20	108
Glossic Hapludalfs	New York	7.7		18	17	69

Table 6.2 (continued)

Aquic Udorthents	New York	7.7	40	10	131
Anthrosol	China	7.9	21	54	71

The CEC_{CE} was measured using the modified compulsive exchange method of Gillman and Sumpter (1986). Nonacid cations were extracted from each sample with 1 *M* NH_4OAc (Brown and Warncke, 1988), Mehlich 3 (Wolf and Beegle, 1995), and Morgan (Morgan, 1941). Water-soluble nonacid cations were extracted by 1:5 H_2O (Soil and Plant Analysis Council, 1999).

Hundredth-molar $SrCl_2$ was substituted for 0.01 *M* $CaCl_2$ in the extraction method of Houba et al. (2000) to allow for direct measurement of Ca in the extract. The shaking time with 0.01 *M* $SrCl_2$ was reduced from 120 minutes to 5 minutes, and the soil:solution ratio was maintained at 1:10, but only 2 g soil and 20 mL 0.01 *M* $SrCl_2$ were used, rather than 10 g soil and 100 mL solution as described by Houba et al. (2000). This simplification of the 0.01 *M* $SrCl_2$ extraction was tested on 31 calcareous and non-calcareous sands and soils. The simplified method extracted equivalent quantities of the nonacid cations (data not shown, $r^2 = 0.98$, linear regression intercept and slope not significantly different from 0 and 1, respectively) when compared to the procedure as outlined by Houba et al. (2000).

All solutions were analyzed for nonacid cations using inductively-coupled plasma spectrometry. From the quantity of nonacid cations extracted by each method, we estimated the CEC by summation of the nonacid cations. We shall refer to this estimate of CEC as CEC_{sum} . The CEC_{sum} was calculated based on formulas modified from Sumner and Miller (1996) to report CEC_{sum} in units of $mmol_c\ kg^{-1}$:

$$CEC_{sum} = Ca + Mg + K + Na \quad [1]$$

where Ca = extracted Ca in $\text{mmol}_c \text{kg}^{-1}$

Mg = extracted Mg in $\text{mmol}_c \text{kg}^{-1}$

K = extracted K in $\text{mmol}_c \text{kg}^{-1}$

Na = extracted Na in $\text{mmol}_c \text{kg}^{-1}$

Thus, five CEC_{sum} estimates were obtained in addition to CEC_{CE} for each of the samples. Exchangeable acidity was measured for each sample with pH below 6 (Tables 6.1 and 6.2); we did not include the exchangeable acidity in our CEC_{sum} calculations.

Soil pH was measured in a 1:5 soil:water suspension. Calcium carbonate equivalent of each sample was measured using the method of Moore et al. (1987). Soil OM was measured by loss on ignition (Schulte, 1995). An empirical relationship based on the investigations of Helling et al. (1964) was used to calculate an expected contribution of organic matter to the sample CEC assuming a conversion factor from organic carbon to organic matter of 1.9:

$$\text{CEC}_{\text{OM}} (\text{mmol}_c \text{kg}^{-1}) = -311 + 268 \times \text{pH} \quad [2]$$

The data were evaluated using least squares linear regression analysis. The CEC_{sum} values for each method were used to predict CEC_{CE} . All statistical analyses were performed using the REG procedure in SAS System Software version 9.1 (SAS, Cary, NC).

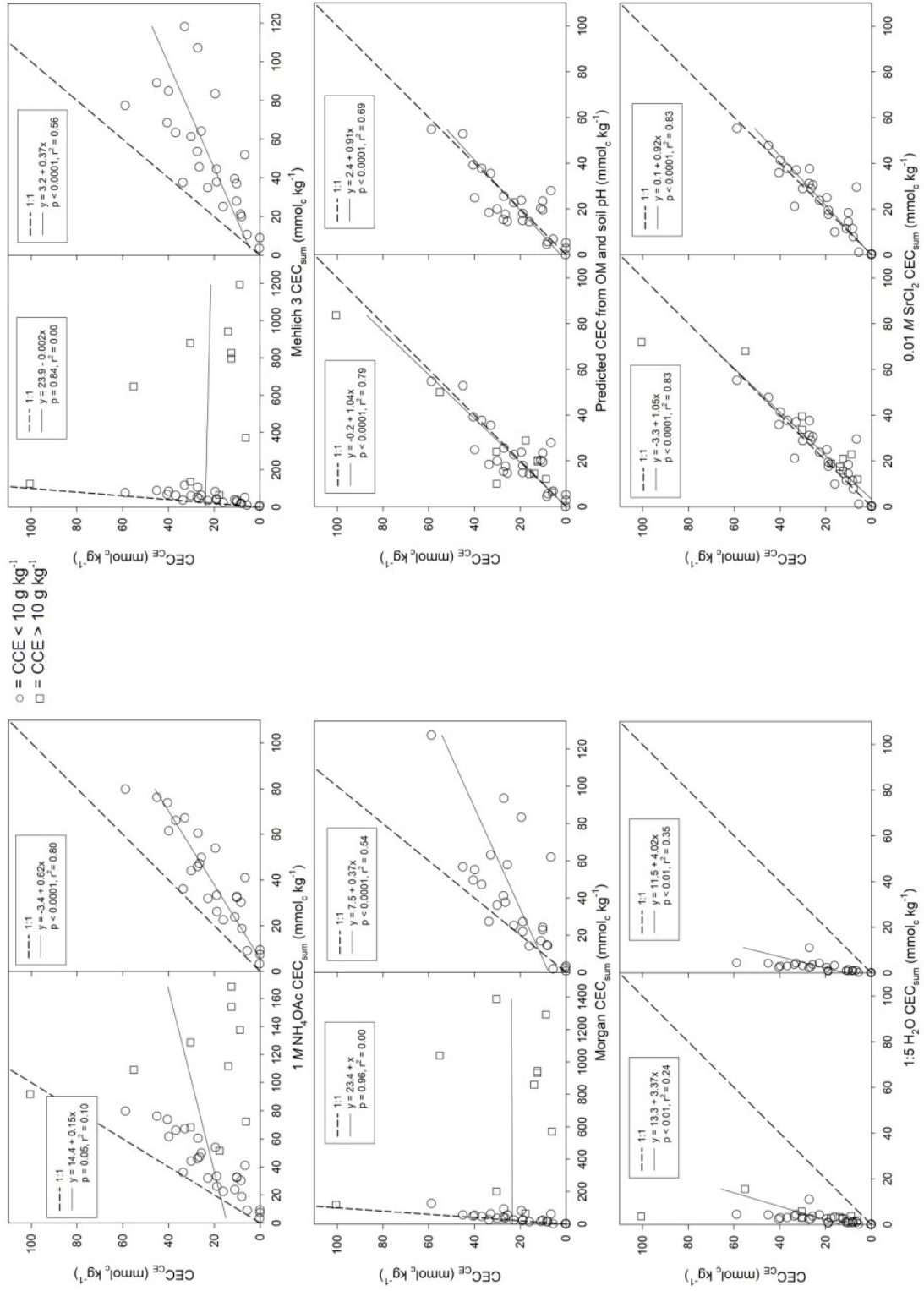
Results and Discussion

Sands

The extraction methods differed in their ability to predict CEC_{CE} of sand rootzones (Fig. 6.1). For the solutions that do not adjust to the sample pH during the extraction process (1 M NH_4OAc , Mehlich 3, and Morgan), an overestimation of CEC_{CE} was observed in the sand samples with $CCE > 10 \text{ g kg}^{-1}$. This overestimation is due to the dissolution of solid-phase calcium or magnesium carbonates during the extraction process. Even when the samples with $CCE > 10 \text{ g kg}^{-1}$ were omitted (Fig. 6.1), the 1 M NH_4OAc , Mehlich 3, and Morgan tests produced CEC_{sum} values that overestimated CEC_{CE} .

The CEC_{OM} estimates were of similar magnitude as CEC_{CE} and were not influenced by CCE (Fig. 6.1). Because organic matter is the preponderant source of CEC in sand rootzones, one expects that OM and pH would predict CEC. The use of equation 2 provides a more accurate estimate of the CEC in sand rootzones than does CEC_{sum} based on 1 M NH_4OAc , Mehlich 3, or Morgan extractions.

Figure 6.1. The relationship between CEC_{sum} based on 1 M NH_4OAc , Mehlich 3, Morgan, 1:5 H_2O , and 0.01 M $SrCl_2$ extractions and corresponding CEC_{CE} for 37 sand samples varying in pH, CCE, and OM. The CEC_{OM} is also shown for comparison. The (\square) represent samples with $CCE > 10 \text{ g kg}^{-1}$, and the (\circ) represent samples with $CCE < 10 \text{ g kg}^{-1}$.

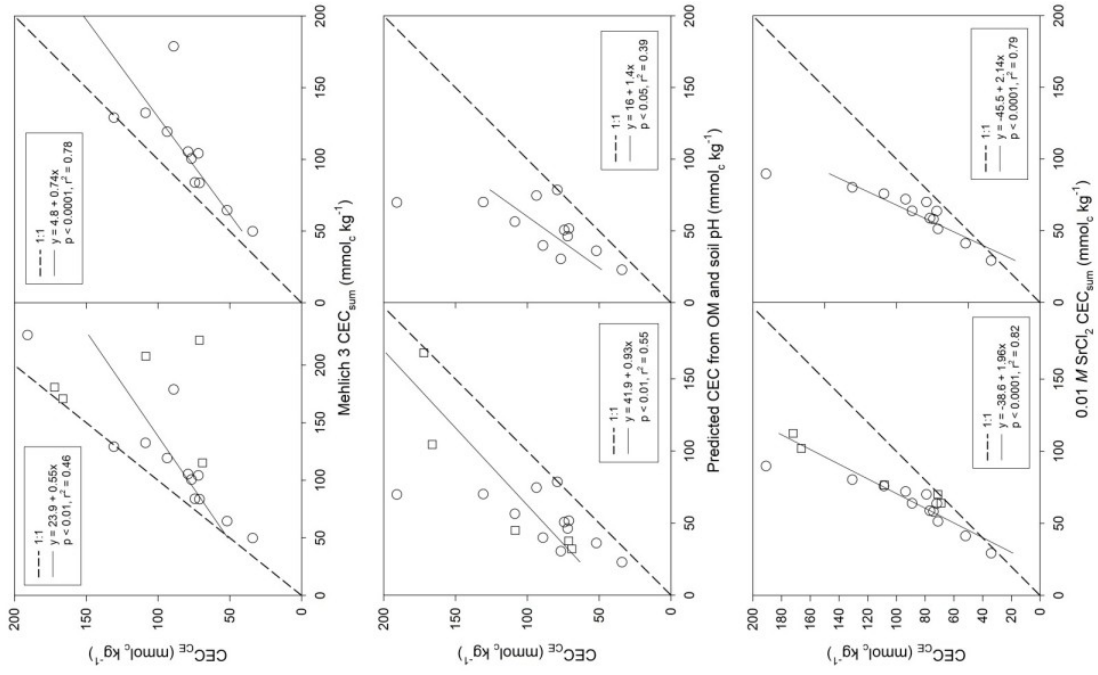


The CEC_{sum} derived from the 1:5 H_2O extractions were always less than CEC_{CE} (Fig. 6.1). The 1:5 H_2O extraction removes only a fraction of the exchangeable nonacid cations, and although there is a positive relationship between CEC_{sum} based on the 1:5 H_2O extraction and CEC_{CE} , it is possible that the sands with higher CEC also have a greater concentration of water soluble nonacid cations.

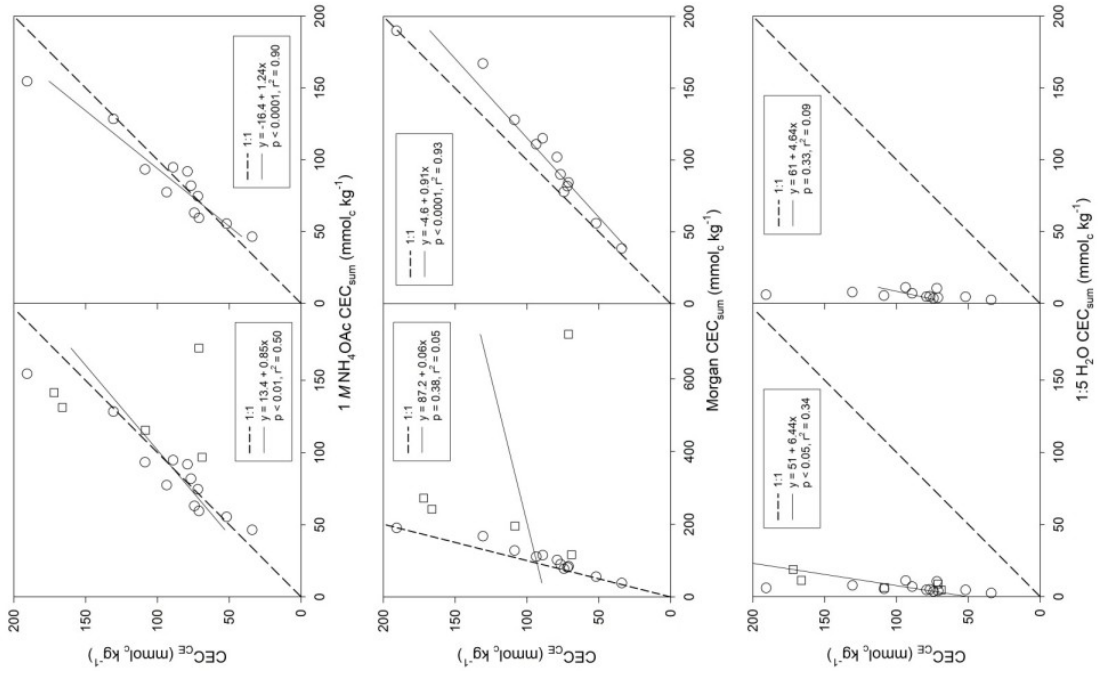
The 0.01 M $SrCl_2$ extraction resulted in CEC_{sum} values that were comparable to CEC_{CE} in all sands, regardless of CCE (Fig. 6.1). The 1 M NH_4OAc , Mehlich 3, and Morgan procedures extract more nonacid cations, even in sands with low CCE, than would be exchangeable under simulated field conditions. However, the 0.01 M $SrCl_2$ method extracted nonacid cations of equivalent charge to those cations on the sample exchange sites.

All but one of the sands included in our analysis had $CEC_{CE} < 60 \text{ mmol}_c \text{ kg}^{-1}$. The recommended maximum organic matter content for sand rootzones maintained as creeping bentgrass [*Agrostis stolonifera* var. *palustris* (Huds.) Farw.] putting greens is 40 g kg^{-1} (Carrow, 2003). At this maximum value of OM, and at a pH of 6.5, the CEC_{OM} (equation 2) would be $57 \text{ mmol}_c \text{ kg}^{-1}$. Because turfgrass managers attempt to maintain the organic matter content of sand rootzones at less than 40 g kg^{-1} (Carrow, 2003), most samples from sand rootzones probably fall within the linear prediction range of CEC_{CE} by the 0.01 M $SrCl_2$ CEC_{sum} .

Figure 6.2. The relationship between CEC_{sum} for 1 M NH_4OAc , Mehlich 3, Morgan, 1:5 H_2O , and 0.01 M $SrCl_2$ extractions and corresponding CEC_{CE} for 17 soil samples varying in pH, CCE, and OM. The CEC_{OM} is also shown for comparison. The (\square) represent samples with $CCE > 10 \text{ g kg}^{-1}$, and the (\circ) represent samples with $CCE < 10 \text{ g kg}^{-1}$.



○ = CCE < 10 g kg⁻¹
 □ = CCE > 10 g kg⁻¹



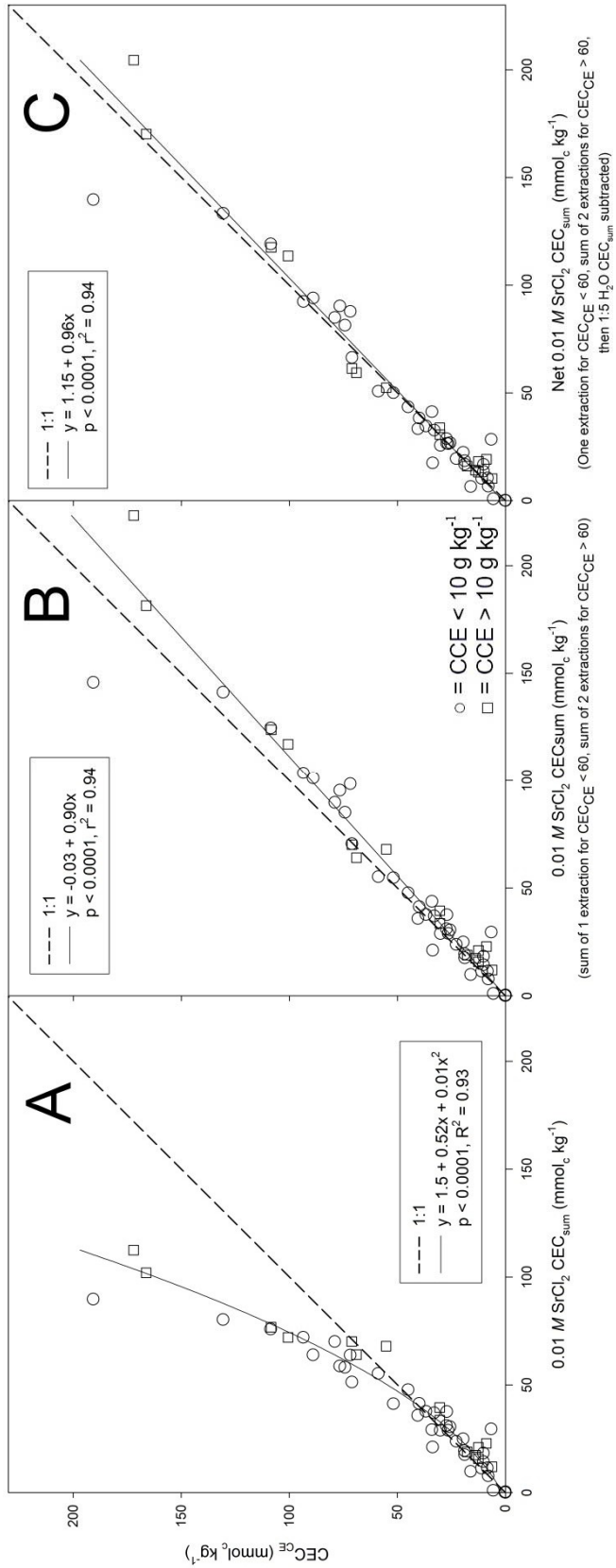
Soils

The CEC_{sum} of soil samples extracted with 1 M NH_4OAc , Mehlich 3, or Morgan solutions were of similar magnitude to CEC_{CE} , particularly in soils with CCE < 10 g kg^{-1} (Fig. 6.2). The CEC_{OM} , which do not take into account the clay content of a soil, were less than CEC_{CE} for these soil samples (Fig. 6.2). The 1:5 H_2O CEC_{sum} estimates were similar to the results from the sands in that they were unaffected by CCE but remained low in comparison with the CEC_{CE} (Fig. 6.2). The predictive relationship between 0.01 M $SrCl_2$ CEC_{sum} and CEC_{CE} is linear with a slope of 1 up to about 60 $mmol_c kg^{-1}$, above which the 0.01 M $SrCl_2$ CEC_{sum} underestimates CEC_{CE} (Fig. 6.2).

All Samples Combined

Of the methods we evaluated for predicting CEC_{CE} , only 0.01 M $SrCl_2$ produces a suitable CEC_{sum} regardless of the sample CEC or CCE. The CEC_{sum} values based on this extraction had a quadratic predictive relationship (Fig. 6.3, A) with CEC_{CE} across all samples. For samples with $CEC_{CE} > 60$ $mmol_c kg^{-1}$, we measured the nonacid cations extracted by performing three consecutive 0.01 M $SrCl_2$ extractions on the same sample. When the CEC_{sum} from the first and second extractions were summed, the quadratic relationship between CEC_{sum} and CEC_{CE} became linear (Fig. 6.3, B). Three consecutive extractions with 0.01 M $SrCl_2$ produced a CEC_{sum} that overestimated CEC_{CE} (data not shown). The accuracy of the CEC_{sum} estimates could be slightly improved by subtracting the water soluble nonacid cations (CEC_{sum} derived from the 1:5 H_2O extraction) from the 0.01 M $SrCl_2$ CEC_{sum} , as shown in Fig. 6.3 (C).

Figure 6.3. The relationship between 0.01 *M* SrCl₂ CEC_{sum} and CEC_{CE} for 54 sand and soil samples varying in pH, CCE, and OM. The CEC_{sum} is shown for one 0.01 *M* SrCl₂ extraction (A), for two consecutive 0.01 *M* SrCl₂ extractions (B), and for two consecutive 0.01 *M* SrCl₂ extractions with 1:5 H₂O CEC_{sum} subtracted (C). The (□) represent samples with CCE > 10 g kg⁻¹, and the (○) represent samples with CCE < 10 g kg⁻¹.



When the nonacid cations are represented as a percentage of the CEC, the implication is that the specified cation occupies the reported percentage of soil exchange sites. Because the aforementioned agronomic testing methods overestimate CEC_{CE} , it is not clear exactly what the nonacid cation percentage values then represent, other than simply a percentage of the cations extracted; it is misleading to consider them exchangeable for sand samples with $CEC_{CE} < 60 \text{ mmol}_c \text{ kg}^{-1}$.

We expect that a single 5 minute extraction with 0.01 *M* SrCl_2 will produce an accurate CEC estimate for most samples collected from sand rootzones or soils with $CEC_{CE} < 60 \text{ mmol}_c \text{ kg}^{-1}$, regardless of CCE. A notable exception is saline samples, from which no CEC_{sum} , regardless of extraction method, will provide an accurate estimate of CEC. It is not known if the 0.01 *M* SrCl_2 extraction results in accurate CEC estimates for sands to which certain types of inorganic or organic amendments have been added; our dataset did not include every possible soil amendment. It is furthermore unknown how accurate the method is in acid sands. However, turfgrass sand rootzones are usually limed to a pH of at least 5.5, so in practice it is unlikely to encounter samples with significant amounts of exchangeable Al. In addition to improved accuracy of the CEC estimates, a dilute salt solution that adjusts to the soil pH can be used to measure plant-available pools of soil P (Wendt and Corey, 1981) and soil micronutrients (McBride et al., 2003).

Conclusion

Nonacid cations extracted by 0.01 *M* SrCl_2 in a rapid 5 minute extraction procedure provided accurate estimates of CEC_{CE} in sands and soils with CEC_{CE} less than $60 \text{ mmol}_c \text{ kg}^{-1}$, independent of the CCE of the samples. Because sand rootzones usually have a CEC_{CE} less than $60 \text{ mmol}_c \text{ kg}^{-1}$, use of a single 0.01 *M* SrCl_2 extraction

will provide accurate estimates of exchangeable nonacid cations, CEC_{sum} , and resultant nonacid cation percentages. If CEC_{CE} is above $60 \text{ mmol}_c \text{ kg}^{-1}$, two consecutive extractions are needed.

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