A Simple Method for Estimating Effective Cation Exchange Capacity, Cation Saturation Ratios, and Sulfur Across a Wide Range of Soils

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Abstract: Cation exchange capacity (CEC) and soil S supply potential are important soil characteristics. The $BaCl_2$-$MgSO_4$ compulsive exchange (CEC_{CE}) method is recommended for measuring effective CEC (ECEC) of both calcareous and acidic soils. However, to reduce costs, soil testing laboratories typically report CEC estimated from agronomic soil test data (summation method; CEC_{sum}), a method that overestimates the ECEC of calcareous soils. Recently, guidance for sulfur (S) management of alfalfa (*Medicago sativa* L.) was derived based on a single, 30-min, 0.01-*M* $CaCl_2$ soil extraction with a 1:5 (wt:vol) soil-to-solution ratio. We tested the hypothesis that a single, 5-min, 0.01-*M* $SrCl_2$ soil extraction with a 1:10 (wt:vol) soil-to-solution ratio can be used to accurately estimate both ECEC and available S across a variety of soil types. Fifty New York agricultural soils (soil pH from 5.1 to 8.4) were analyzed for CEC_{CE} and cations extracted with Morgan, Mehlich 3, 1 *M* NH_4OAc, 1 *M* NH_4Cl, and 0.01 *M* $SrCl_2$ (single and double extractions). The CEC_{sum} based on Mehlich 3, Morgan, 1 *M* NH_4OAc, and 1 *M* NH_4Cl extraction solutions greatly overestimated ECEC as measured by CEC_{CE}, whereas the CEC_{sum} based on a single extraction with 0.01 *M* $SrCl_2$ correlated well with CEC_{CE} across all soils (slope, 1.0451; $R^2 = 0.8538$). Extractable S in the 5-min 0.01-*M* $SrCl_2$ solution correlated well with results of the 30-min 0.01-*M* $CaCl_2$ extraction (slope, 0.9685; $R^2 = 0.9976$). We conclude that a single 5-min 0.01-*M* $SrCl_2$ extraction with 1:10 soil-to-solution ratio is a simple, rapid, and inexpensive method of estimating ECEC and plant-available S.

Key Words: Cation exchange capacity, strontium chloride, compulsive exchange, sulfur

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Cation exchange capacity (CEC) is widely used to assess soil's ability to retain and supply calcium (Ca), magnesium (Mg), and potassium (K) to plants. In addition, percent base saturation, which requires a CEC determination, is a criterion used for separation of soil orders (Horn et al., 1982) and, by some practitioners, to derive K and Mg recommendations for crops (Buchholz, 2004).

The various methods developed to determine soil's CEC can give different results (Bache, 1976), primarily driven by conditions under which the CEC is measured. The ammonium acetate (NH_4OAc) method buffered at a pH of 7.0 is the most widely used method among those that determine CEC at a specified pH, and many state agencies have traditionally required CEC to be measured by this procedure (Ross, 1995). The barium chloride–triethanolamine method of Mehlich (1938) is also buffered but at a pH of 8.2.

Although CEC determination at a buffered pH can be useful for soil classification purposes, CEC estimates at a pH that is not the pH of the soil as it is being managed for agricultural purposes can be misleading (Gillman et al., 1983; Hendershot and Duquette, 1986). For management purposes, determination of the CEC of a soil at its actual soil pH and ionic strength, hereafter referred to as effective CEC (ECEC), is more useful. The $BaCl_2$-$MgSO_4$ compulsive exchange (CEC_{CE}) method developed by Gillman and Sumpter (1986) is the recommended method for determining ECEC. This method can be used for many soils including saline and nonsaline calcareous soils but is very time consuming and hence expensive to conduct in the laboratory. In addition, this method generates a hazardous waste ($BaCl_2.2H_2O$).

Because of the costs and time associated with use of the $BaCl_2$-$MgSO_4$ compulsive exchange method, many soil analysis laboratories do not routinely measure the ECEC of soils but rather estimate a soil's CEC from its agronomic soil test results (summation of cations method; CEC_{sum}). In this approach, CEC_{sum} is determined by summation of exchangeable K, Ca, Mg, and, where applicable, also sodium (Na) extracted by the test used to derive agronomic recommendations. For soils with a pH less than 6, exchangeable acidity should be taken into account as well.

The cation summation method is known to result in inaccurate estimates for calcareous soils as most agronomic soil test procedures extract cations at a low pH. For example, the pH of the Mehlich-3 extraction is 2.3 (Wolf and Beegle, 1995), whereas the Morgan extraction has a pH of 4.8 (Morgan, 1941). However, also for other soils, overestimation of the ECEC can occur when the summation method is used. Ross and Ketterings (2011) recommend not using the summation method if the soil pH is greater than 7.5 or the soil has been recently limed or fertilized. Woods (2006) reported that the ECEC derived by summation of cations extracted by the Mehlich 3, Morgan, and 1 *M* NH_4OAc extraction solutions overestimated the ECEC of low organic matter sands.

To improve the $BaCl_2$-$MgSO_4$ compulsive exchange method developed by Gillman (1979), Matsue and Wada (1985) proposed the use of 0.01 *M* $SrCl_2$ instead of $BaCl_2$ for soils with a specific adsorption of SO_4^{2-} because there is a greater opportunity of selectivity preferences for Sr than for Ca, Mg, or the monovalent cations (Dolcater et al., 1968). This modified 0.01 *M* $SrCl_2$ method of Matsue and Wada (1985) also required consecutive centrifuge washings and 48 h of equilibration and exchange and, therefore, it was also not suitable for routine soil testing. More recently, Woods (2006) found that a single extraction with 0.01 *M* $SrCl_2$ produced an accurate ECEC estimate in a data set of 37 sands collected from golf courses in the Philippines, Thailand, Japan, China, Spain, and the United States (Hawaii, Oregon, California, New York, and Georgia) and 17 agricultural soils samples (16 from New York and one from China). Woods (2006) further reported that, in soils with a CEC_{CE} >60 $cmol_c\ kg^{-1}$, two consecutive extractions with 0.01 *M* $SrCl_2$ and summation of nonacid

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TABLE 1. List of Soil Samples Included in the CEC Study With OM, M3-P Content, Soil pH (1:1 H_2O), and CEC_{CE} and 0.01 M $SrCl_2$ Method (CEC_{sum})

Soil Number	Name	Soil Series	OM†	M3-P	pH	CEC_{CE}	CEC_{sum}
			g kg^{-1}	mg kg^{-1}		cmol$_c$ kg^{-1}	
1	Chenango	Chenango Loamy-Skeletal, Mixed, Superactive, Mesic Typic Dystrudepts	27	80	5.1	1.74	0.64
2	Volusia	Volusia Fine-Loamy, Mixed, Active, Mesic Aeric Fragiaquepts	27	69	5.2	3.24	2.67
3	Bath	Bath Coarse-Loamy, Mixed, Active Mesic Typic Fragiudepts	37	104	5.8	5.34	5.77
4	Madalin	Madalin Fine, Illitic, Mesic Mollic Endoaqualfs	32	31	5.9	7.51	7.08
5	Braceville	Braceville Coarse-Loamy, Mixed, Active, Mesic Typic Fragiudepts	29	59	6.0	5.07	6.02
6	Ovid	Ovid Fine-Loamy, Mixed, Active, Mesic Aeric Endoaqualfs	18	55	6.1	4.96	4.90
7	Rhinebeck	Rhinebeck Fine, Illitic, Mesic Aeric Endoaqualfs	15	34	6.3	6.02	5.46
8	Madrid	Madrid Coarse-Loamy, Mixed, Active, Mesic Haplic Glossudalfs	23	69	6.3	3.49	3.51
9	Lordstown	Lordstown Coarse-Loamy, Mixed, Active, Mesic Typic Dystrudepts	44	59	6.3	6.37	6.90
10	Volusia	Volusia Fine-Loamy, Mixed, Active, Mesic Aeric Fragiaquepts	35	36	6.4	5.71	6.12
11	Trout River	Trout River Sandy-Skeletal, Mixed, Frigid Entic Haplorthods	55	66	6.4	10.24	10.58
12	Hamlin	Hamlin Coarse-Silty, Mixed, Active, Mesic Dystric Fluventic Eutrudepts	28	46	6.5	5.77	6.46
13	Malone	Malone Coarse-Loamy, Mixed, Active, Nonacid, Frigid Aeric Epiaquepts	37	22	6.6	7.82	8.17
14	Niagara	Niagara Fine-Silty, Mixed, Active, Mesic Aeric Endoaqualfs	15	172	6.6	3.00	2.88
15	Mardin	Mardin Coarse-Loamy, Mixed, Active, Mesic Typic Fragiudepts	86	85	6.6	6.25	6.82
16	Bath	Bath Coarse-Loamy, Mixed, Active Mesic Typic Fragiudepts	31	224	6.8	6.27	5.81
17	Arkport	Arkport Coarse-Loamy, Mixed, Active, Mesic Lamellic Hapludalfs	11	228	6.8	2.82	2.59
18	Ontario	Ontario Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	18	189	6.9	4.39	3.89
19	Colonie	Colonie Mixed, Mesic Lamellic Udipsamments	16	123	7.0	4.93	4.87
20	Lima	Lima Fine-Loamy, Mixed, Active, Mesic Oxyaquic Hapludalfs	51	387	7.0	10.27	8.46
21	Adjidaumo	Adjidaumo Fine, Mixed, Active, Nonacid, Frigid Mollic Endoaquepts	29	28	7.1	12.09	11.48
22	Lupton	Lupton Euic, Frigid Typic Haplosaprists	98	29	7.1	17.87	14.69
23	Munuscong	Munuscong Coarse-Loamy Over Clayey, Mixed, Active, Nonacid, Frigid Mollic Epiaquepts	59	32	7.1	11.98	12.14
24	Hogansburg	Hogansburg Coarse-loamy, Mixed, Semiactive, Frigid Aquic Eutrudepts	36	120	7.2	7.14	8.09
25	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	50	na	7.2	11.62	9.76
26	Hogansburg	Hogansburg Coarse-loamy, Mixed, Semiactive, Frigid Aquic Eutrudepts	44	184	7.3	9.17	9.38
27	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	11	na	7.3	5.63	5.25
28	Mardin	Mardin Coarse-Loamy, Mixed, Active, Mesic Typic Fragiudepts	26	935	7.4	8.36	6.70
29	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	38	na	7.4	15.76	13.72
30	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	23	82	7.4	6.86	7.62
31	Ontario	Ontario Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	29	81	7.5	9.58	8.43
32	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	45	na	7.5	10.53	7.63
33	Hogansburg	Hogansburg Coarse-loamy, Mixed, Semiactive, Frigid Aquic Eutrudepts	53	152	7.5	9.38	9.00
34	Hogansburg	Hogansburg Coarse-loamy, Mixed, Semiactive, Frigid Aquic Eutrudepts	41	137	7.5	9.75	10.28
35	Ontario	Ontario Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	25	100	7.5	6.78	8.19
36	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	44	na	7.5	10.98	8.23
37	Hudson	Hudson Fine, Illitic, Mesic Glossaquic Hapludalfs	22	22	7.5	9.47	10.01
38	Appleton	Appleton Fine-Loamy, Mixed, Active, Mesic Aeric Endoaqualfs	18	116	7.6	5.93	7.02
39	Rhinebeck	Rhinebeck Fine, Illitic, Mesic Aeric Endoaqualfs	38	28	7.6	13.99	13.41
40	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	48	na	7.6	9.58	7.49
41	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	29	20	7.6	11.22	13.24
42	Appleton	Appleton Fine-Loamy, Mixed, Active, Mesic Aeric Endoaqualfs	49	50	7.6	9.07	9.76
43	Hudson	Hudson Fine, Illitic, Mesic Glossaquic Hapludalfs	21	19	7.6	8.32	9.19
44	Ontario	Ontario Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	21	46	7.7	5.65	6.01
45	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	43	na	7.9	10.70	8.16
46	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	42	na	8.0	8.86	10.14
47	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	32	na	8.2	4.76	7.02
48	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	24	na	8.2	5.20	7.01
49	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	22	na	8.3	5.45	6.93
50	Honeoye	Honeoye Fine-Loamy, Mixed, Active, Mesic Glossic Hapludalfs	19	na	8.4	5.78	6.85

†OM determined by loss-on-ignition; samples dried at 105°C for moisture determination followed by ashing for 2 h at 500°C (Storer, 1984).

CEC_{CE}: CEC by compulsive exchange; M3-P: Mehlich 3–extractable phosphorus content; na: not available; OM: organic matter.

cations measured in both extracts provided the most accurate estimate of CEC_{CE}. The single- or double-extraction approaches with $SrCl_2$ at a low ionic strength (I = 0.01 M) can more easily be implemented as a routine test in soil testing laboratories than the $BaCl_2$-$MgSO_4$ compulsive exchange method of Gillman and Sumpter (1986). However, additional work is needed to evaluate the accuracy of the single- or double-extraction approaches with $SrCl_2$ for agricultural soils of relevance to the northeastern United States.

In recent years, a comparison of soil test S methods resulted in the release of a new soil S test for detecting S deficiencies in alfalfa in New York (Ketterings et al., 2011a). This method uses a 30-min 0.01 M $CaCl_2$ extraction procedure with a 1:5 soil-to-solution ratio. Given similar characteristics of Sr and Ca and identical ionic strength for both tests, we hypothesized that a single 5-min extraction with 0.01 M $SrCl_2$ at a 1:10 soil-to-solution ratio can be used to accurately estimate both ECEC and available S, allowing a laboratory to extract S and estimate ECEC and cation saturation ratios using one single extraction procedure.

The objectives of the study were to evaluate (i) the accuracy of the summation method based on five different agronomic soil tests in predicting the ECEC across a range of 50 New York agricultural soils, (ii) single versus double consecutive extractions with 0.01 M $SrCl_2$ for their ability to accurately estimate ECEC, (iii) accuracy of commonly used summation methods in determining Ca, Mg, and K base saturation ratios; and (iv) potential of a single extraction with 0.01 M $SrCl_2$ for both ECEC and S determination in soil. The five extractants used were Mehlich 3, Morgan, 1 M NH_4OAc buffered at pH 7, 1 M NH_4Cl, and 0.01 M $SrCl_2$. Results for each method were compared with ECEC values obtained for the soils based on the $BaCl_2$-$MgSO_4$ compulsive exchange method.

MATERIALS AND METHODS

Determination of ECEC and Saturation Ratios

Fifty New York agricultural soils were collected from production fields (0–20 cm depth; see Table 1 for relevant soil properties). The samples were oven-dried at 50°C and sieved through a 2-mm sieve. The soils ranged in pH from 5.1 to 8.4 (1:1 soil-to-water ratio), with an organic matter (OM) level from 11 to 98 g kg^{-1} based on loss-on-ignition (LOI) with samples

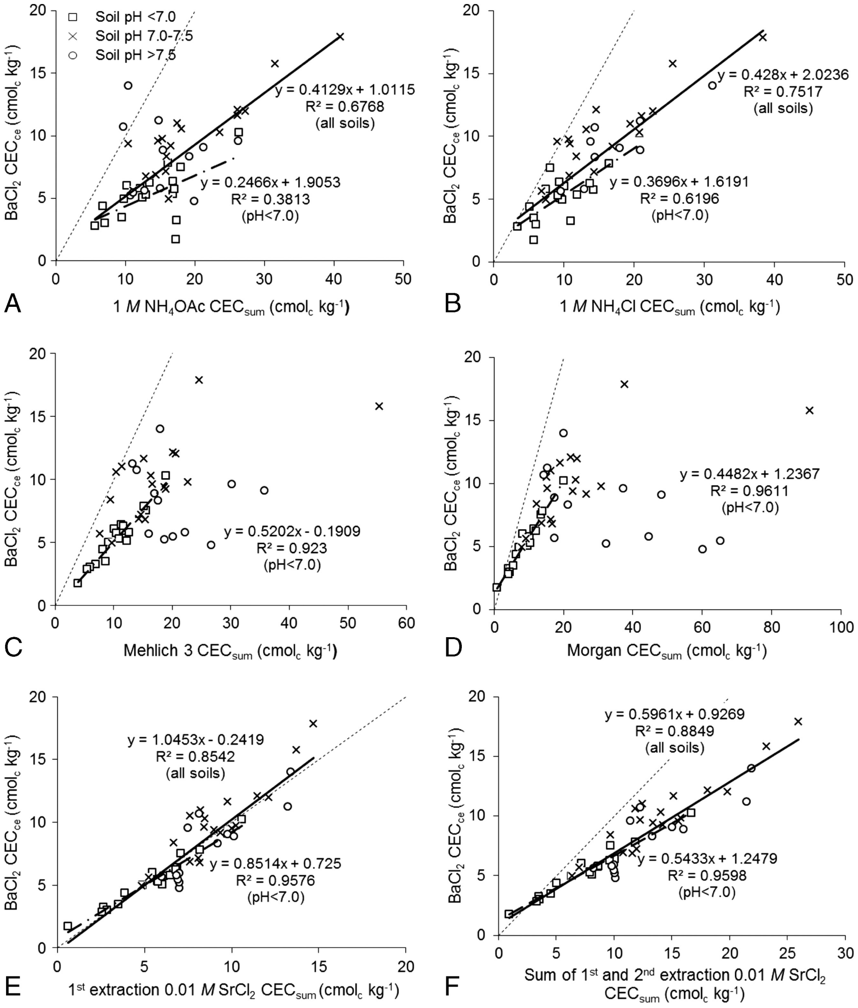

FIG. 1. Regression of ECEC measured with the compulsive exchange method (CEC_{CE}) and derived from NH_4OAc, Mehlich 3, Morgan, and $SrCl_2$ extractable cations for 50 and NH_4Cl for 44 New York soils. In all figures, a linear regression was fit to the soils with pH less than 7.0 (N = 18; dashed line). In A, B, E, and F, a linear regression was also fit to the entire data set (N = 50; pH range from 5.1 to 8.4; solid line); the 1:1 dashed lines are shown as well.

TABLE 2. Linear Regression Equations of $SrCl_2$ Determined K, Ca, and Mg Saturation and Saturation Estimates Derived From Morgan or Mehlich 3 Soil Test Results

				Intercept (a)			Slope (b)		
Dependent Parameter		r^2	**RMSE**	**a**	SE_a	**Prob. A = 0**	**b**	SE_b	**Prob. B = 1.0**
Saturation ratio across all soils									
Morgan-based K saturation		0.95	0.46	0.257	0.085	0.004	0.757	0.025	<0.0001
Mehlich3–based K saturation		0.81	0.90	−0.598	0.218	0.009	1.016	0.071	<0.0001
Morgan-based Ca saturation		0.86	2.42	5.973	4.378	0.180	0.919	0.052	<0.0001
Mehlich3–based Ca saturation		0.72	3.47	14.652	6.088	0.020	0.841	0.075	<0.0001
Morgan-based Mg saturation		0.83	2.44	−0.310	1.064	0.772	1.115	0.072	<0.0001
Mehlich 3–based Mg saturation		0.71	3.19	−0.093	1.473	0.950	1.012	0.092	<0.0001
Saturation ratio for specific soil pH classes									
Morgan-based K	Soil pH <7.0	0.98	0.37	−0.105	0.122	0.399	0.784	0.024	<0.0001
	Soil pH 7.0–7.5	0.92	0.39	0.198	0.140	0.176	0.881	0.063	<0.0001
	Soil pH >7.5	0.75	0.46	0.487	0.177	0.019	0.695	0.115	<0.0001
Mehlich3–based K	Soil pH <7.0	0.84	1.17	−1.408	0.509	0.014	1.269	0.134	<0.0001
	Soil pH 7.0–7.5	0.87	0.50	−0.036	0.198	0.858	0.751	0.070	<0.0001
	Soil pH >7.5	0.78	0.44	0.015	0.221	0.948	0.696	0.106	<0.0001
Morgan-based Ca	Soil pH <7.0	0.89	2.33	−3.472	7.408	0.646	1.048	0.091	<0.0001
	Soil pH 7.0–7.5	0.85	2.40	6.252	7.410	0.411	0.903	0.089	<0.0001
	Soil pH >7.5	0.83	1.89	17.720	9.035	0.076	0.787	0.102	<0.0001
Mehlich3–based Ca	Soil pH <7.0	0.68	3.89	1.773	13.094	0.894	0.996	0.164	<0.0001
	Soil pH 7.0–7.5	0.73	3.24	22.829	8.399	0.015	0.731	0.105	<0.0001
	Soil pH >7.5	0.65	2.70	32.210	11.360	0.016	0.651	0.134	<0.0005
Morgan-based Mg	Soil pH <7.0	0.91	1.70	−3.960	1.569	0.023	1.280	0.097	<0.0001
	Soil pH 7.0–7.5	0.79	2.81	−0.509	2.233	0.823	1.196	0.143	<0.0001
	Soil pH >7.5	0.82	1.76	2.630	1.284	0.065	0.838	0.113	<0.0001
Mehlich3–based Mg	Soil pH <7.0	0.81	2.54	−2.219	2.272	0.343	1.170	0.141	<0.0001
	Soil pH 7.0–7.5	0.62	3.91	1.965	3.046	0.528	0.927	0.176	<0.0001
	Soil pH >7.5	0.72	2.28	1.946	1.892	0.326	0.742	0.139	<0.0002

dried at 105°C to estimate moisture content followed by ashing for 2 h at 500°C (Storer, 1984). Soil texture varied from sand to clay (Table 1).

Soils were analyzed for ECEC using the $BaCl_2$-$MgSO_4$ compulsive exchange method of Gillman and Sumpter (1986), and results were compared with data obtained with the summation method based on the Morgan extraction (Morgan, 1941), Mehlich 3 (Wolf and Beegle, 1995), 1 *M* NH_4OAc buffered pH at 7.0 (Brown and Warncke, 1988), 1 *M* NH_4Cl (McClenahan and Ferguson, 1989), and the single and double extractions with 0.01 *M* $SrCl_2$ (Woods, 2006).

For the 0.01 *M* $SrCl_2$ extractions, soil was shaken for 5 min at a soil-to-solution ratio of 1:10 (2 g soil and 20 mL 0.01 *M* $SrCl_2$). Samples were centrifuged for 10 min at about 721*g*. To evaluate if centrifugation is needed, five samples were analyzed both with and without the centrifugation step. These results indicated that the centrifugation step did not impact the final results, so this step can be excluded. The supernatant of the first extraction was filtered through a Whatman 15.0-cm grade 2V filter paper before analyses for exchangeable cations. For the second extraction, an additional 20 mL of 0.01 *M* $SrCl_2$ was added, followed by the same extraction and determination procedure as previously mentioned. All extracted solutions were analyzed to quantify K, Ca, and Mg using an inductively coupled plasma atomic emission spectroscopy (IRIS Advantage, Thermo Jarrell Ash Crop, Ottawa, Ontario, Canada) at 766.4, 317.9, and 279.0 nm, respectively. The CEC_{sum} was calculated by summation of nonacid cations (molar basis, Ca, Mg, K) after subtraction of the cation content of two blank samples that were included for each batch of samples. Sodium or NH_4^+ in extraction was not included because of the low levels of Na and NH_4^+ in relation to the total nonacid cations present in New York's agricultural soils. No adjustments were made based on soil pH.

Sulfur Evaluation

The sulfur extraction comparison was done using 135 soil samples (0–20 cm depth) that were collected in experimental plots under alfalfa production located in western, central, and eastern New York. These samples were evaluated because they (i) reflect agricultural soils in New York state used for alfalfa production and (ii) included sites that are deficient (S <8 g kg^{-1}) and soils that are high (S ≥8 g kg^{-1}) in available S (Ketterings et al., 2011b). Samples were dried in a forced air oven at 50°C and ground to pass a 2-mm sieve before analyses. Soil pH and OM were determined following the same protocols as previously described.

Each soil sample was extracted with 0.01 *M* $CaCl_2$ and 0.01 *M* $SrCl_2$. Briefly, 10 g of soil was shaken in 50 mL of 0.01 *M* $CaCl_2$ (1:5 soil-to-solution ratio; wt:vol) for 30 min as described in Ketterings et al. (2011a). For $SrCl_2$ extraction, soil was shaken for 5 min at a soil-to-solution ratio of 1:10 wt:vol (2 g soil and 20 mL 0.01 *M* $SrCl_2$), identical to the procedure used to determine CEC (excluding the 10 min centrifugation step). Each extract was filtered using Whatman 15.0-cm grade 2V folded filter paper. The filtered solution was analyzed for S with an inductively coupled plasma atomic emission spectroscopy

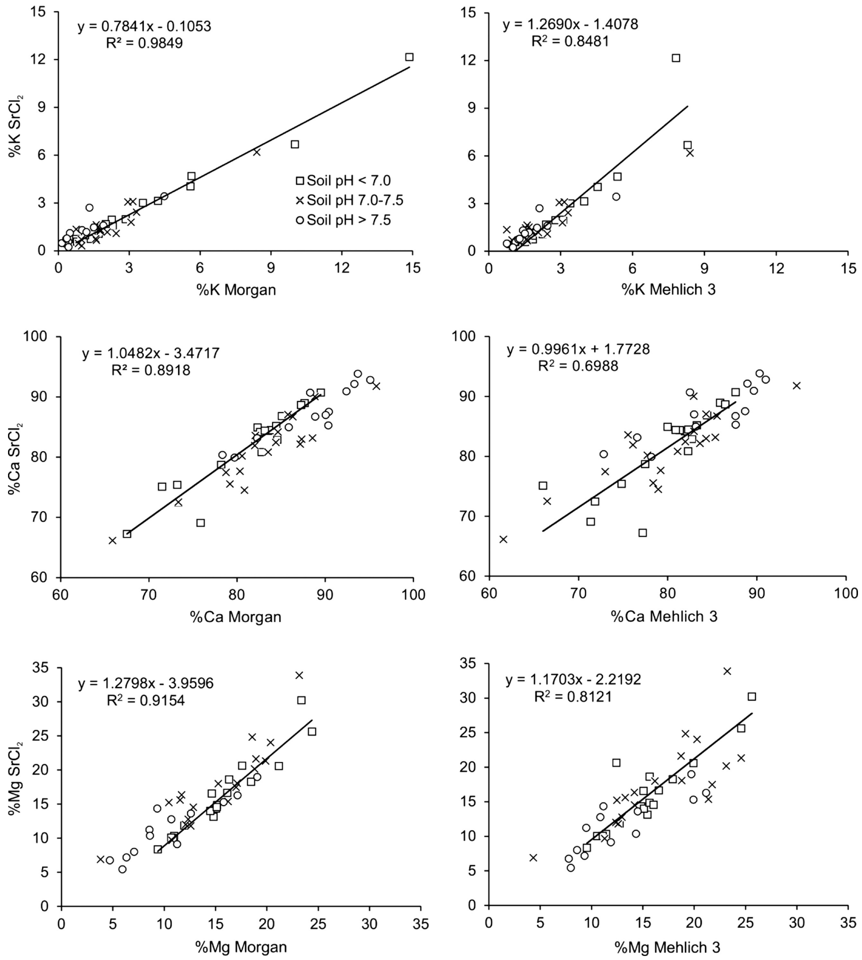

FIG. 2. Regression of percentage K, Ca, and Mg saturation estimated with the 0.01 *M* $SrCl_2$ extraction method and cation summation methods based on Morgan and Mehlich 3 soil test data. A linear regression was fit to the soils with pH less than 7.0 only ($N = 18$).

(IRIS Advantage, Thermo Jarrell Ash Crop) at 182 nm. Two blank samples were included in each batch, and S values of blank samples were subtracted.

Data Analysis

Linear regression models were fit to the CEC_{CE} and 0.01 *M* $CaCl_2$ extractable S data (dependent variables) and CEC_{sum} and 0.01 *M* $SrCl_2$ extractable S (independent variable), respectively, using PROC REG of SAS (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Soil CEC_{CE}

The CEC_{CE} of the soils ranged from 1.74 $cmol_c\ kg^{-1}$ soil for the soil with the lowest pH (pH 5.1) and organic matter level of 27 $g\ kg^{-1}$ to 17.87 $cmol_c\ kg^{-1}$ for the soil with the highest amount of organic matter (98 $g\ kg^{-1}$) and a soil pH of 7.1 (Table 1).

Soil organic matter explained 38% of the variability in CEC_{CE} across all 50 soils ($P < 0.0001$) with CEC_{CE} ($cmol_c\ kg^{-1}$) = −3.62 +0.12*OM ($g\ kg^{-1}$), $R^2 = 0.3834$, and RMSE = 2.65 $cmol_c\ kg^{-1}$. The large intercept suggests that factors other than OM contribute to the CEC. When soil pH was included in the model, together with OM, 50% of the variability in CEC_{CE} across all 50 soils was explained ($P < 0.0001$) with CEC_{CE} ($cmol_c\ kg^{-1}$) = −8.00+1.65*pH+0.12*OM ($g\ kg^{-1}$), $R^2 = 0.4989$, and RMSE = 2.37 $cmol_c\ kg^{-1}$. Improvements in predictions can possibly be made if soil clay content is known in addition to soil organic matter (Helling et al., 1964; Wright and Foss, 1972). For example, Wright and Foss (1972) reported that OM contributed about

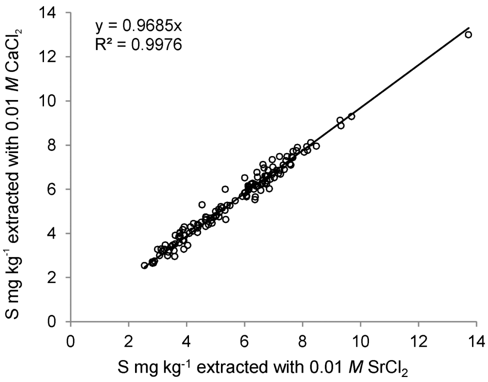

FIG. 3. Soil sulfur determined using a 0.01 *M* $SrCl_2$ extraction (1:10 wt:vol soil-to-solution ratio; 5-min shaking time) and a 0.01 *M* $CaCl_2$ extraction method (1:5 wt:vol soil-to-solution ratio; 30-min shaking time) for 135 agricultural soils in New York.

50% to the ECEC of the Coastal Plain soils in Maryland where clay mineralogy was fairly uniform. However, clay content determination in the laboratory is time consuming and hence expensive and, as a result, textural analyses are not typically done for farmer samples. In addition, estimates of ECEC derived from OM and clay content may only be accurate within a limited geographic and climatic zone where clay composition and type and organic fractions are essentially homogeneous (Hallsworth and Wilkinson, 1958).

Buffered pH and Summation Method Results

Both the 1 M NH_4OAc at pH 7 and 1 M NH_4Cl methods overestimated the soil's ECEC (Fig. 1A, B). Ammonium acetate overestimated the ECEC across the entire pH range of the 50 soils, with greater overestimation for the low pH soils. These results are consistent with Kalisz and Stone (1980) who found that CEC determined with NH_4OAc at pH 7 was two to four times higher than that estimated with unbuffered $BaCl_2$ saturating solution at the field pH according to Bascomb (1964). Likewise, Gillman et al. (1983) also observed that the NH_4OAc-derived CEC values were generally higher than those for silver thiourea and compulsive exchange methods, sometimes up to three times greater in variable charge soils, further showing the limited usefulness of use of methods buffered at a pH considerably higher than the actual pH of the soil.

The CEC_{sum} estimates based on Mehlich 3 or Morgan greatly overestimated the ECEC as measured by the $BaCl_2$-$MgCl_2$ compulsive exchange method as well, especially in the soils with pH greater than 7 (Fig. 1C, D). In our study, when the soil pH was less than 7, the ECEC based on cations extracted using the Mehlich 3 or Morgan chemistries still overestimated the ECEC, but results were well correlated (Fig. 1C, D). Thus, a summation method based on Mehlich-3 or Morgan extractions does not result in accurate estimates of ECEC; the method can be used for soils with a pH less than 7.0 but conversion equations are needed. These results are consistent with Woods (2006) who reported that the ECEC derived by summation from the NH_4OAc, Mehlich 3, and Morgan extractions all overestimated CEC_{CE} in 37 sand samples with a pH range from 4.4 to 9.0, likely reflecting dissolution of solid-phase calcium or magnesium carbonates during the extraction process.

Single Versus Double Consecutive Extractions With 0.01 M $SrCl_2$

The single extraction with 0.01 M $SrCl_2$ resulted in ECEC estimates that shows no significant intercept and correlated well with CEC_{CE} across all soils (Fig. 1E): CEC_{CE} ($cmol_c\ kg^{-1}$) = 1.04*CEC_{sum} ($cmol_c\ kg^{-1}$) ($R^2 = 0.8538$; RMSE = 1.29 $cmol_c\ kg^{-1}$). The addition of a 2nd 0.01 M $SrCl_2$ extraction as suggested by Woods (2006) resulted in an overestimation of CEC_{CE} (Fig. 1F) without improving the accuracy of the ECEC prediction. These results suggest that a single 5-min extraction with 0.01 M $SrCl_2$ is the most cost-effective and accurate approach to predicting a soil's ECEC, independent of soil pH and soil type.

Cation Saturation Ratios

The R^2 and RMSE results of the regression of saturation ratios showed the difficulty in accurately determining the K, Ca, and Mg saturation based on either the Morgan and Mehlich-3 extraction methods, especially for soil with a pH greater than 7 (Table 2). The ratios derived from Ca, Mg, and K measured in the Morgan solution were better correlated to the saturation ratios determined with the 0.01 M $SrCl_2$ method than the Mehlich-3–derived ratios across all soils (Fig. 2). This is not surprising given the difference in extraction pH 2.3 for Mehlich-3 versus 4.8 for the Morgan solution versus pH of the soil for the 0.01 M $SrCl_2$ method and the CEC_{CE} method. These results further support the statement that the summation method should not be used to derive nonacid cation saturation ratios for high pH soils.

Sulfur

The 0.01 M $SrCl_2$ extraction method with 5-min shaking time and 1:10 soil-to-solution ratio resulted in extractable S data that were directly comparable to those obtained with the 0.01 M $CaCl_2$ extraction method with 30-min shaking time and 1:5 soil-to-solution ratio reported in Ketterings et al. (2011a): $CaCl_2$ extractable S (mg kg^{-1}) = 0.97*$SrCl_2$ extractable S (mg kg^{-1}), $R^2 = 0.9976$, and RMSE = 0.28 mg kg^{-1} (Fig. 3). These results suggest that the 0.01 M $SrCl_2$ method can be used to derive extractable S data that can be interpreted as reported in Ketterings et al. (2011b).

CONCLUSIONS

Agronomic soil test data (Morgan or Mehlich 3) can be used to estimate ECEC when soil pH is less than 7, but conversion equations are needed to derive accurate predictions as both extraction methods result in an overestimation of the soil's actual ECEC. A single 0.01 M $SrCl_2$ extraction with a 1:10 soil-to-solution ratio and 5-min shaking time is a simple, rapid, and inexpensive method of estimating ECEC and cation saturation ratios. The same extraction method can be used to determine soil available S. We recommend the single extraction procedure with 0.01 M $SrCl_2$ be implemented for routine testing of both soil ECEC and plant-available S.

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