An alternative method for determination of cations in solution of small soil samples[1]

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ABSTRACT

A series of equations based on relations between exchangeable and soil solution ions were evaluated to find an appropriate procedure to determine the activity of cations in soil solution of small soil samples. Correlation coefficiency values (R) of 0.98, 0.98, and 0.96 were obtained for the relation between predicted and observed values of Ca^{+2}, Mg^{+2}, and Al^{+3} in solution, respectively, when a procedure based on the following relations was employed, where the subscripts, s and e refer to ions in solution and exchangeable phase, respectively:

1) $\frac{Ca_s^{1/2}}{Mg_s^{1/2}}$ on $\frac{Ca_e^{1/2}}{Mg_e^{1/2}}$;

2) $\frac{Al_s^{1/3}}{(Ca_s+Mg_s)^{1/2}}$ on $\frac{Al_e^{1/3}}{(Ca_e+Mg_e)^{1/2}}$;

3) pAl on pH.

The effectiveness of the developed equations was maintained even when the sample was submitted to variations in the type of salt added to the soil in the soil water ratio (SWR) used to extract the ions in solution.

RESUMEN

Un método alterno para determinar cationes en solución de muestras pequeñas de suelo

Se evaluó una serie de ecuaciones basadas en la relación entre iones en solución y en la fase intercambiable del suelo para desarrollar un método que permitiese determinar cationes en solución en muestras de suelo bien pequeñas. Se obtuvo una gran correlación (valores de R de 0.98, 0.98, 0.96) entre actividades de Ca^{+2}, Mg^{+2}, y Al^{+3} en solucción determinados analíticamente y por medios empíricos, respectivamente, mediante un procedimiento desarrollado a partir de las siguientes relaciones:

1) $\frac{Ca_s^{1/2}}{Mg_s^{1/2}}$ sobre $\frac{Ca_e^{1/2}}{Mg_e^{1/2}}$;

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2) $$\frac{Al_s^{1/3}}{(Ca_s+Mg_s)^{1/2}} \text{ sobre } \frac{Al_e^{1/3}}{(Ca_e+Mg_e)^{1/2}};$$

3) $$pAl \text{ sobre } pH$$

(Los subscritos s y e se refieren a cationes en solución y en la fase intercambiable, respectivamente).

La efectividad de las ecuaciones desarrolladas no se vió afectada por el tipo de sal añadida al suelo ni por los cambios en la proporción agua:suelo utilizada para obtener los cationes en solución.

INTRODUCTION

One of the factors which have prevented scientists from completely understanding the chemistry of soil solutions is the inability to work with soils under field moisture conditions. It is well known that a parameter measured in an altered system may perfectly describe that particular system, but be only an approximation to the system under different moisture conditions (10).

This limitation becomes particularly critical when working in areas such as the rhizosphere (5, 6). For instance, Kirlew and Bouldin (8, 9) found that corn roots growing in a limed [$Ca(OH)_2$] subsoil changed the chemistry of the rhizosphere soil. Their results indicated that the root-soil interfacial zone (rhizosphere) was more acid, had less KCl-extractable Ca^{+2} and more KCl-extractable Al^{+3} than the bulk soil. Presumably, this change came as a result of an excess of cation (Ca^{+2}) uptake relative to anions by the roots. This in turn created a charge imbalance in the soil solution that forced the roots to excrete H^+ in order to keep the soil solution balanced. They believed that as the concentration of H^+ in the soil solution increased, some $Al(OH)_3$ was dissolved causing an increase in the KCl-extractable Al^{+3} and a decrease in the KCl-extractable Ca^{+2}.

However, further analyses of the system were restrained by two obstacles:

1) Soil samples obtained from the rhizosphere are small.
2) The soil solution must usually be diluted in order to have enough solution for analysis.

In view of the obstacles that these limitations present to a better knowledge of the chemistry of soil solutions, we performed some chemical studies. The objective was to develop a method to estimate the concentration of cations in the soil solution of acid soils, on the basis of measurable properties of very small soil samples taken from the rhizosphere.

We carried out the studies on the basis of the following principles: soil samples of a gram or less can be analyzed for KCell-extractable cations. Therefore, if a relationship between the exchangeable and soluble cations can be identified in bulk samples (where sample size is not a limitation), a reasonable estimation of the composition of the soil solution of small soil samples can be accomplished with the aid of such a relation and a knowledge of the composition of the exchangeable phase.

We hypothesized that the following relations would exist:

$$1)\quad \frac{(Ca_s)^{1/2}}{Mg_s)^{1/2}} = KD_1\frac{(Ca_e)^{1/2}}{(Mg_e)^{1/2}}$$

$$2)\quad \frac{(Ca_s)^{1/2}}{(K_s)} = KD_2\frac{(Ca_e)^{1/2}}{(K_e)}$$

$$3)\quad \frac{(Ca_s)^{1/2}}{(NH_{4s})} = KD_3\frac{(Ca_e)^{1/2}}{(NH_{4e})}$$

$$4)\quad \frac{(Al_s)^x}{(Ca_s + \text{other dominant cation})^y} = \frac{KDT\,(Al_e)^x}{(Ca_e + \text{other dominant cation})^y}$$

$$5)\quad \begin{array}{rcl} Al_s\,(OH)^3 & = & KSP \\ \text{or } Al_s & = & Ksp \times (H+)^3 \\ & & (Kw)3 \end{array}$$

The subscripts "s" and "e" describe solution and exchangeable ions, respectively; KD_x, KTD, Ksp, x and y are constants and Kw is the dissociation constant for water.

We assumed that although the values of KD_x, KDT, Ksp, x and y vary among soils as the suite of exchangeable cations changes markedly, they are relatively constant over a limited range of concentrations in a given soil.

If KD_x, KDT and Ksp are determined with bulk samples, and we assume that the values remain constant over the range of conditions which are likely to occur in the rhizosphere, we can use equations 1 to 5 to calculate the ionic composition of the soil solution from pH measurements and concentrations of exchangeable cations only.

MATERIALS AND METHODS

A subsoil from the Cornell University, Mount Pleasant research farm (coarse, loamy, mixed, mesic, typic, fragiocrept) was used in these

TABLE 1.—*Charge balance analysis for the Mt. Pleasant subsoil*

Treatment	Anions (Cl, NO$_3$, SO$_4$)[1]	Cations (Ca, Al)[2]	Cations (Ca, Mg, Al)[3]
Control	4.73e-4	2.08e-4	4.14e-4
Ca (OH)$_2$	4.80e-4	2.83e-4	4.76e-4
Ca (Cl)$_2$	8.01e-4	4.68e-4	7.30e-4
Ca (NO$_3$)$_2$	7.07e-4	4.98e-4	7.54e-4

[1] Refers to the sum of activities (moles/L) of anions (Cl, No$_3$, SO$_4$) in solution.

[2] Refers to the sum of activities (moles/L) of calcium and aluminum in solution.

[3] Refers to the sum of activities (moles/L) of cation (Ca, Mg, and Al) in solution.

studies. A series of treatments (Control, $Ca(OH)_2$, $CaNO_3$, and $MgSO_4$) were applied as follows:

Five hundred grams of air dry soil (sieved to pass a 0.5 mm screen) was used in each treatment. The moisture content of the soil was determined and the amount of salt necessary to add 1×10^{-6} moles of Ca^{+2} or Mg^{+2} to the soil was calculated. A solution was prepared by diluting that amount of salt with enough water to bring each soil to 20% moisture content.

TABLE 2.—*Soil chemical analyses of the Mt. Pleasant subsoil*

Treatment	SWR (mL/g)	CA$_s$ (m/L)	Mg$_s$ (m/L)	Al$_s$ (m/L)	Ca$_e$ (m/g)	Mg$_e$ (m/g)	Al$_e$ (m/g)
Control	0.5	1.70e-4	1.21e-4	3.60e-5	1.12e-6	6.13e-7	1.68e-5
	1.0	1.36e-4	9.70e-5	3.22e-5	1.08e-6	6.03e-7	1.65e-5
	2.0	1.03e-4	7.82e-5	2.76e-5	7.69e-7	4.67e-7	1.43e-5
	3.0	8.54e-5	6.24e-5	2.40e-5	7.69e-7	4.49e-7	1.55e-5
Ca(OH)$_2$	0.5	--	--	--	1.91e-6	5.58e-7	1.42e-5
	1.0	2.87e-4	8.89e-5	2.40e-5	1.99e-6	5.58e-7	1.42e-5
	2.0	1.69e-4	7.03e-5	1.95e-5	1.71e-6	4.94e-7	1.39e-5
	3.0	1.83e-4	6.06e-5	1.72e-5	1.79e-6	4.94e-7	1.43e-5
Mg(SO$_4$)	0.5	158e-4	2.94e-4	3.18e-5	1.04e-6	1.46e-6	1.56e-5
	1.0	1.49e-4	2.82e-4	3.30e-5	1.00e-6	1.33e-6	1.48e-5
	2.0	1.13e-4	2.07e-4	2.76e-5	9.26e-7	1.09e-6	1.48e-5
	3.0	9.40e-5	1.75e-4	2.40e-5	8.09e-7	9.82e-7	1.52e-5
CA(NO$_3$)$_2$	0.5	8.38e-4	2.16e-4	9.99e-5	1.79e-6	5.58e-7	1.46e-5
	1.0	5.41e-4	1.41e-4	7.58e-5	1.91e-6	5.58e-7	1.50e-5
	2.0	3.31e-4	9.27e-5	4.28e-5	1.31e-6	4.49e-7	1.42e-5
	3.0	2.70e-4	7.93e-5	3.96e-5	1.24e-6	4.49e-7	1.47e-5

The solutions were applied with a spray bottle. The soils were continuously stirred during the application of the treatments to ensure uniform distribution. The treatments were left reacting for 1 week near field capacity. Water extracts at four different soil-water ratios (0.5, 1, 2, and 3 ml/g of soil) were obtained from each treatment. This constituted the soil solution phase. The same samples were then submitted to a KCell extraction to obtain the exchangeable ions. Each extract was analyzed for Ca^{+2}, Mg^{+2}, and Al^{+3}. Calcium was determined by atomic absorption, whereas magnesium and aluminum were measured by a fluorometric technique. (1, 3, 4, 7).

The collected data were used to solve the equations and predict the concentration of cations in solution. We evaluated the effectiveness of the procedure by comparing the predicted values with the ones obtained previously by direct determination.

RESULTS AND DISCUSSION

A charge balance check was performed in a prior study to ensure that all the dominant cations (those which contributed most of the positive charges to the soil solution) were being considered. Calcium, magnesium

TABLE 2. (continued to the right)

Ratio 1 Ca_s^(0.5)/ Mg_s^(0.5)	Ratio 2 (Ca_e^(0.5)/ Mg_e^(0.5)	Kl (rl/r2)	Ratio 3 Al_s^(1/3)/ (Ca_s+Mg_s)^(0.5)	Ratio 4 Al_e^(1/3)/ (Ca_e+Mg_e)^(0.5)	r3/r4 (K2)	pH	%Al+3[1]
1.19	1.35	0.88	1.94	19.46	0.10	4.03	91
1.18	1.34	0.88	2.08	19.62	0.11	4.12	89
1.15	1.28	0.89	2.25	21.83	0.10	4.17	88
1.17	1.31	0.89	2.37	22.59	0.11	4.19	87
--	1.85	--	--	15.41	--	4.18	--
1.80	1.89	0.95	1.49	15.17	0.10	4.22	86
1.55	1.86	0.83	1.74	16.20	0.11	4.25	85
1.74	1.90	0.91	1.65	16.06	0.10	4.27	85
0.73	0.84	0.87	1.49	15.80	0.09	4.12	89
0.73	0.87	0.84	1.55	16.08	0.10	4.18	87
0.74	0.92	0.80	1.69	17.29	0.10	4.19	87
0.73	0.91	0.81	1.76	18.51	0.10	4.19	87
1.97	1.79	1.10	1.43	15.95	0.09	3.82	94
1.96	1.85	1.06	1.62	15.70	0.10	3.96	92
1.89	1.71	1.11	1.70	18.26	0.09	4.00	91
1.85	1.66	1.11	1.82	18.85	0.10	4.07	90

[1] Refers to the percentage of the monomeric species of aluminum in solution constituted by Al+3.

and aluminum were the most significant ions (table 1), and, therefore, were the only ones considered in the evaluation of the equations.

Table 2 shows soil analyses data. Using linear least square regression analysis (2), we fit the values obtained to relations 1, 4, and 5 for each soil water ratio.

The resulting best fit equations were obtained:

$$1)\quad \frac{(Ca_S)^{1/2}}{(Mg_S)^{1/2}} = \frac{1.15\,(Ca_e)^{1/2} - 0.28}{(Mg_e)^{1/2}} \qquad r^2 = 0.96$$

$$2)\quad \frac{(Al_s)^{1/3}}{(Ca_s + Mg_s)^{1/2}} = \frac{0.11\,(Al_e)^{1/3} - 0.174}{(Ca_e + Mg_e)^{1/2}} \qquad r^2 = 0.96$$

$$3)\quad pAl = 1.6\,pH - 2.15 \qquad r^2 = 0.92$$

Table 3 shows the measured values of cation activity ratios in solution and those calculated from measured exchange phase composition, pH, and equations 1 to 3. Plots of the predicted vs observed values are shown in figures 1 through 3. Also included are the results of a regression performed on the relation predicted vs observed values.

TABLE 3.—*Predicted and observed values of dominant cations in soil solution*

Treatment	SWR	Ca_s mol/L predicted	Ca_s mol/L observed	Mg_s mol/L predicted	Mg_s mol/L observed	Al_s mol/L predicted	Al_s mol/L observed
Control	0.5	205E-04	1.70E-04	1.26E-04	1.21E-04	4.57E-05	3.63E-05
	1	1.61E-04	1.36E-04	1.00E-04	9.70E-05	3.31E-05	3.23E-05
	2	1.09E-04	1.03E-04	7.64E-05	7.82E-05	2.75E-05	2.75E-05
	3	9.84E-05	8.54E-05	6.55E-05	6.24E-05	2.57E-05	2.40E-05
$Ca(OH)_2$	0.5	--	--	--	--	--	--
	1	2.82E-04	2.87E-04	7.88E-05	8.89E-05	2.29E-05	2.40E-05
	2	2.24E-04	1.69E-04	6.49E-05	7.03E-05	2.04E-05	1.95E-05
	3	2.21E-04	1.83E-04	6.10E-05	6.06E-05	1.90E-05	1.74E-05
$MgSO_4$	0.5	1.34E-04	1.58E-04	2.86E-04	2.94E-04	3.31E-05	3.16E-05
	1	1.19E-04	1.49E-04	2.30E-04	2.82E-04	2.63E-05	3.31E-05
	2	1.10E-04	1.13E-04	1.82E-04	2.07E-04	2.57E-05	2.75E-05
	3	9.35E-05	9.40E-05	1.59E-04	1.75E-04	2.57E-05	2.40E-05
$Ca(NO_3)_2$	0.5	6.57E-04	8.38E-04	2.08E-04	2.16E-04	1.00E-04	1.00E-04
	1	4.87E-04	5.41E-04	1.43E-04	1.41E-04	5.89E-05	7.59E-05
	2	3.05E-04	3.31E-04	1.07E-04	9.27E-05	5.13E-05	4.26E-05
	3	2.35E-04	2.70E-04	8.87E-05	7.93E-05	3.98E-05	3.98E-05

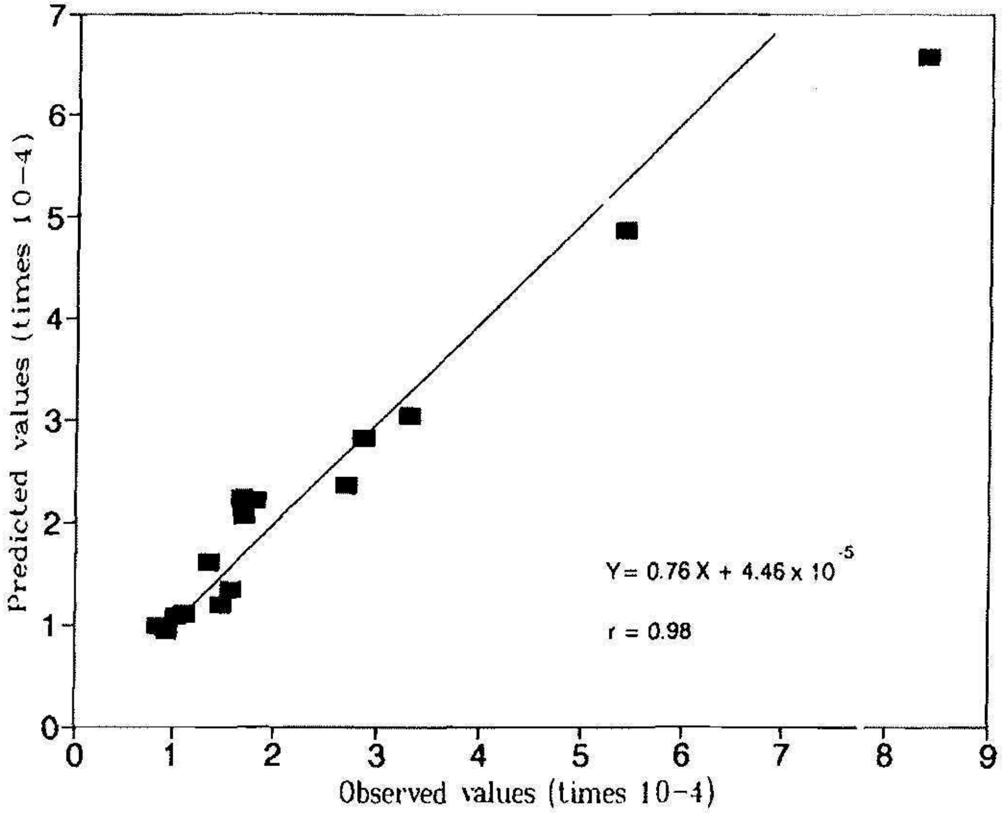

Fig. 1.—Relation between predicted and observed values of calcium in solution. Points are observations, and the 1:1 response line is included for observational purposes.

The predicted values agree reasonably well with the observed values in most cases; therefore, a good estimation of the composition of the soil solution can be achieved with this approach. The relations were not affected by changes in the soil-water ratio (within the 0.5 to 3 range) used to extract the ions or by the type of salt added. These results agree with our hypothesis that over a limited range of concentrations, we can estimate the composition of the soil solution in samples of small size by measuring pH and cations in the exchange phase.

The results reported are only for SWR values between 0.5 and 3. However, one could probably use the same relations to estimate the composition of the soil solution at the 0.2 SWR level, which is more typical of the value at which most plants grow.

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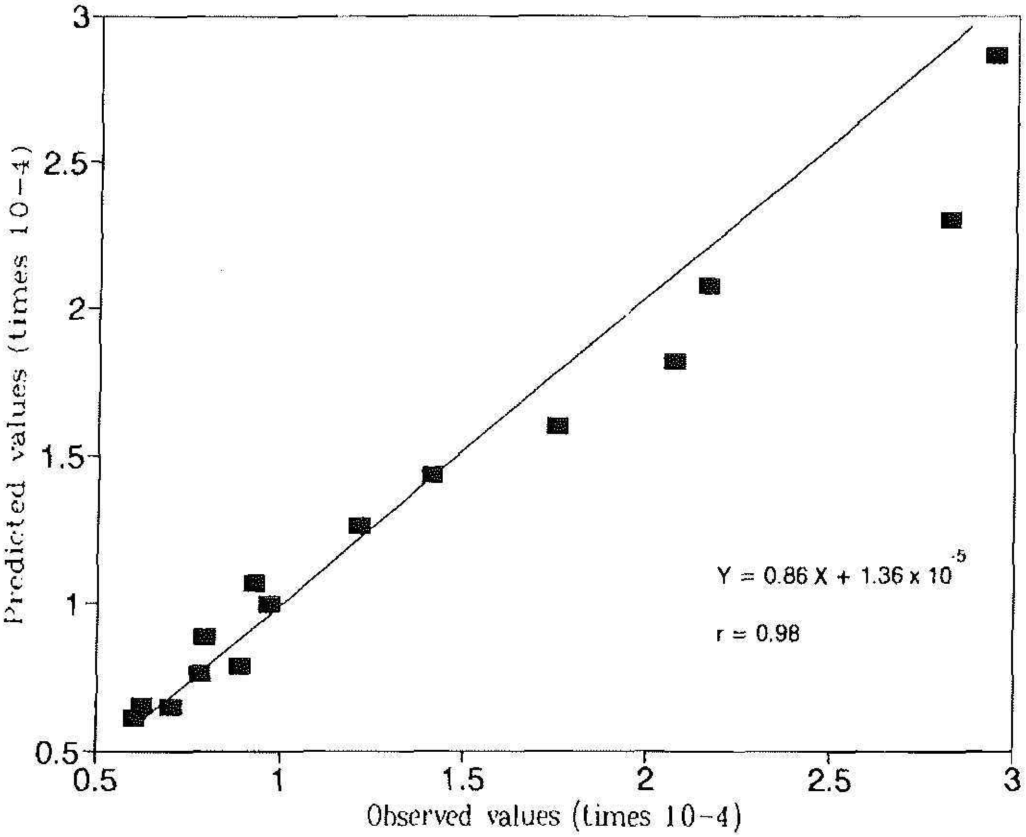

Fig. 2.—Relation between predicted and observed values of magnesium in solution. Points are observations, and the 1:1 response line is included for observational purposes.

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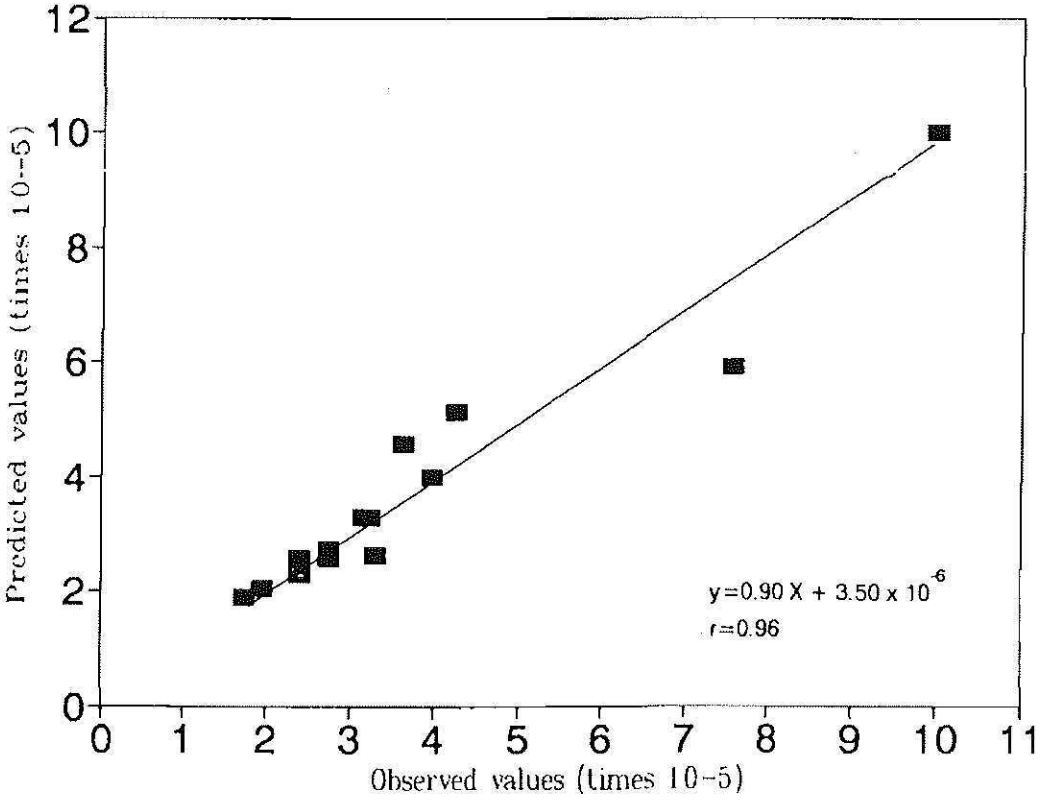

Fig. 3.—Relation between predicted and observed values of aliminum in solution. Points are observations, and the 1:1 response line is included for observational purposes.