

Soil Solution Studies on Weathered Soils from Tropical North Queensland

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Abstract

Solutions obtained from six soils in tropical North Queensland after incubation at a moisture tension of 0.1 bar were analysed to obtain data on their ionic strengths. Soil extracts, at soil:solution ratios of 1:1, 1:2.5, 1:5, and 1:10 were also examined. Determinations on the aqueous phase included electrical conductivity, pH, ammonium, calcium, magnesium, potassium, sodium, bicarbonate, chloride, sulphate, and nitrate.

Ionic concentrations of the soil solutions were found to be low when compared with many of the values reported in the literature. The upper limit for the ionic strength was about 0.005. Ionic strength was well correlated with the electrolytic conductivity of the soil solution itself, and also of the soil extracts.

Relationships found between the soil solution and soil extracts in respect of total cation (and anion) content and also cation ratios, allow predictions about the soil solution to be made from soil extract data.

Consideration of the ionic ratio of calcium to total cations in these soils suggests that the soils may have suboptimal levels of calcium for the growth of many plant species.

Introduction

The soil solution has been defined as the aqueous component of a soil at field-moisture contents consisting of dissolved electrolytes, gases and other water soluble compounds (Adams 1971). Because it is the source of nutrients for plants and since most soil chemical reactions involve this phase, it could be assumed that studies on soil solution composition would have been extensive. That this is not so might be attributed to the emphasis in recent years on soil exchange phenomena and also to the difficulty often experienced in obtaining sufficient quantities of true soil solution for analysis.

Current research on the charge characteristics of weathered soils, the minerals of which are dominated by 1:1 type clay silicates and iron and aluminium oxides, has demonstrated the dependence of surface charge on (amongst other things) the ionic strength of the ambient medium (van Raij and Peech 1972; Keng and Uehara 1974; El-Swaify and Sayegh 1975; Gillman and Bell 1976). The commonly used methods for assessing the cation exchange capacity of soils were developed primarily for temperate region soils which are dominated by colloids of constant surface charge (negative) and frequently involve saturating salts of high ionic strength (e.g. 1M ammonium acetate). Since highly weathered soils possess both cation and anion exchange capacity which are dependent on ionic strength, the methods of assessing these capacities should be related to the ionic strength of the soil solution prevailing in the field if they are to have agronomic significance.

Most of the soil solution studies conducted so far (e.g. Le Roux and Sumner 1967; Larsen and Widdowson 1968; Adams 1971) have not included the more highly weathered humid tropical soils, through Larsen and Widdowson (1968) did include a Rhodesian red clay of undefined mineral composition, and the Natal oxisols and ultisols examined by Le Roux and Sumner (1967) would, according to their classification, be weathered soils.

The principal object of the present investigation was to measure the concentrations of those cations and anions which would contribute to the ionic strength of the soil solution in a number of weathered soils from tropical north Queensland, and then to test whether the ionic strength value obtained could be predicted from the easily determinable electrolytic conductivity. A further object was to measure the concentrations of the same species in convenient soil extracts to see whether predictions about the composition and ionic ratios in soil solution could be made from such data.

Experimental

Soils

Eighteen samples were used in the study and included from two to four samples from various depths from each of a krasnozem, euchrozem, xanthozem, red podzolic, red earth, and yellow earth from north Queensland (Table 1). The chemical, physical, and mineralogical characteristics of these samples have been described previously by Gillman and Bell (1976).

Method of Obtaining Soil Solution

Soil solution was obtained using a modification of the centrifuge method of Davies and Davies (1963). One or 2 kg of < 2 mm air dry soil was moistened to 0.1 bar with distilled water and equilibrated for a predetermined time at 25°C in a 5 l., polythene-lined, plastic bucket covered with 0.025 mm polythene film. The incubated soil was then loaded into special centrifuge vessels, 70 mm in diameter and 70 mm in height, each designed to hold 250 g of soil, and was centrifuged at 2000 rpm (relative centrifugal force, *c.* 900*g*) for 45 min. A full description of the apparatus and reasons for choosing the centrifuge technique have been given by Gillman (1976).

Establishment of Suitable Equilibration Times

Ten of the soils were incubated at a moisture tension of 0.1 bar for up to 64 days, and the soil solution removed by centrifugation. The pH, electrolytic conductivity *C*, calcium, and magnesium concentrations of the solutions were determined for all soils. Additionally, nitrate and ammonium were determined for the solutions obtained from surface soils.

A krasnozem surface soil and a red earth subsurface soil were equilibrated for 1, 2, and 3 days at 1:1, 1:5, and 1:10 soil:solution ratio and *C*, calcium, magnesium, sodium, and chloride determined on the extract.

Soil Solution and Soil Extract Analysis

Soil solution obtained by centrifugation was filtered through a 0.22 μ m Millipore filter, brought to 25°C in a water bath, and *C* measured. After the determination of pH (combination glass/calomel electrode), bicarbonate was measured by titrating

to a methyl orange end point with 0.0025M sulphuric acid. Nitrate (Schall and Hatcher 1968) and ammonium (steam distillation over magnesium oxide; Bremner 1965) were determined within 24 h. Calcium, magnesium, potassium, sodium, iron, aluminium, and manganese were analysed by atomic absorption spectrophotometry. Sulphate was determined by reduction to hydrogen sulphide (Johnson and Nishita 1952) but with a titrimetric finish using mercuric acetate (Archer 1956). Chloride was measured by titration with silver nitrate (Jackson 1958).

Analysis of 1:1, 1:2.5, 1:5, and 1:10 soil:solution filtered extracts was the same as described above except that nitrate + chloride was estimated by difference between the sum of cations and other anions.

Phosphate analysis was attempted using an automated analytical procedure based on the Murphy and Riley (1962) method, but soil solutions and extracts contained $< 0.005 \mu\text{g/ml}$ phosphorus ($< 2 \times 10^{-4}$ mM phosphorus). At this concentration phosphate has negligible effect on the ionic strength.

Table 1. Selected site data for the north Queensland soils

Great Soil ^A Group	Location	Parent material	Mean rainfall (mm)	Mean ^B temperature (°C)		Profile drainage	Vegetation
				Jan.	July		
Krasnozem (Acrohumox)	Gregory Falls Innisfail 385786 ^C	Basalt	3050	Max. 32 Min. 22	24 15	Free	Rain forest
Euchrozem (Ustocrept)	Talavera Clarke R. 334519	Basalt	630	Max. 34 Min. 22	24 11	Free	Eucalypt open woodland
Xanthozem (Acrohumox)	Paluma Townsville 424616	Dacite	2030	Max. Not Available Min.		Free	Rain forest
Red Podzolic (Acrohumox)	Paluma Townsville 420616	Dacite	2030	Max. Not Available Min.		Free	Rain forest
Red Earth (Eustrustox)	Pentland Hughenden 325426	Lateritized Sediments	630	Max. 36 Min. 23	25 10	Free	Eucalypt woodland
Yellow Earth (Haplustox)	Heathlands Jardine R. 575507	Mesozoic Sandstone	1700	Max. 31 Min. 23	29 18	Free	Closed heath

^A U.S. Soil Taxonomy classification given in parenthesis.

^B Estimates only.

^C Australian Map Grid Reference 1:250,000.

Treatment of Data

The analytically determined concentrations were corrected for ion pair formation using an iterative procedure as described by Adams (1974) which allows the calculation of ion activities of each species. The Debye-Huckel equation was used to calculate activity coefficients (f_i):

$$-\log f_i = \frac{0.509A_i^2 I^{\frac{1}{2}}}{1 + 0.329A_i I^{\frac{1}{2}}}$$

where Z is the ionic valency, I the ionic strength and A_i is an ion size parameter.

The ionic strength of the solutions was calculated using the formula

$$I = 0.5 \sum c_i Z_i^2,$$

where Z_i is the ionic valency and c_i is the ionic concentration (molality \equiv molarity in these dilute solutions).

Results and Discussion

Soil Solution Data

The time-of-incubation experiment showed that equilibrium between the soil and the soil solution at a moisture tension of 0.1 bar was reached in 16 days for red and yellow earths, and 8 days for all other samples except the krasnozem sample, where strongly increasing nitrate and ammonium values showed that organic matter was still being mineralized after 64 days. In this latter case, an incubation period of 28 days was chosen for convenience.

Analytical results for the soil solutions are presented in Table 2. The concentrations in these tropical soils are generally much lower than those presented by Larsen and Widdowson (1968) for some British and Rhodesian soils and in their summary of other workers' results. Data compiled by Altman and Dittmer (1966) from the results of many workers show typical values for calcium, magnesium, and potassium in soil solution from temperate regions to be 2.5–5 m.e./l, 4–8 m.e./l, and 0.5–1 m.e./l respectively. The concentrations of calcium, magnesium, potassium, and sodium, are, however, similar to those reported by Le Roux and Sumner (1967) for Natal soils. Our results illustrate the high degree of leaching that these soils experience under humid tropical conditions. It is only in the surface horizons of soils with organic matter contents greater than 10% that the ionic strength was much greater than 0.003, and it is probable that the values for these samples have been artificially raised by mineralization of organic matter in the incubation process.

An examination of Table 2 shows an acceptable balance between the sums of cations and anions considering the low levels encountered, thus confirming that all significant cations and anions have been measured. Further examination reveals a considerable amount of variation in the ionic composition between soils, particularly in the anions. Some soil solutions were dominated by sulphate, others by chloride, while the bicarbonate ion concentration was appreciable in one or two samples. Considering the cations, calcium plus magnesium concentrations usually exceeded those of sodium plus potassium, and in the majority of cases, magnesium was more abundant than calcium. In many samples, sodium appeared to dominate the cation suite calcium, magnesium, potassium, and sodium, a phenomenon also noted by Le Roux and Sumner (1967). This could arise because sodium is not as strongly held electrostatically as are the other cations, but it might also be due to salt accession, since many of these samples have been taken from regions of relatively high rainfall within 25–30 km of the coast. The proportionally high ammonium values in the solutions from soil samples rich in organic matter are due in some degree to the laboratory incubation process. This aspect will be discussed later.

The concentrations of iron, aluminium, and manganese have not been reported in Table 2. The value for each of these species was less than 0.5 ppm except in the surface horizons. In the time-of-incubation experiment, it was observed that in some surface soils the iron and aluminium values initially increased and the solutions obtained were dark brown. As incubation proceeded, the concentrations of iron and aluminium decreased to very low values and the solution extracted was colourless. Results for the surface krasnozem are presented in Table 3. Combining this observation with the fact that a balance between cations and anions was achieved without these species, it is assumed that iron, aluminium, and possibly manganese present in solutions from the surface horizons were chelated to colloidal organic matter, and were thus not likely to affect the ionic strength.

Table 2. Electrical conductivity, ionic composition, and ionic strength of the soil solution from samples of north Queensland soils

Sample	Depth range (cm)	0.1 bar moisture (%)	C (mS/cm)	pH	NH ₄	Cation concentration (m.e./l)			Anion concentration (m.e./l)			Ionic strength × 10 ⁻³			
						Ca	Mg	K	Na	HCO ₃	Cl	SO ₄	NO ₃	Uncorrected	Corrected ^A
Krasnozem	(0-10)	34	0.600	5.9	5.50	0.11	0.15	0.27	0.25	0.76	2.12	2.55	0.63	7.65	7.43
	(30-60)	36	0.064	5.5	0.22	<0.01	0.02	0.04	0.16	0.06	0.30	0.04	0.05	0.50	0.50
	(210-240)	29	0.034	5.5	0.10	<0.01	0.01	0.01	0.14	0.08	0.10	0.05	<0.01	0.28	0.28
	(450-480)	37	0.035	5.3	0.02	<0.01	0.01	0.01	0.13	0.04	0.12	0.05	<0.01	0.22	0.22
Euchrozem	(0-10)	37	0.290	7.9	0.03	1.28	0.88	0.30	0.07	2.12	0.34	0.22	<0.01	3.85	3.73
	(60-90)	34	0.057	6.6	<0.01	0.10	0.09	0.04	0.14	0.14	0.22	0.04	<0.01	0.51	0.51
Xanthozem	(0-10)	37	0.820	4.1	4.03	0.56	1.72	0.39	0.69	<0.01	2.22	3.97	0.68	10.33	9.48
	(30-40)	19	0.245	4.6	0.92	0.04	0.19	0.16	0.38	0.08	0.80	0.34	0.47	2.00	1.98
	(90-120)	15	0.170	4.6	0.20	0.10	0.10	0.03	0.40	0.08	0.78	0.14	0.03	1.12	1.12
Red Podzolic	(0-10)	33	1.000	5.0	5.22	0.79	1.45	0.79	0.86	1.62	4.60	3.06	0.53	12.31	11.59
	(20-30)	24	0.320	5.8	1.52	0.01	0.17	0.18	0.30	0.12	1.50	0.45	0.05	2.46	2.43
	(90-120)	31	0.063	4.8	0.03	<0.01	0.03	0.01	0.28	<0.01	0.25	0.09	<0.01	0.43	0.43
Red Earth	(0-10)	16	0.222	7.4	0.17	0.44	0.42	0.45	0.29	0.46	0.80	0.45	0.04	2.51	2.43
	(30-45)	16	0.140	5.3	0.03	0.19	0.14	0.17	0.22	0.10	0.62	0.34	<0.01	1.30	1.28
	(150-165)	21	0.087	5.5	0.13	0.11	0.14	0.03	0.20	0.06	0.48	0.07	<0.01	0.74	0.74
Yellow Earth	(0-10)	15	0.190	4.2	0.67	0.02	0.11	0.10	0.27	0.10	1.04	0.20	0.05	1.47	1.47
	(60-75)	12	0.071	5.1	0.02	<0.01	0.02	0.03	0.22	0.02	0.32	0.04	0.05	0.42	0.42
	(120-135)	18	0.044	5.0	0.08	<0.01	0.02	0.01	0.18	0.02	0.25	0.05	0.01	0.36	0.36

^A Corrected for ion pair formation.

Ionic strengths of the soil solutions were calculated from the measured concentrations and also from the concentrations calculated after correcting for ion pair formation (Adams 1974). The results in Table 2 show that such a calculation was hardly necessary in these soils; the solutions were so dilute that ion pair formation was not extensive. Nevertheless, the corrected values have been used in all calculations in this paper.

Table 3. The soil solution concentration of iron and aluminium at various times of incubation for the 0–10 cm krasnozem sample

Incubation time (days)	Iron (ppm)	Aluminium (ppm)
2	7.1	10.7
4	10.0	15.0
8	25.6	24.5
16	7.7	7.5
32	1.2	1.0
64	<0.1	<0.1

Ionic Strength and Electrolytic Conductivity

There was a strong relationship between C and ionic strength (Fig. 1). The regression equation was:

$$I = 0.0120C - 0.0004 \quad r = 0.993 (P < 0.001).$$

This equation which covered an electrolytic conductivity up to about 1 mS/cm, is remarkably similar to that obtained by Griffin and Jurinak (1973) for a range of soil saturation paste extracts and river waters with electrolytic conductivities up to 30 mS/cm. The Griffith and Jurinak equation is:

$$I = 0.0127C - 0.0003 \quad r = 0.996 (P < 0.001).$$

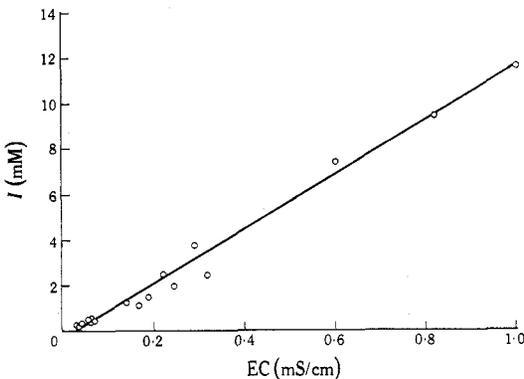


Fig. 1. Relationship between ionic strength and electrolytic conductivity for soil solution removed from soils at 0.1 bar soil moisture tension for a range of weathered soils from north Queensland.

The high value of the correlation coefficient shows that the ionic strength of the soil solution of these highly weathered soils can be estimated by simply determining the electrolytic conductivity. The similarity between the equation calculated here and that of Griffin and Jurinak (1973) suggests that the ionic strength of soils possessing a great variety of ion species and concentrations can be easily estimated.

Soil Extracts

Equilibration studies showed that equilibrium was achieved in two days, and ionic concentrations measured from 1:1, 1:2.5, 1:5, and 1:10 soil:solution extracts were given the same mathematical treatment as in the soil solution studies in calculating the ionic strength. At each soil to solution ratio, the ionic strength was highly correlated with C and the regression of ionic strength on C was similar to that obtained for the soil solution. When all of the data from soil solution and soil extracts was considered together, the regression was:

$$I = 0.0109C - 0.0002 \quad r = 0.984 (P < 0.001).$$

In addition, C at each soil:solution ratio was strongly correlated with the C at 0.1 bar (Table 4), which means that C at any moisture content should be well correlated with

Table 4. Relationship between electrical conductivity (mS/cm) of a soil extract and electrical conductivity of the soil solution

Soil extract	Regression equation	r
1:1	$C(1:1) = 0.721 C_{(0.1 \text{ bar})} - 0.188$	0.982
1:2.5	$C(1:2.5) = 0.492 C_{(0.1 \text{ bar})} - 0.168$	0.966
1:5	$C(1:5) = 0.258 C_{(0.1 \text{ bar})} - 0.021$	0.971
1:10	$C(1:10) = 0.139 C_{(0.1 \text{ bar})} - 0.014$	0.984

the ionic strength of the soil solution. This relationship was indeed observed; for instance, the relationship between ionic strength of the soil solution $I_{(0.1)}$ and $C_{(1:5)}$ of the 1:5 soil extract was:

$$I_{(0.1)} = 0.0446C_{(1:5)} - 0.000173 \quad r = 0.980 (P < 0.001).$$

Therefore the soil solution ionic strength could be simply estimated from the electrolytic conductivity of a 1:5 soil extract for the weathered soils used in this study.

Adsorbed Cations

Using Langmuir theory, Khasawneh and Adams (1967) demonstrated that an acid Magnolia sandy clay loam subsoil, saturated with calcium and potassium, desorbed these cations as the soil:solution ratio of soil extracts was decreased. Their data fitted the derived equation

$$V/S = a/S_t + V/S_0,$$

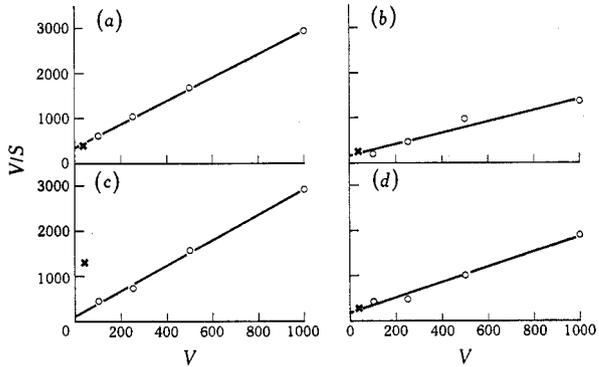
where V is the volume of solution (ml) in equilibrium with 100 g soil, S is the total cations in solution (milli-equivalents), S_t is the total milli-equivalents of cations in the system (i.e. solution plus those adsorbed on the soil), and a is a constant reflecting the intensity of adsorption. The value of S_t can be calculated from the slope of the plot of V/S versus V . It is important to realize that the Langmuir model is being applied here in a special (limiting) case, i.e. in dilute solution with concentration approaching zero. It would therefore be unwise to assume adsorption according to the complete Langmuir model, but using the equation in this special case could be useful in predicting soil solution composition from soil extract data.

Ulrich and Khanna (1972) were only partly successful in fitting this equation to four soils they studied. In a plot of V/S versus V , a straight line was obtained only

up to $V = 80$ ml/100 g. These authors claimed that the presence of desorbable (i.e. initially adsorbed) salts will cause an overestimation of the exchangeable cation value.

In the present study, linear plots of V/S against V were obtained in most cases up to 1000 ml/100 g, for those samples where the solution concentrations were high enough to be accurately measured (viz. eight samples from upper horizons). Four of these samples are depicted in Fig. 2 where S (milli-equivalents) is the sum of ammonium, calcium, magnesium, potassium and sodium.

Fig. 2. Langmuir plots for salt adsorption for four soils where V is the volume of the solution (ml) in equilibrium with 100 g soil, and S is the sum of calcium, ammonium, magnesium, potassium, and sodium in V (ml).
 o Soil extract.
 x Soil solution (0.1 bar).
 (a) Euchrozem.
 (b) Red Podzolic.
 (c) Krasnozern.
 (d) Xanthozern.
 All 0–10 cm.



We believe that the desorption of cations (and anions) with decreasing soil:solution ratio is due to the ionic strength—and pH—dependence of charge in these soils which contain appreciable amounts of constant potential type clay minerals. Thus as the ionic strength is decreased by dilution, positive and negative charge is equally reduced by the mutual cancellation of electrolytic double layers (Sumner 1963) and cations (and anions) are released. The sample used by Khasawneh and Adams (1967) was sesquioxidic, whereas Ulrich and Khanna (1972) possibly used soils dominated by clay of the constant charge type.

If the mechanism proposed here is correct, then the desorbable ions measured are in fact, exchangeable, and their presence does not cause an overestimation of the sum of exchangeable cations. The interesting result is, however, that for these weathered soils, the sum of cations (and therefore anions) in the soil solution at any moisture content can be predicted by determining their sum in three of four convenient extracts.

Cation Activity Ratio

It is well known that cation ratios in soil solution influence the plant uptake of such cations. The activity ratio between potassium and the divalent cations, calcium and magnesium,

$$R_{A,K} = a_K/[a_{Ca} + a_{Mg}]^{\frac{1}{2}}$$

is a good example. The equilibrium value for this ratio $R_{A,K,E}$ is determined in a rather tedious way from a curve of $R_{A,K}$ versus adsorbed potassium, but Le Roux and Sumner (1967) showed that for a range of Natal soils, this value could be more easily obtained by actually measuring the potassium, calcium, and magnesium concentrations in the soil solution. The values they obtained were well correlated with those determined by the conventional ionic equilibria procedure.

It was therefore of interest to determine whether $R_{A,K,E}$ (the value obtained from the soil solution data) could be predicted from soil extract data in these particular soils. Sufficiently accurate data were available for about half of the samples studied, and it was found that $R_{A,K}$ was linearly related to \sqrt{V} , where V is the volume of solution in equilibrium with 100 g of soil. Plots for four samples are given in Fig. 3.

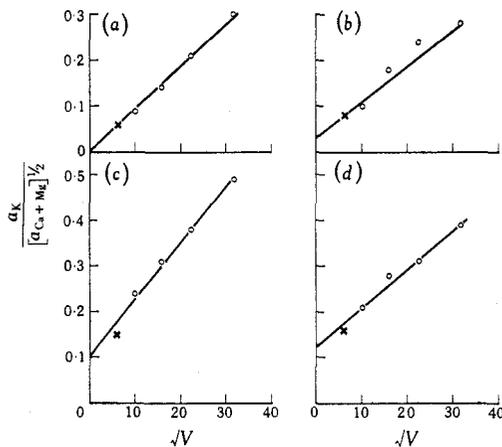


Fig. 3. Cation activity ratio plots for four soils where a is the molar activity of cation in equilibrium with 100 g of soil.
 o Soil extract.
 x Soil solution (0.1 bar).
 (a) Euchrozem.
 (b) Xanthozem.
 (c) Krasnozem.
 (d) Red Podzolic.
 All 0–10 cm.

Calcium/ Σ Cations

Adams (1966) and Bennett and Adams (1970) demonstrated that if the ratio of the calcium activity to the sum of cationic activities in the soil solution is less than 0.15, calcium deficiency (even in a limed soil) could be expected. The results in Table 5 show that calcium deficiency might be a real problem in these weathered soils for introduced economic plants. The euchrozem is the only soil having such a ratio above the critical value.

Probert (1978) found that the application of increased amounts sodium dihydrogen phosphate in the absence of lime to a yellow earth similar to that studied here, depressed the yield of *Stylosanthes guyanensis*. Also, calcium biphosphate gave better yields than sodium dihydrogen phosphate at equivalent phosphorus rates. Such evidence points to calcium deficiency *per se*, which could have been deduced from the cationic activity ratio. Kerridge *et al.* (1972) demonstrated a very high phosphorus requirement for krasnozem soils, similar to that studied here, but as the phosphorus was added as calcium dihydrogen phosphate, an examination of the cation ratio in Table 5 suggests that some of the response could have been due to the alleviation of calcium deficiency.

General Discussion

This preliminary assessment of the composition of the soil solution of weathered soils has been necessarily artificial in that the soils were wetted to a common moisture tension (0.1 bar) and incubated. Such conditions do not reflect those existing in the field where moisture content is constantly changing. Periodic changes in soil solution composition would also be expected to occur as a result of such effects as leaching and plant uptake of mineralized components. Results not presented here showed that the soil solution from moist samples of some of these soils collected

directly in the field had only small amounts of ammonium. Furthermore, solution calcium and magnesium concentrations were usually much lower than those obtained under incubated conditions.

In spite of these limitations, some important relationships between soil solutions and soil extracts have emerged. It has been shown that even at concentrations difficult to measure accurately and with a variety of ionic species, there is a strong correlation between the ionic strength and C . Thus, in an extensive study of soil solution embracing seasonal and site variation, the ionic strength could be estimated by an extremely simple method.

A number of very useful relationships between the soil solution and soil extracts have been demonstrated, and these avoid the difficulty encountered in trying to obtain true soil solution. Firstly, the ionic strength of soil solution was well correlated with the C of a convenient soil extract. Secondly, the sum of the major cations and anions may be estimated from the results of three or four more convenient extract determinations. Finally, it has been possible to predict from soil extract data the relative quantities of soil solution cations, parameters so important in plant nutrition studies.

The ionic strength for some of the soil solutions were overestimated because of the mineralization of organic matter. For instance, using C of 1:5 soil extract for 0–10 cm krasnozem sample after 1 day equilibration, and the regression of $I_{(0.1)}$ on $C_{(1.5)}$, an ionic strength of 0.004 was calculated, about half of the value reported in Table 1. A realistic upper limit for the ionic strength of the soil solution of these weathered soils is 0.005, with values less than 0.002 being common for the majority of horizons in each of the six soils. These values are far removed from that used in most methods for estimating the cation exchange capacity of soil, viz. 1.0. (If an alcohol washing step is included the ionic strength is indefinite.) The difference in net charge between ionic strengths of 0.002 and 1.0 can be appreciable, as demonstrated by Gillman and Bell (1976) where differences between these two ionic strength values at the soil pH were as much as 400%.

The possibility of calcium deficiency indicated by the soil solution cation ratios show that studies on soil solution composition could profitably be included in plant nutrition assessment of these weathered soils.

Acknowledgments

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