Estimates of Soil Solution Ionic Strength and the Determination of pH in West Australian Soils

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Abstract

The average ionic strength of 20 West Australian soils was found to be 0·0048. The effects of three electrolytes (deionized water, $CaCl_2$ and KNO_3), three ionic strengths (0·03, 0·005 and soil ionic strength at field capacity, I_s) and two soil liquid ratios (1:5 and 1:10) on the pH of 15 soils were investigated. pH measurements in solutions of ionic strength 0·005 differed the least from measurements made at I_s. The differences that occurred in comparisons with distilled water or $CaCl_2$ of ionic strength 0·03 (0·01 M) were much greater ($\geq$0·4 pH units). An extractant with an ionic strength of 0·005 may provide a more realistic measure of pH in the field than distilled water or 0·01 M $CaCl_2$ for West Australian soils.

Introduction

The pH of a soil is an important parameter for assessing the suitability of a soil for the growth of plants. However, measurement of pH is fraught with difficulties (Russell 1973). Not only can soil variability cause large variations in pH within one paddock (up to 1 pH unit; Russell 1973), but also the method of measurement can strongly influence the value obtained and the precision of that value (White 1969).

In Australia, soil pH has usually been determined in a 1:5 soil-water ratio but now 0·01 M $CaCl_2$ (ionic strength of 0·03) is being used with increasing frequency (e.g. Williams 1980; Bromfield *et al.* 1983; Jarvis and Robson 1983; Vimpany and Bradley 1984). Schofield and Taylor (1955), White (1969) and Russell (1973) have suggested that the main criteria for selecting an extractant for pH measurement is that it should cause a minimum of disturbance to the distribution of ions between soil surfaces and the soil solution. An extractant that has the same ionic strength as the soil solution and is made up of the most common ions present in the soil may provide the most realistic pH measurement. However, such an approach would be very time consuming, as the ionic strength of each soil would have to be determined before pH measurement. A compromise would have to be achieved by using an ionic strength that represented the average value in a certain group of soils. Hence Gillman (1981), on the basis that some tropical soils have quite a low ionic strength (Gillman and Bell 1978), suggested that pH measurements at an ionic strength of 0·005 may be more realistic for the tropical soils he studied. However, the ionic strength of West Australian soils has not been measured, and so it is difficult to assess which medium would be the most appropriate for pH measurements.

Consequently, the aim of this work was to estimate the ionic strength of West Australian soil solutions from both cultivated and uncultivated soils by using the relationship between I_s and electrical conductivity (Richards 1954; Griffin and Jurinak 1973; Gillman and Bell 1978). Subsequently, the pH of several soils, measured in commonly used media and at the average ionic strength determined above, were compared with the pH measured at the estimated ionic strength for each individual soil.

Materials and Methods

Soils

Surface samples from 20 soils were collected from the agricultural regions of Western Australia. Some of their properties are given in Table 1. Soils 1–10 are from virgin sites, whereas soils 11–20 are cultivated (mainly wheat-legume rotation). Samples of a lateritic podzolic soil (Table 1, soils 8 and 16–20) with similar histories of agricultural management, but which had been used for crop production for different lengths of time, were collected for ionic strength comparisons only. All the soils were air-dried and sieved through a 2 mm mesh sieve before use.

Ionic Strength Measurements

The ionic strength of each soil was estimated by measuring the electrical conductivity of a 1:5 soil-water suspension. Triplicate samples were shaken for 16 h, centrifuged and filtered before measuring the conductivity. The formula of Gillman and Bell (1978) was used to estimate the ionic strength of the soil solution at field capacity (I_s):

$$I_s = 0\cdot0446C - 0\cdot000173, \tag{1}$$

where C is the electrical conductivity in mS cm^{-1}. The assumption that it was valid to use this equation for West Australian soils was tested by comparing the values for I_s estimated by using C of a 1:5 soil-water mixture and C of the soil solution at field capacity for four soils considered representative of those used in the study. C at field capacity was measured by using the method of Gillman and Bell (1978) except that for each soil type, six centrifuge tubes (of 40 g soil capacity) were centrifuged at 3000 rpm for 10 min after 8–9 days' incubation with deionized water. For soils 1, 4, 5 and 6 the predicted values were 85, 113, 98 and 89% of the measured values, respectively.

pH Measurements

The effects of deionized water, $CaCl_2$ (at ionic strengths of 0·03, 0·005 and I_s) and KNO_3 (at ionic strengths of 0·005 and I_s) at two soil:liquid ratios (1:5 and 1:10) on the pH of soils 1–10 were investigated. The only exception was for soils 3–6; the pHs were not measured in KNO_3 ($I = I_s$) at a soil:liquid ratio of 1:10. This resulted in 56 different comparisons for studying the effect of soil:liquid ratio. Soils 11–15 were included to provide extra data for cultivated soils after an initial study into the effects of soil:liquid ratio and electrolyte type. Consequently, pHs of soils 11–15 were only determined in $CaCl_2$ (at $I = I_s$, 0·005 and 0·03) and water at a soil:liquid ratio of 1:5.

The electrolyte cations, soil:liquid ratios and 0·03 ionic strength were selected because of their common usage as media for pH measurements (White 1969). The ionic strength of the soil was chosen because it was thought to cause the least disturbance of the distribution of ions in the soil. An ionic strength of 0·005 was selected on the basis of the average ionic strength determined in the other part of this work. Triplicate samples of each soil were shaken for 16 h with each treatment and then centrifuged and filtered to produce a clear supernatant liquid. pH measurements were made with a Radiometer PHM64 Research pH meter, using a combination electrode immersed in the supernatant solution. pH readings were taken after the rate of change of pH $<0\cdot015$ per 90 s interval.

Results

Ionic Strength of the Soil Solution

Of the 20 soils 14 had an estimated ionic strength $<0\cdot0053$, reflecting the generally low fertility and buffer capacity of West Australian soils (Table 1).

Table 1. Soil properties

No.	Soil[A]	Great Soil Group	Northcote classification	Organic matter (%)	CEC (C g^{-1})	$10^3 \times I_s$	pH[B]			
							Distilled water	$CaCl_2$		
								I_s[C]	$I_{0\cdot005}$	$I_{0\cdot03}$
1	Lancelin	siliceous sand	Uc 5·1	1·3	8·0	2·0±0·3	5·83	5·8	5·30	5·11
2	Warranine	non-calcic brown	Dr 2·11	5·95	31·0	3·7±0·2	7·34	6·46	6·34	6·06
3	Kojonup	gleyed podzolic	Dy 5·81	2·14	6·0	1·2±0·1	5·80	5·48	5·13	4·84
4	Balkuling	lateritic podzolic	Dy 5·51	4·92	11·2	2·3±0·1	6·12	5·53	5·48	5·15
5	Malebelling	yellow podzolic	Gn 2·44	3·04	8·0	5·3±0·2	5·73	5·43	5·28	4·97
6	Yalanbee	lateritic podzolic	KS-Uc 4·21	2·46	6·0	1·0±0·1	5·97	5·84	5·17	4·85
7	Merredin (subsoil)	yellow earth	Gn 2·24	0·09	1·2	2·4±0·3	4·51	4·35	4·19	4·07
8	Gairdner River	lateritic podzolic	Dy 5·51	1·85	—	3·5±0·2	5·16	4·88	4·76	4·50
9	Merredin	yellow earth	Gn 2·24	1·49	3·0	14·9±0·2	6·22	5·60	5·88	5·48
10	Badgingarra	earthy sand	Uc 5·2	0·83	3·2	1·5±0·1	6·00	5·31	5·04	4·67
11	York	non-calcic brown	Dr 2·22	4·33	21·9	7·6±0·1	5·94	5·54	5·64	5·40
12	Waroona A	alluvial	Gn 3·42	5·62	10·0	6·6±0·02	4·96	4·55	4·60	4·26
13	Roleystone	yellow podzolic	Dy 4·61	8·01	7·0	2·3±0·05	5·60	5·14	5·02	4·66
14	Waroona B	gleyed lateritic podzolic	Dy 5·81	2·15	2·0	1·7±0·006	4·99	4·38	4·30	4·07
15	Beverley	red earth	Gn 2·14	1·46	10·0	3·2±0·006	6·65	5·97	5·89	5·53
16	GR 3[D]	lateritic podzolic	Dy 5·51	1·66	—	3·9±0·82	—	—	—	—
17	GR 8	lateritic podzolic	Dy 5·51	2·20	—	4·8±0·12	—	—	—	—
18	GR 11	lateritic podzolic	Dy 5·51	2·38	—	8·3±0·34	—	—	—	—
19	GR 15	lateritic podzolic	Dy 5·51	3·46	—	9·6±0·18	—	—	—	—
20	GR 25	lateritic podzolic	Dy 5·51	3·34	—	9·1±0·44	—	—	—	—

[A] Soils 11–20 are cultivated soils. All soils sampled from 0–10 cm depth except No. 7 (30–60 cm depth).

[B] 1:5 soil liquid ratio.

[C] I_s estimated from equation 1.

[D] Number refers to years of cultivation.

The average estimated I_s for all the soils was 0·0048, similar to the value found by Gillman and Bell (1978) for North Queensland soils. For the 10 cultivated soils, the average estimated I_s was 0·0057, whereas the average for the virgin soils was 0·0038. Even though there was an increase in the ionic strength of the soil solution with years of cultivation (Table 1, soils 8, 16–20), it is not a marked effect and appears to reach a maximum after about 15 years.

pH Measurements

Examples of the variation of pH measured in deionized water and $CaCl_2$ solutions are given in Table 1.

Table 2. The mean difference in pH measured by different soil treatments

Extractant	Soil-liquid ratio	$\Delta pH^{A,D}$	$\Delta pH_{ca}^{B,D}$	$\Delta pH_{k}^{C,D}$
Distilled water	1:5	0·15±0·10(5)	0·44±0·24(1)^{E}	0·30±0·23(1)
	1:10		0·48±0·20(1)	0·41±0·19(0)
$I_{0\cdot005}$ $CaCl_2$	1:5	0·06±0·07(7)	0·20±0·18(1)^{E}	—
	1:10		0·21±0·62(2)	—
$I_{0\cdot005}$ KNO_3	1:5	0·12±0·07(3)	—	0·26±0·19(0)
	1:10		—	0·13±0·10(0)
$I_{0\cdot03}CaCl_2$	1:5	0·09±0·08(4)	0·46±0·22(0)^{E}	0·65±0·19(0)
	1:10		0·39±0·17(0)	0·52±0·25(0)
I_s $CaCl_2$	1:5	0·10±0·11(5)	—	0·15±0·11(3)
	1:10		—	0·13±0·12(3)
I_s KNO_3	1:5	0·09±0·05(1)	0·15±0·11(3)	—
	1:10		0·13±0·12(3)	—

[A] ΔpH: the difference in pH between the 1:10 and 1:5 soil liquid ratios for each solution.

[B] ΔpH_{ca}: the difference in pH between measurements in $CaCl_2$ at $I = I_s$ and other treatments.

[C] ΔpH_k: Same as B except KNO_3 is the solution.

[D] All ΔpH values are the mean for soils 1–10±standard deviation. Figures in brackets refer to the number of soils for which ΔpH is not significant at $P < 0\cdot05$.

[E] As for D except the ΔpH values are the mean of soils 1–15.

Effect of Soil:Liquid Ratio

For all the treatments used (except distilled water) the difference in pH determined from the two soil:liquid ratios was ≤0·12 pH units (Table 2). The differences were not statistically significant ($P < 0\cdot05$) for 24 of the 56 possible comparisons. It would appear that changes in the soil:liquid ratio of ≤50% do not have a large effect on pH measurements.

Effect of Extractant Type and Ionic Strength

For the purposes of this investigation, the pH measured in media with the same ionic strength as the soil (I_s) will be compared with the other treatments.

The smallest difference in pH was observed between the $CaCl_2$ and KNO_3 media both at $I = I_s$ (Table 2), indicating that at constant ionic strength, changes in pH due to type of electrolyte were not a major factor.

The average pH difference between $CaCl_2$ at $I = I_s$ and other measurements was in the order (Table 2):

$$0 \cdot 03\ CaCl_2 > \text{water} > 0 \cdot 005\ CaCl_2 > I_s, KNO_3.$$

The same trend was observed for the pH difference between KNO_3 at $I = I_s$ and other treatments (Table 2). As anticipated from the results of previous work (reviewed by White 1969), the variation in the ionic strength of the media appears to be the major contributor to pH differences measured by the different treatments.

Discussion and Conclusions

pH measurements in solutions of $I = 0 \cdot 005$ differed the least from measurements made in solutions of ionic strength equal to that of the soil. Even though the pH values at I_s and $I = 0 \cdot 005$ were significantly different, the difference was less than that which occurs from soil variability. On the other hand, the differences that occurred in comparisons with distilled water or 0·01 M $CaCl_2$ were much greater ($\leqslant 0 \cdot 4$ pH units).

If changes are to be made in the most commonly used method for pH measurement in Australia and the criteria for its choice is that it causes the least disturbance of the distribution of ions in the soil, then it would appear that 0·01 M $CaCl_2$ shows no distinct improvement over distilled water as a medium for pH measurement in West Australian soils. An extractant of $I = 0 \cdot 005$ may provide a more realistic compromise. This is similar to Gillman's (1981) findings, even though the soils he studied (acrohumoxs, an eutrostox and a haplustox) are not common agricultural soils in Western Australia. $CaCl_2$ would probably be the most suitable electrolyte because of the dominance of Ca in most agricultural soils.

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