EFFECT OF SOIL/SOLUTION RATIO ON DETERMINING THE CHEMICAL POTENTIALS OF PHOSPHATE IONS IN SOIL SOLUTIONS

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SCHOFIELD[1] suggested that an index of soil phosphate availability could be given by the negative chemical potential of monocalcium phosphate—the 'phosphate potential'—defined as $(\frac{1}{2}pCa + pH_2PO_4)$ and determined in a 0·01 M calcium chloride extract. Aslyng[2] found, however, that this potential varied markedly with the soil/solution ratio and he attempted to correct for this 'dilution effect' by extrapolation of his experimental results to 'zero dilution'; others[3,4] have adopted this procedure. However, this is not a justifiable correction because, as shown by Aslyng's own results and those of others[5,6], there is no approach to a limiting value towards zero dilution.

Larsen and Court[6] suggested a number of possible explanations for the effect of soil/solution ratio on the phosphate solubility but were unable to decide which was operative. Olsen *et al.*[7], using soils comparatively rich in soluble phosphate (about 100 times more than in most other soils), found that the negative dicalcium phosphate potential ($pCaHPO_4$) of the 0·01 M calcium chloride extracts decreased with the amount of soil in the suspension. They equilibrated the soils with calcium chloride for 4 days at a constant carbon dioxide pressure and measured the concentration of bicarbonate ions in the extracts. This was found to increase with the amount of soil and they attributed the increase in phosphate concentration (decrease in negative phosphate potential) to the ability of carbonate ions to displace HPO_4 ions from surfaces containing phosphate. When the chemical potential of monocalcium phosphate is calculated from the experimental results of Olsen *et al.*[7] it is independent of the soil/solution ratio (Table 1). This suggests that the observed effect of soil/solution ratio on the phosphate potential $(\frac{1}{2}pCa + pH_2PO_4)$ may be due to accumulation of carbon dioxide produced by microbial activity during equilibration with the calcium chloride solution, since this usually occurs in stoppered bottles mounted on an end-over-end shaker.

To test this assumption, varying aliquots of soil 5 from the experiment of Larsen and Court[6] were equilibrated for 16 h with 0·01 M calcium chloride under three contrasting conditions: (1) in stoppered bottles placed in an end-over-end shaker; (2) open bottles on a roller shaker; (3) bubbled with atmospheric air, previously moisture saturated by passing through a wash bottle containing 0·01 M calcium chloride; wrist action shaking.

From the results (Table 2) it can be seen that when stoppered bottles were used there was a reduction in pH, increase in phosphate concentration and decrease in phosphate potential with increasing weight of soil in the suspension. When the bottles were left open the same trends were observed but to a smaller degree. However, when atmospheric air was passed through while shaking, all three values became independent of the amount of

Table 1. EFFECT OF SOIL/SOLUTION RATIO ON SOIL PHOSPHORUS SOLUBILITY *

g soil/ 50 ml.	pH			$C_P \times 10^6$			$\frac{1}{2}pCa + pH_2PO_4$†		
	1	2	3	1	2	3	1	2	3
5	6·75	6·70	6·46	474	103	224	5·76	5·39	4·99
10	6·82	6·75	6·52	455	136	331	5·79	5·29	4·83
20	6·92	6·84	6·62	593	149	403	5·75	5·29	4·79
40	7·02	6·95	6·73	600	149	406	5·78	5·35	4·82

Soil 1, Pierre clay
Soil 2, Apisha silt clay loam } equilibrated 4 days in 0·01 M CaCl₂
Soil 3, Rocky fine sandy loam } at $- \log P_{CO_2} = 1·42$

* Data of Olsen, Watanabe and Cole[7].
† Calculated by the equation: $\frac{1}{2}pCa + pH_2PO_4 = pCaHPO_4 - pK_2 + (pH - \frac{1}{2}pCa)$, where pK_2 is the 2nd dissociation constant of phosphoric acid and equals 7·20.

soil in the suspension. Similar results were obtained with other soils.

In a separate experiment the amount of carbon dioxide produced by the soil was measured by absorption in sodium hydroxide using the apparatus described by Kent-Jones and Taylor[8]. The carbon dioxide pressure was calculated from the solubility of carbon dioxide in 0·01 M calcium chloride at room temperature[9], and the volume of the bottles. The results (Table 3) show that the amount of carbon dioxide produced was proportional to the amount of soil in the suspension. This suggests that the production of carbon dioxide at the individual soil/solution ratios fully explains the variation of pH with the soil/solution ratio.

Table 2. EFFECT OF SOIL/SOLUTION RATIO AND CARBON DIOXIDE EQUILIBRATION ON SOIL PHOSPHORUS SOLUBILITY *

g soil/ 50 ml.	pH			$C_P \times 10^6$			$\frac{1}{2}pCa + pH_2PO_4$		
	a	b	c	a	b	c	a	b	c
1	7·23	7·31	7·36	0·71	1·04	1·11	7·79	7·68	7·68
2	7·16	7·32	7·41	0·93	1·16	1·13	7·63	7·65	7·72
4	7·04	7·31	7·43	1·16	1·25	1·16	7·47	7·60	7·73
8	6·98	7·25	7·42	1·35	1·42	1·19	7·37	7·51	7·70
16	6·94	7·20	7·40	1·53	1·59	1·07	7·30	7·42	7·74

* Soil 5 of Larsen and Court (ref. 6).
a, Stoppered bottles, end-over-end shaking for 16 h.
b, Open bottles, roller shaking for 16 h.
c, Bubbled with atmospheric air, previously moisture saturated by passing through a wash bottle containing 0·01 M calcium chloride; wrist action shaking.

Table 3. EFFECT OF CARBON DIOXIDE ON SOIL pH

g soil/ 50 ml. 0·01 M CaCl₂	$P_{CO_2} \times 10^3$	$pH\alpha$	$pH\beta$
1–16	(0·3)	(7·43)	(7·55)
1	2·6	7·32	7·42
2	3·2	7·22	7·32
4	5·5	7·14	7·17
8	11·8	7·01	7·07
16	21·2	6·94	7·00

$pH\alpha$ measured after shaking for 16 h in stoppered bottles.
$pH\beta$ measured when soil suspensions (10 g soil/50 ml. solution) were equilibrated in the presence of carbon dioxide buffers.
Figures in brackets obtained when the suspensions were equilibrated with atmospheric air.

Using the method of Pardee[10], carbon dioxide buffers were made up to give carbon dioxide pressures corresponding to those calculated when the soil suspensions were shaken in stoppered bottles. 10-g aliquots of the soil suspended in 50 ml. 0·01 M calcium chloride were then shaken overnight with an atmosphere that was in equilibrium with these buffers. The values of the soil suspensions (Table 3) compare closely with those obtained when varying soil/solution ratios were shaken in stoppered bottles without carbon dioxide absorption.

These findings have a bearing on the interpretation of lime and phosphate potentials, for the carbon dioxide content of soil air varies greatly in the field[11] because of variation in biological activity and soil aeration.

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