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CHARACTERIZING SOIL FERTILITY BY ION DIFFUSIVE FLUX MEASUREMENTS*

by T. W. MASSEE, R. A. OLSEN and E. O. SKOGLEY**

SUMMARY

The general acceptance of diffusion as a rate-limiting step in transferring ions to plant roots was considered in characterizing soil fertility. Soil ion diffusive flux measurements to an exchange resin were measured with two soil: resin cells, one with untreated soil, the other with the same soil fertilized with P, K, and Cl. The P, K, and Cl that diffused to the resin of each cell was extracted and determined. Using only these measurements and some simplifying assumptions of diffusion theory, calculations were made of the soil's P and K solution concentration, adsorbed concentration, a capacity factor, transmission factor, and quantity of fertilizer needed to attain any desired flux. Excellent to fair correlations existed between these calculated values and traditionally measured chemical quantities. Plant uptake of P and K was generally well correlated with diffusive flux measurements as well as traditional chemical measurements.

INTRODUCTION

Agronomists generally accept that diffusive flow accounts for most of the movement of certain nutrient ions (P, K, and most trace elements)[13] to plant roots. Two important aspects of this concept are: (a) There is a plant-regulated reduction of solution ion concentration at the root surface. The resulting concentration gradient is the driving force for ion movement to the plant root; and (b) the release of soil-adsorbed ions to the solution phase in the region affected by the gradient can be quantified by a 'capacity factor'.

Several workers have provided fairly convincing supportive evi-

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dence for the diffusive flow mechanism controlling ion uptake. First, the validity of the soil solution hypothesis in mediating transfer of ions from soils to plants was established[12] in contrast to a contact exchange transfer. Then, from mathematical considerations, estimates of diffusive ion flow to roots were shown to be consistent with measured plant uptake quantities[14 16]. The existence of soil ion gradients near plant roots has been visually shown with autoradiographs of soils or agar using a radioactive isotope[2]. Reasonably accurate quantitative soil measurements of ion diffusion gradients have since been made by sectioning soils adjacent to onion roots[8].

A 'capacity factor' may be related to a dissolution reaction plus diffusion (Crank[6], pages 121 to 122), and this approach has been commonly used. In studying phosphorus diffusion, a capacity factor value was taken as the linear portion of the adsorption isotherm obtained by plotting labile P as a function of solution P[14]. Validity of this use was established from comparing phosphorus flux in soils under both steady state and transient conditions[15].

In view that diffusion might be a rate-limiting step in ion uptake by plants, surprisingly few diffusion experiments have been used to evaluate soil fertility. Vaidyanathan and Nye[22] placed exchange resin strips on moist soils and measured diffusive ion uptake by the resin. They showed that the accumulative flow for any ion versus the square root of time was constant for a given soil and proposed this term to characterize soils. Next, it was shown that similar quantities of K diffused to onion roots as to the resin strips[4]. However, in another evaluation of this method, they found the resin strips accumulated less P than expected, and attributed the apparent discrepancy to the resin strips for failing to maintain the soil: strip boundary concentration near zero[23]. Others[24] used a similar technique to determine the effect of soil physical conditions on diffusion of added Zn and Cl. The transmission values they obtained from ^{36}Cl diffusion to the resin strip did not indicate the boundary rate-limiting step. Under greenhouse conditions, the quantity of P fertilizer needed on individual soils for barley production was closely predicted after initially determining the components of diffusive flow. The predicted solution concentration needed varied with soil, *e.g.*, a clay needed only 13 percent that of a sandy loam[16].

The objective of this research was to develop simple methods to measure fertility and assess fertilizer needs by using both untreated and treated (fertilized) soils placed in contact with resin sinks, and then measuring the accumulation of ions in the resin.

THEORETICAL CONSIDERATIONS

Assumptions

The method is based on a simplified diffusion model in which an ion has a constant diffusion coefficient and which assumes the process is not affected by other processes, such as ion pair formation, chelation, codiffusion, osmotic and electrical potential gradient effects. In addition, two ion conditions, solution phase and adsorbed phase, are assumed to contribute to diffusion. While in the solution phase, the ion is free from the effects of clay and organic matter charges as compared with its equilibrium adsorbed phase in which the ion does not contain sufficient energy to escape. The same soil transmission value of P and K ions is used as is determined for chloride. The adsorption isotherm is taken to be linear with a zero intercept, so that the following relations apply: The adsorbed concentration is in equilibrium with the solution concentration, so that both will vary when there is an addition or subtraction of the respective ion, according to a constant R:

$$C_s = RC \qquad [1]$$

$$\text{'Capacity factor'} = R + 1 = \frac{C_s + C}{C} = \frac{\Delta C_s + \Delta C}{\Delta C} \qquad [2]$$

Notations used

C	soil solution concentration; for P it is g/cm³ of soil solution, and for K and Cl is eq/cm³ of soil solution. C_0 designates that it is the 'original' (initial) concentration, as prior to diffusing elsewhere or having fertilizer added.
C_s	is the amount of adsorbed ion, and from being in equilibrium with C it may eventually contribute to the diffusion process. To maintain continuity, it has units like C, and so it is the amount that reacts with a cm³ of soil solution.
D	diffusion coefficient of an aqueous solution; cm²/sec. The values for Cl, H_2PO_4, and K ions were taken to be 1.82×10^{-5}, 5.0×10^{-6}, and 1.98×10^{-5} cm²/sec, respectively[18].
erf	the error function, found in mathematics tables.
F	concentration of material, as fertilizer K, P, or as Cl, added per soil solution basis (to be comparable to C); g/cm³ or eq/cm³.
I	transmission (also termed 'impedance') factor for denoting an effective diffusion coefficient in a soil solution (D_e) as compared to an aqueous solution (D) and, therefore, is D_e/D.
M	quantity of material diffusing through a planar area to a sink in time t; g/cm² or eq/cm². M_f indicates that the quantity was from a fertilized soil.

(R + 1) the 'capacity factor', equal in value to the slope of sorption isotherm, where $C_s = RC$, and, therefore, is the ratio of $(C_s + C)$ to C.
t time; sec.
x distance; cm.
θ the volumetric soil water content.
π the constant pi, equal to about 3.14.

Derivation of formulas used

In a laboratory system, a moist soil surface is exposed to an exchange resin sink, which maintains the boundary solution ion concentration near zero (Fig. 1 B). If, in actuality, the resin reduces the boundary solution concentration a lesser amount than to zero, flux will be reduced accordingly as M (and M_f) is proportional to $(C_0 - C_{\text{boundary solution}})$. The rate of ion movement from the soil across the boundary under these transient conditions is of prime interest. Following an applicable derivation [9], amended to include volumetric water content [3 19], the soil solution concentration at some given distance from the resin and given time after the soil and resin are brought together is determined by

$$C_{(xt)} = C_0 \operatorname{erf}[x(R+1)^{1/2}/2(DIt)^{1/2}] \qquad [3]$$

Also, rate of diffusion across the boundary into the resin has a solution given on the right-hand side of Equation [4]

$$DI\theta(dC/dx)|_{x=0} = C_0\theta[DI(R+1)]^{1/2}/(\pi t)^{1/2} \qquad [4]$$

Equation [4] can be integrated over time, which solves the mass accumulated in the resin after some time, t:

$$M = 2C_0\theta[DIt(R+1)]^{1/2}/\pi^{1/2} \qquad [5]$$

In the special case of Cl diffusion, it is considered as being nonadsorbed, but remaining entirely in soil solution. For Equations [3], [4], and [5], the (R + 1) term then becomes equal to 1 and drops out. For future reference in this paper these will be, respectively, [3a], [4a], and [5a]. [3a, 4a, 5a]

So far, these equations have referred to experimentally unfertilized soils. With the duplicate cell where fertilizer was initially added to the soil, and assuming that the fertilizer remains entirely in solution and in adsorbed forms, there is an addition to the soil concentration which is also related to the capacity factor, see Equation [2].

$$F = \Delta C_0 + \Delta C_s = \Delta C_0 (R+1) \qquad [6]$$

For Cl, the ΔC_s in Equation [6] is 0, and (R + 1) is equal to 1.

Solving for the transmission factor from using Cl diffusion measurements, Equation [5a] may be rewritten for a fertilized soil where C_0 is increased by F.

$$M_f = 2(C_0 + F)\theta(DIt)^{1/2}/\pi^{1/2} \qquad [5b]$$

and, upon dividing [5b] by [5a], it is found that the original unfertilized soil solution concentration of Cl is given by:

$$C_0 = MF/(M_f - M) \qquad [7]$$

Although C_0 for Cl was not studied directly here as provided by Equation [7], this relation was used to derive I. Proceeding, Equation [5a] may be squared and solved in terms of I. Then, where 'C_0' appears in the resulting equation, the term is replaced with the laboratory measured terms appearing on the right-hand side of Equation [7]. Thus,

$$I = (M_f - M)^2 \pi/4F^2\theta^2Dt \qquad [8]$$

and M_f, M, F, and D in Equation [8] are for Cl, and is the solution needed to calculate I from a laboratory diffusion experiment.

The remaining derivations will be for P and K (although I, from Cl diffusion, will be used to estimate soil transmission properties for these other elements).

A ΔC_0 relation may be obtained after first amending Equation [5] with this term for a soil fertilized with P or K. (The change in the adsorbed concentration from fertilizing is hidden in the constant capacity factor (R + 1).)

$$M_f = 2(C_0 + \Delta C_0)\theta[DIt(R+1)]^{1/2}/\pi^{1/2} \qquad [5c]$$

On dividing Equation [5c] by Equation [5],

$$\Delta C_0 = (M_f/M)\, C_0 - C_0 \qquad [9]$$

With this relationship of ΔC_0 known, C_0 may be found. To do this, Equation [5] is written with $F/\Delta C_0$ replacing the (R + 1) term as allowed by Equation [2]. Next, the terms on the right-hand side of Equation [9] are substituted for ΔC_0, and

$$C_0 = \frac{(M_f - M)M\pi}{4DItF\theta^2} \qquad [10]$$

Thus, a diffusive calculated solution concentration is available for P or K, using laboratory-measured M_f, M, and F, together with a table value of D, and the I value previously determined with the same two cells. Also, enough relations have been found to almost immediately derive C_s for P or K. With the linearity of the adsorption isotherm assumed in Equation [1], it is possible to write

$$C_s = C_0\, \Delta C_s/\Delta C_0 \qquad [11]$$

while the unsolved for ΔC_s term may be replaced by $(F - \Delta C_0)$ as per Equation [6], and

$$C_s = C_0(F - \Delta C_0)/\Delta C_0 \qquad [12]$$

The terms on the right-hand side of Equation [12] have been derived here in measured terms, and

$$C_s = \left[\frac{MF}{(M_f - M)} - \frac{(M_f - M)M\pi}{4DItF\theta^2}\right] \qquad [13]$$

which estimates C_s from diffusion measurements.

Also, enough terms are known to easily obtain a capacity factor, (R + 1),

either by substituting values for its identity as $F/\Delta C_0$ or $(C_s + C_0)/C_0$, and

$$(R + 1) = \frac{4DIt\, F^2\theta^2}{(M_f - M)^2\pi} \qquad [14]$$

From rearranging Equation [14], a fertilizer requirement F may be derived that will indicate quantity needed for a desired M_f quantity. Therefore, in Equation [15], the (R + 1) and M values previously found from experiment are used, and F is evaluated at some value substituted for M_f.

$$F = \frac{(M_f - M)\,(R + 1)^{1/2}\,\pi^{1/2}}{2\,(DIt)^{1/2}\theta} \qquad [15]$$

METHODS AND MATERIALS

Twenty-one soils, including those having a wide range of properties, were collected from throughout the United States. General characterization was made by usual methods[5], including mechanical analysis, pH_{CaCl_2}, CEC, exchangeable cations (Ca, Mg, K, Na), and organic matter.

The soils were also tested by the diffusion cell used to measure soil ion flow to an exchange resin sink (M, M_f) as shown in Fig. 1. The nylon mesh in Fig. 1 entirely surrounded the sink and was held in place by an O-ring. A mixture of resieved and regenerated[21] medium porosity Amberlite IR-120 H-ion and Amberlite IRA-410 OH-ion resins was used. The two resins were mixed to equalize anion and cation exchange capacities.

Soil to be added to the cell compartment was fertilized with 0, 5, and 10 ml/100 g soil of a near-neutral aqueous solution containing 2.16 g K Cl, 0.725 g K H_2PO_4, and 1.442 g $K_2H\ PO_4.3H_2O$/liter. (Even though only two fertilizer rates, a nonfertilized plus another, were shown to be needed in the previous mathematical derivations, the third rate was used here as an added experimental point.) Then, enough water was added and mixed with the soil to produce a nearly saturated, but fairly rigid, paste, with a consistency that allowed future mixing but which would not shrink away from the sink during the diffusion period. The wetted soil was then placed in a strong plastic bag, sealed, and placed in a large round capped jar which was slowly rolled on a rock tumbler for 24 hours.

After mixing, a part of the soil was used to fill the soil portion of the cell. A vibrator aided getting the soil packed uniformly. The top was smoothly leveled off with a spatula. The filled cell (of known tare and volume) was weighed, so that by use of Equations [16] and [17], volume per cent water and bulk density could be determined for future unit conversions. Using the same approach as has been taken[26] with a saturated soil

$$\theta = \left[\, 1 - \frac{(W - V)\,(0.606)}{V} \,\right] \qquad [16]$$

$$\text{Bulk density} = W/V - \theta \qquad [17]$$

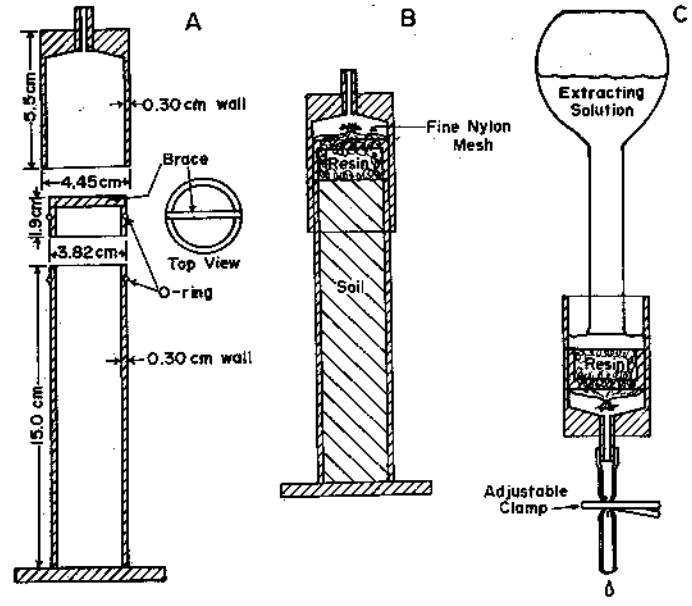

Fig. 1. Diffusion cell, showing A: dimensions, B: in operation, and C: extracting ions from sink.

wherein W = grams of wetted soil, V = cm^3 of wetted soil. The resin sink and cap were then fitted in place as shown in Fig. 1-B, the sink:soil contact was rechecked, and diffusion was allowed to take place at near constant room temperature (20°C) for 24 h. Visual observations of the soil's and resin's moistness before and after the diffusion period did not indicate any mass flow. Afterwards, as shown in Fig. 1-C, resin extraction was done with *N* H_2SO_4 (one drop per second) with 100 ml extract collected for determining M (or M_f) of Cl, K, and P. Chloride was determined by potentiometric titration with 0.005 *N* Ag NO_3, using a Ag reference and Ag Ag Cl electrode. Potassium was determined by flame spectroscopy, and P by molybdenum blue color development in ascorbic acid[25].

From a portion of soil not used in the diffusion cell, a suction extract was taken for comparing traditional soil solution P and K with results from diffusion tests.

For comparative chemical estimations of labile P and labile K, soils fertilized as mentioned were wetted and dried four cycles. Labile K was estimated by the method of Graham and Kampbell[10] where repeated extractions are made with 0.01 *M* $CaCl_2$. Labile P was estimated by measuring anion exchange resin uptake of this element in a soil-water-resin mix according to the method of Amer *et al.*[1] and which has been used by others[17] for similar purposes. Adsorbed P or K, (C_s), was considered to be labile minus the suction water extract (C_0) amounts.

For determining relative P and K uptake by plants from the soils, the short-term of DeMent, Stanford and Bradford[7] was used. Barley (*Hordeum distichon* var. Piroline) was grown with 2 replications in a growth chamber with 16 hours of full light (500 to 600 microeinsteins/(m²)(sec) within the 400–700 nm range) at 24°C, and with an 8-h night temperature of 18°C. Harvesting was done with roots and tops combined for analysis. The samples were ground and digested for P and K according to a TCA method[11].

RESULTS

Transmission values

From the diffusion cell resin extraction, about 40 to 90 μeq of Cl were obtained from soils treated with the 10 ml fertilizer solution, which was sufficient for easy laboratory determinations. The average

TABLE 1

Transmission (I) values, solution (C_0) and sorbed (C_s) potassium content of unfertilized soils

Soil types	Order	Transmission (from Cl diffusion)	Potassium (μeq/cm³ soil solution)			
			Measured by standard chemical methods		Estimated fro diffusion cell	
		(I)	C_0	C_s	C_0	C
Amsterdam silt loam	Mollisol	0.84	0.78	34.9	0.39	1
Astoria clay loam	Inceptisol	.29	.09	4.7	.22	1
Camas Creek sandy loam	Mollisol	.49	.26	11.7	.25	3
Dayton silty clay loam	Alfisol	.60	.87	18.7	.71	9
Door loam	Mollisol	.82	.22	7.4	.20	3
Drummer silty clay loam	Mollisol	.61	.88	16.8	1.40	8
Frankfort clay	Alfisol	.45	.80	19.0	.47	1
Jory silt loam	Ultisol	.24	.64	18.3	.52	8
Lloyd clay	Oxisol	.25	.23	5.0	.18	1
Minidoka sandy loam	Aridisol	.48	4.09	30.2	4.23	9
Portneuf silt loam	Aridisol	.73	.55	27.6	.17	1
Portneuf subsoil silt loam	Aridisol	.79	.39	20.2	.31	1
Sagemoor sandy loam	Aridisol	.63	.41	21.0	.23	1
Stanton sandy loam	Entisol	.39	.10	4.6	.18	6
Tetonia silt loam	Mollisol	.73	.82	44.3	.59	1
Tracy sandy loam	Alfisol	.65	.33	3.8	.35	1
Wahluke loam	Aridisol	.66	.25	7.8	.05	8
Whitney loam	Alfisol	.67	1.45	20.0	.85	1
Williams loam	Mollisol	.46	.71	28.6	.46	1
Willamette silty clay loam	Mollisol	.62	.11	6.8	.06	3
Winchester loamy sand	Entisol	.36	.83	24.7	.80	9
Average		0.56	0.70	17.9	0.60	8

deviation of the calculated (per Equation [8]) transmission values, for a single soil was 3.8 per cent from using the 10- and 0-ml fertilizer solution and these are shown in Table 1. The I transmission values ranged from 0.24 to 0.84. When comparing these values to other soil characteristics including percent silt, pH, percent organic matter, percent clay, volumetric water percent, and bulk density, the I values were only weakly correlated with silt content ($r = 0.46$, significant at 5 percent level), and to a non-significant degree with the other mentioned variables, either by simple or multiple regression.

Transmission values herein have been mathematically defined in essentially the same manner as was previously done by Porter *et al.*[20], who also measured Cl flux, and so these results should be comparable.

Potassium – diffusive flux and traditional determinations

The quantity of K extracted from the resin ranged from about 2 (nonfertilized soils) to 40 μeq/100 ml for soils with the 10 ml fertilizer solution. These amounts were within easy analytical range, and are converted to soil C_0 and C_s values in Table 1 using Equations [10] and [12], respectively. The C_0 measured by chemical methods for all the soils averaged 0.70 μeq/cm³ of water saturation extract, and 0.60 μeq/cm³ from diffusive flux. Comparing individual soil C_0 quantities by the two methods gives a 0.97 correlation coefficient (r). The r for the diffusion *versus* traditional methods for the sorbed (C_s) values was 0.90. However, the mean C_s measured by traditional methods was just over twice the value found from the diffusion method (17.9 *versus* 8.7 μeq/cm³).

Fixation of the added fertilizer K (which was 18 percent as denoted from not being recovered by the 0.01 *M* $CaCl_2$ extracts) would result in decreased M_f values and therefore in an overestimating of total diffusible K, ($C_0 + C_s$), as it is equal to $MF/(M_f - M)$. Instead, the mentioned underestimation as compared to the chemical (solution + NH_4OAc) extracts (Table 1) may indicate that the NH_4OAc extract removed ions not only participating in diffusion, but some that were more tightly bound.

The capacity factor used here is simply $(C_0 + C_s)/C_0$, and averaged 36 for chemical methods and 33 for diffusion methods, although individual comparisons were not usually this close (Table 1). Sandy soils tended to have low capacity factor values, especially the Mini-

TABLE 2

Solution (C_0) and sorbed (C_s) phosphorus content of unfertilized soils

	Phosphorus, μg/cm³ of soil solution			
	Measured by standard chemical methods		Estimated from diffusion cell	
	C_0	C_s	C_0	C_s
Amsterdam	.13	73.8	5.11	99.1
Astoria	.04	33.5	0.02	384.4
Camas Creek	.22	139.0	3.16	107.4
Dayton	.23	244.4	1.82	300.7
Door	.07	145.3	0.25	274.4
Drummer	.26	218.6	1.76	337.0
Frankfort	.52	383.4	1.53	593.0
Jory	.04	66.8	0.05	131.6
Lloyd	.03	83.6	0.03	832.3
Minidoka	.60	137.4	9.78	53.9
Portneuf	.90	195.7	3.04	393.2
Portneuf subsoil	.43	81.5	1.35	109.4
Sagemoor	.30	93.3	1.59	206.4
Stanton	.09	43.2	0.29	149.1
Tetonia	.54	123.9	4.70	299.2
Tracy	.17	345.6	0.08	213.5
Wahluke	.83	138.5	1.01	65.2
Whitney	2.65	283.1	10.54	207.6
Williams	.43	121.3	2.37	213.0
Willamette	.04	142.0	0.34	107.3
Winchester	.30	151.2	6.84	51.9
Average	.42	154.5	2.65	244.3

doka sandy loam which had been heavily fertilized in previous years as reflected by the high C_0 in Table 1.

For comparing the computed *versus* the actual amount of potassium fertilizer F needed to bring about a predetermined M_f value, as per Equation [15], the M_f value obtained with the 5 ml solution fertilizer rate may be chosen as though the fertilizer rate were not known. Equation [15] was then computed using the data from the 10- and 0-ml rates. From doing this, the average computed F value was 85.1 percent (with a standard deviation of 19.8 percent) of the actual amount used to obtain M_f at 5-ml fertilizer rate. Thus, using this equation and procedure on the average slightly underestimated the needed quantity. If only the fertilizer rates to achieve a M_f quantity are of interest, Equation [15] may be simplified. For example, if F_1 and F_2 are rates that produce M_{f-1} and M_{f-2}, respectively, there is a linear relationship so that

$$F_2/F_1 = (M_{f-2} - M)/(M_{f-1} - M)$$

and it is necessary to test only one F rate and solve for the other at some desired M_f level substituted into the equation.

Phosphorus-diffusive flux and traditional determinations

The quantity of P in resin extracts was sufficient for laboratory determination. However, the soil water-saturation extracts of Lloyd, Jory, and Astoria soils were so low in P that conventional determinations (shown in Table 2) were not as reliable as others. Diffusion estimated solution (C_0) and sorbed (C_s) quantities were made by using Equations [10] and [12] (as done for K). As seen in Table 2, diffusion C_0 values, averaging 2.65 μg P/cm³, exceeded the traditional measurements of 0.42 μg/cm³, with an r value of 0.67. The C_s values for both methods averaged closer, (154.5 μg/cm³ for traditional compared to 244.3 for diffusion). However, the r value from comparing soils was only 0.23.

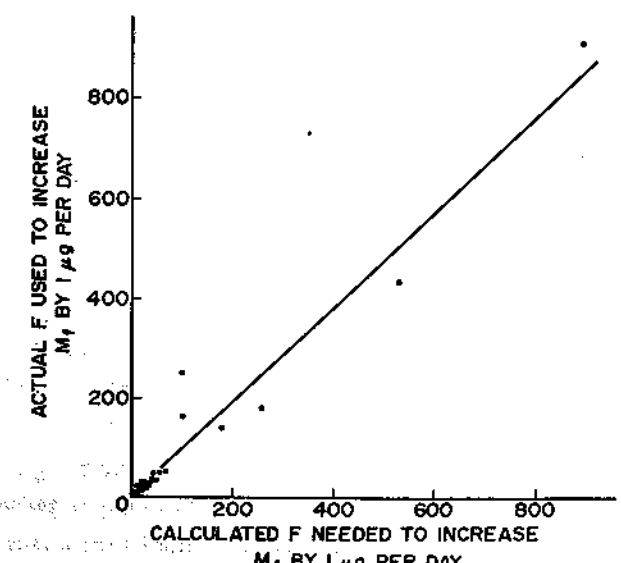

Fig. 2. Comparison of calculated fertilizer phosphorus (F) needed to increase M_f by 1 μg/day *versus* actual quantity found from experiment.

By theory, $C_0(R + 1)^{\frac{1}{2}}$ denotes a diffusion 'strength'. When these 'strengths' from diffusion versus traditional chemical methods were calculated and compared, the r value was higher, 0.78. Although fixation was measured chemically, as with K, the r value was n't increased by mathematically correcting the diffusion terms for fixation.

To assess the validity of computing P fertilizer needed, as per Equation [15], the same approach was used as for K. The average computed amounts of F were 99 percent (with a standard deviation of 30 percent) of the amounts actually used to obtain a predetermined M_f. There were large differences in the efficiency of P fertilizer for changing diffusive flux among soils, and these are shown in Fig. 2 with the regression line.

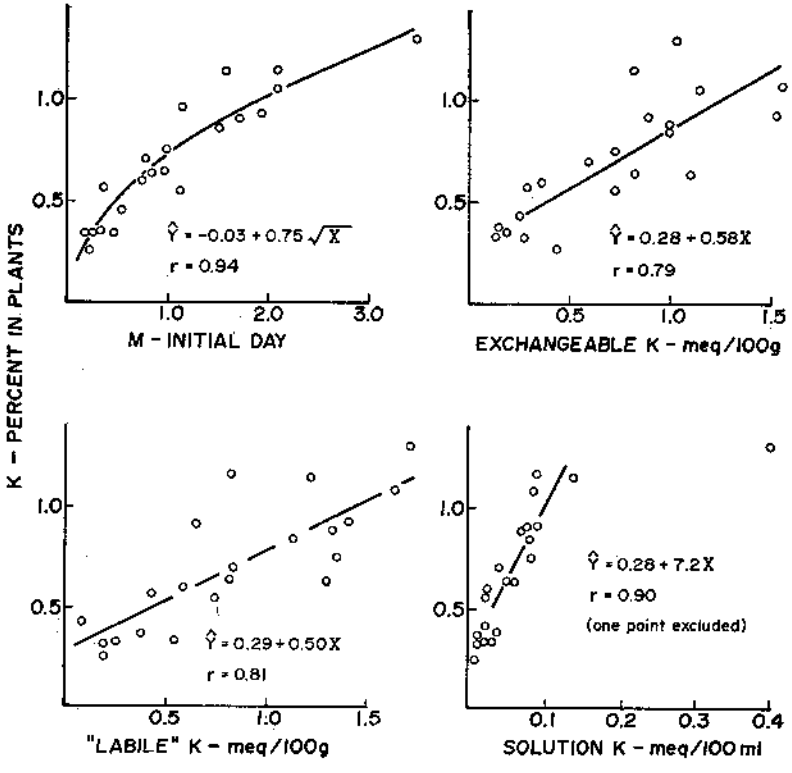

Fig. 3. Plant K percent in barley (DeMent-Standford test) *versus* (a) diffusion M results, (b) exchangeable K, (c) an estimate of labile K, and (d) saturated soil solution extract (wherein the point excluded at upper right was for Minidoka soil).

Plant potassium and phosphorus uptake vs. *chemical and diffusion tests*

When the percent K in the barley plants, grown according to the DeMent-Stanford[7] method, was compared to a 24-h measured M, good curvilinear correlation existed (r = 0.94). These results and traditional chemical tests are shown in Fig. 3. Traditional tests were not quite as closely related to plant K, as indicated by their r values. The total P uptake in the DeMent-Stanford[7] test was curvilinearly related to soil chemical and diffusion tests. Fig. 4 shows regressions resulting from the form $\hat{Y}_{P\text{-uptake}} = a + bX^n$ with comparable correlations. From these comparisons in Figs. 3, 4, the utility of this diffusion test is suggested, especially for K, as is the credibility of the proposed test[22] for the value of $M/t^{\frac{1}{2}}$.

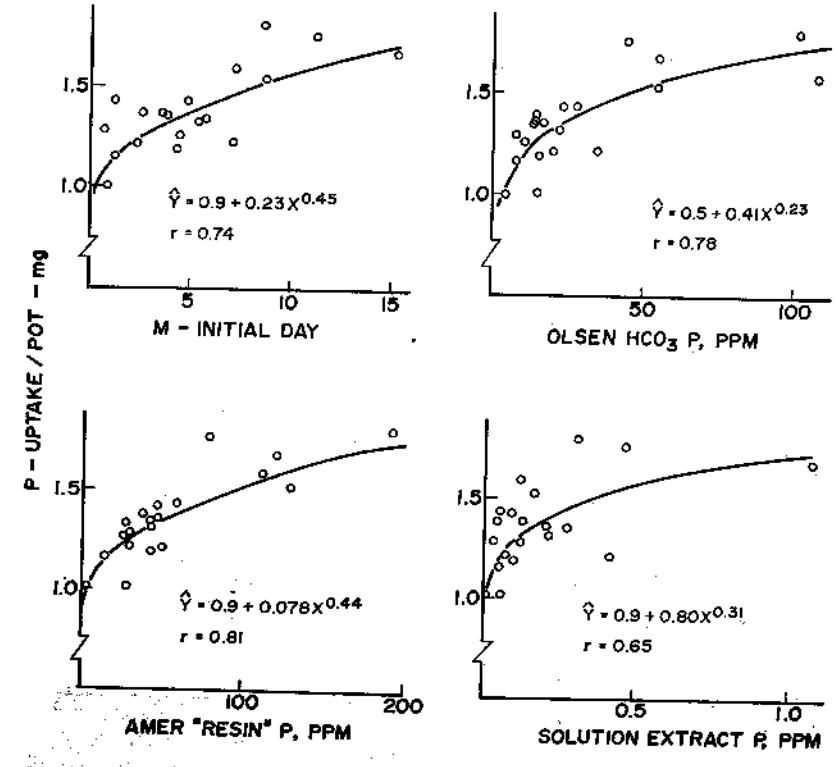

Fig. 4. Plant P uptake per pot in barley (DeMent-Stanford test) *versus* (a) diffusion M results, (b) Olsen's bicarbonate test, (c) Amer's resin test, and (d) saturated soil solution extract.

The nonlinear relations between M and plant uptake may result from a plant root sink not reducing the boundary solution concentration to a constant value but rather varying with a plant's ability to partially compensate for variation in soils, as was previously found when measuring diffusive flow to onion roots[4].

Concentration gradients in diffusion cell

To view how the mechanics of the diffusion setup may influence the comparative accuracy and precision of estimates of P, K, and Cl, the calculated concentration distributions at the end of a 24-h diffusion time are shown in Fig. 5 for Williams loam, a soil of average fertility. Diffusion results and Equations [3] and [3a] were used to obtain data for these curves. They show that Cl, then next K, and then P diffusion take place over shorter and shorter distances. Therefore, the physical resin: soil contact would be most critical for P, then K, etc. These gradients also indicate the relative distances at which diffusion may take place in the soil rhizosphere, although with roots the concentration at the root: soil boundary would be greater than zero and also the mathematics would be slightly changed for diffusion to a cylindrical root rather than a planar surface.

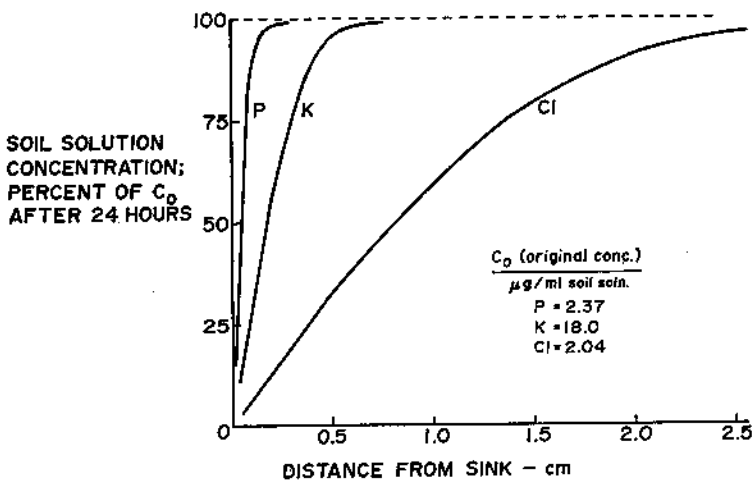

Fig. 5. Calculated soil solution concentration (as percent of original concentration, C_0) of P, K, and Cl as a function of distance from adsorbing sink after 1-day diffusion period for Williams soil.

CONCLUSIONS

The authors consider that using diffusion measurements to characterize fertility is now in the developmental stage. Coinciding with findings that a diffusion mechanism is a primary driving force for transferring certain ions to plant roots, is the aspect that chemical equilibria conditions in the root rhizosphere may be simulated in the laboratory by creating a soil concentration gradient with an ion exchange resin. Also, the quantitative evaluation of diffusion experiments with diffusion theory provides opportunities not available from traditional tests.

We consider that diffusion theory was upheld with the new approach taken here. The utility of diffusion tests seems apparent after obtaining plant response correlations on this first attempt that compared favorably with traditional tests which have taken years to develop. Also, estimating a capacity factor and a fertilizer requirement should be useful, especially in areas where field correlations are limited.

This test was somewhat time consuming. From four to five soils could be completely analyzed daily.

Further research applications may arise from being able to make the estimates without undue chemical alteration of the soil, *e.g.*, like that needed in measuring the efficiency of fertilizer materials, timing the recovery of temporarily depleted soil zones, or in conjunction with measuring plant root sink strengths.

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REFERENCES

1. Amer, F., Bouldin, D. R., Black, C. A. and Duke, F. R., Characterization of soil phosphorus by anion exchange resin adsorption and P^{32} equilibration. Plant and Soil 6, 391–408 (1955).
2. Barber, Stanley A., A diffusion and mass-flow concept of soil nutrient availability. Soil Sci. 93, 39–49 (1962).
3. Barfield, B. J., Personal communication (1974).
4. Graham, R., Vaidyanathan, L. V. and Nye, P. H., An evaluation of the pro-

perties of soil potassium influencing its supply by diffusion to plant roots in soil. J. Agric. Sci., **73**, 1–14 (1969).

5 Black, C. A. (Editor-in-chief), Methods of Soil Analysis, Part 2. Chemical and microbiological properties. Am. Soc. Agron., Inc., Madison, Wisconsin, U.S.A. (1965).

6 Crank, J., The mathematics of diffusion. Oxford Univ. Press, Oxford (1956).

7 DeMent, Jack P., Stanford, George, and Bradfield, B. N., A method for measuring short-term nutrient absorption by plants. Soil Sci. Soc. Am. Proc. **23**, 47–50 (1959).

8 Farr, E., Vaidyanathan, L. V. and Nye, P. H., Measurement of ionic concentration gradients in soil near roots. Soil Sci. **107**, 385–391 (1969).

9 Gardner, W. R., Movement of nitrogen in soil. *In* Soil Nitrogen. Amer. Soc. Agron. Inc., Madison, Wisconsin, U.S.A. (1965).

10 Graham, E. R. and Kampbell, P. H., Soil potassium availability and reserve as related to the isotopic pool and calcium exchange equilibria. Soil Sci. **100**, 101–106 (1968).

11 Leggett, Glen E. and Westermann, Dale T., Determination of mineral elements in plant tissue using trichloroacetic acid extraction. Agric. Food Chem. **21**, 65–69 (1973).

12 Olsen, R. A. and Peech, Michael, The significance of the suspension effect in the uptake of cations by plants from soil-water systems. Soil Sci. Soc. Am. Proc. **32**, 660–664 (1960).

13 Olsen, S. R. and Kemper, W. D., Movement of nutrients to plant roots. *In* Norman, A. G. (Editor), Advances in Agron. **20**, 91–151, Academic Press, New York (1968).

14 Olsen, S. R., Kemper, W. D. and Jackson, R. D., Phosphate diffusion to plant roots. Soil Sci. Soc. Am. Proc. **26**, 222–227 (1962).

15 Olsen, S. R., Kemper, W. D. and van Schaik, J. D., Self-diffusion coefficients of phosphorus in soil measured by transient and steady-state methods. Soil Sci. Soc. Am. Proc. **29**, 154–158 (1965).

16 Olsen, S. R. and Watanabe, F. S., Diffusion of phosphorus as related to soil texture and plant uptake. Soil Sci. Soc. Am. Proc. **27**, 648–653 (1963).

17 Olsen, S. R. and Watanabe, F. S., Diffusive supply of phosphorus in relation to soil textural variations. Soil Sci. **110**, 318–327 (1970).

18 Parsons, R., Handbook of electrochemical constants. Butterworth Scientific Publications, London (1959).

19 Phillips, Ronald E., Personal communication (1974).

20 Porter, L. K., Kemper, W. D., Jackson, R. D. and Stewart, B. A., Chloride diffusion in soils as influenced by moisture content. Soil Sci. Soc. Am. Proc. **24**, 460–464 (1960).

21 Rohn and Haas Company, Amberlite ion exchange resin laboratory guide. Philadelphia, Pennsylvania, U.S.A. (1964).

22 Vaidyanathan, L. V. and Nye, P. H., The measurement and mechanism of ion diffusion in soils. II. An exchange resin paper method measurement of the diffusive flux and diffusion coefficient of nutrient ions in soil. J. Soil Sci. **17**, 175–183 (1966).

23 Vaidyanathan, L. V. and Nye, P. H., The measurement and mechanism of ion diffusion in soils. VI. The effect of concentration and moisture content on the counter-diffusion of soil phosphate against chloride ion. J. Soil Sci. **21**, 15–27 (1970).

24 Warncke, D. D. and Barber, S. A., The diffusion of zinc in soils: I. The influence of soil moisture. Soil Sci. Soc. Am. Proc. **36**, 39–42 (1972).

25 Watanabe, F. S. and Olsen, S. R., Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. Soil Sci. Soc. Am. Proc. **29**, 677–678 (1965).

26 Wilcox, L. V., A method for calculating the saturation percentage from the weight of known volume of saturated soil paste. Soil Sci. **72**, 233–237 (1957).

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