Soil characterization by diffusion measurements
by Truman Winfield Massee

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Crop and Soil Science
Montana State University

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Reasonable precision was obtained in measuring impedance factors from determining the quantity of added chloride that diffused, and resulting values were similar to ones previously published. The calculated solution and adsorbed quantities of potassium (from diffusion) were usually nearly the same as were measured from routine chemical methods determining solution and labile amounts. There was variation in the quantity of calculated solution and adsorbed phosphorus from diffusion methods depending on the quantity of spiking done. This variation was believed to be associated with non-linear adsorption isotherms as were depicted from the chemical extractions done.

Plant uptake of phosphorus on various soils fairly well Correlated with diffusive flux from these soils, while potassium-plant correlations were much better. A potential was evident for estimating fertilizer needs from diffusion flux measurements, expe-cially for potassium.

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August, 1973

ABSTRACT

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ACKNOWLEDGEMENTS

The listing of persons who contributed to this study is lengthy, and space does not allow a detailed description of each individual's contribution. Even so, the author greatfully acknlwledges their assistance and expresses his appreciation and gratitude with the alphabetical listings of the following persons, placed under several general subject matter categories.

My Graduate Committee: Drs. C. Scott Cooper, A. Hayden Ferguson, Ralph A. Olsen, James R. Sims, and Earl O. Skogley (Chairman), all of Montana State University.

Advice on diffusion theory and application: Drs. W. Doral Kemper, Colorado State University; Phillip Low, Purdue University; Robert L. Nickelson, Montana State University; Sterling R. Olsen, ARS-USDA, Fort Collins, Colorado; Phillip H. Nye, Oxford University; and Ronald E. Phillips, University of Kentucky.

Laboratory and Shop Assistance: Asael Dilworth, ARS-USDA, Kimberly, Idaho; Jeanne Earl, Murtaugh, Idaho; Clarence Hayden, ARS-USDA, Kimberly, Idaho; my family -- Beverly, Rachel, Rebecca, and Daniel Massee, Twin Falls, Idaho; and Harold Waggoner, ARS-USDA, Kimberly, Idaho.

Soils collection and identification: Steven Booth, California resident; A. L. Black, ARS-USDA, Sidney, Montana, Charles Case, SCS-USDA, Gooding, Idaho; Dr. William

R. Gill, ARS-USDA, Auburn, Alabama; Ronald Githens, Junction City, Oregon, Farmer; Robert Hagenow, Indiana farmer; Dr. Dordon Huntington, University of California; Alvin Kohl, Illinois farmer; Herbert Kohl, Illinois farmer; and George E. Otte, SCS-USDA, Hillsboro, Oregon.

Resin Technology: Dr. Walter Dean, Mallinckrodt Chemical Works, St. Louis, Missouri.

Mathematics: Charles Brockway, University of Idaho; Dr. Robert Burman, University of Wyoming; H. Dale Fisher, ARS-USDA, Kimberly, Idaho; Dr. W. R. Gardner, University of Wisconsin; Pedro Hernandez, University of Idaho; Ben J. Pratt, ARS-USDA, Kimberly, Idaho; and Jos de Sonneville, University of Idaho.

Manuscript review: Warren W. Rasmussen, ARS-USDA, Kimberly, Idaho.

Manuscript typing: Doris Adams, Jerome, Idaho; Beverly Massee, Twin Falls, Idaho; and Dala Walton, Burley, Idaho.

Use of laboratory and library facilities: Drs. Marvin E. Jensen and Henry F. Mayland, ARS-USDA, Kimberly, Idaho.

To these named, and to others, who have been patient, encouraging, critical, and concerned, the author will always be indebted.

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INTRODUCTION

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Although the diffusion process was explained on a scientific basis by Fick more than a century ago, it was only since 1950 that it was recognized as an important phenomenon regulating the transport of many nutrient ions to plant roots. In addition to the academic intrigue associated with this relationship, valuable applications may be implemented. These include the measurement and regulation of soil fertility, and probably plant management and genetic selection.

In 1855 Fick, a medical physiologist at the University of Zurich, was the first to show how the heat flow equations developed by Fourier could be applied to diffusion. Thus, even though only a comparatively few analytical solutions (of diffusion-like phenomena) were known then, the fundamental principle(s) were established. It is not surprising that it took such a long time for agronomists to recognize the significance of this. First, the quantity of solution flow (sometimes termed transpiration, viscous, or mass flow) could also conceivably account for large quantities of ions being transferred to plant roots - which was a valid assumption for certain nutrients. This transfer process was believed to be accompanied by a renewal of solution ions from mineral reserves, another plausible process. These two facets were firmly linked together by Cameron (1911) in one of the first detailed works dealing with the soil solution.

Since then, a great deal of speculation has existed on how to measure the activity of soil solutions so that direct interpretations could be made. For example, Hoagland, in his first lecture given at Harvard University under the Prather Lectureship (1944), told of the background of the initial work in California prior to 1920. He said "much had been written about the soil solution and controversy had not ceased. It was apparent that experimental evidence was most inadequate. Generally, chemical analysis had been made on field samples of soil under no adequate control." To obtain better control, he told how 13 soils from the State were selected and two-ton samples of each were sent to Berkeley for soil solution analysis while being cropped. This had been done for 27 years at the time of the Lectureship. Some concluding remarks about these studies were ". . . it has become apparent that soil solutions can often be more dilute than those of our original set of soils, and still plants will not necessarily fail to absorb adequate amounts of nutrient ions. Thus the concept of 'supplying power' and the interrelation of the solid to the liquid phase of the soil became considerations of paramount significance and they are so today." A nutrient of particular consideration in these remarks was phosphorus. It had been found to be below one ppm in many solution samples, even at the beginning of the cropping period. Also, potassium was low - usually less than 20 ppm.

Byers et al (1938) expressed similar thoughts in 1938 in writing about the soil solution, and speculated on methods of extracting ". . .

none of which is wholly satisfactory. When such soil extracts are obtained, it is generally found that the concentration of the soluble salts in the solution is less than is required in artificial nutrient solutions to produce corresponding results . . . . It seems that part of these relations are to be ascribed to the presence of colloids in the soils. In general, the concentration of any solution is usually greatest in the film adjacent to any solid surface . . . ." Thus, they, as did Hoagland, questioned why the extracted soil solution is too low to account for proper plant growth, and propose that extraction methods do not duplicate what a plant root may encounter.

More recent data by Barber (1962) and Barber (1968), still indicate large differences in measured activities of soil solutions for various productive soils. This fact substantiates the impracticality of using averages for drawing conclusions. For phosphorus, Olsen, et al (1962) concluded (with applicable literature quotations not shown herein) "Fertile soils usually contain 0.2 to 0.3 ppm P in the soil solution, and a corn plant takes up 250 to 350 g of water per g of dry matter. Thus, viscous flow of water used by the plant would supply 2 to 4% of the total P taken up by the plant." Barber et al (1962), after studying 145 predominantly midwest soils and by using the same reasoning as Olsen et al (1962), concluded that only one percent of the phosphorus and 10 percent of the potassium could be transferred to the root by mass flow alone. Research on other nutrients, summarized in the more recent review by Olsen and Kemper (1968) indicated that usually the transport of iron, manganese, boron, copper, zinc, molybdenum and sometimes nitrogen and sulfur must be supplemented by mechanism(s) in addition to mass flow.

Early attempts to describe the means (in addition to mass flow) by which ions were transferred to roots have created an array of interesting concepts. One which provoked much thought and controversy was that of "contact exchange" which was developed by Jenny and Overstreet (1939) in 1939. They proposed that exchangeable soil cations, and also cations on the plant root surface, moved about in an oscillating volume. These volumes overlapped, and whenever a neighbor pair of ions simultaneously happened to be closer to each other's original attractive site than their own, they traded sites. In this manner ions exchanged between plant roots and charged soil particles - and by a similar action, between sites on soil particles at will. From this concept it was concluded that the soil solution was not necessary to account for the transfer of ions. Bray (1954), however, argued "A single root, to be functional, must secure many times the amounts of nutrients that are to be found on the immediate surface of a clay mineral particle with which it may be in contact. Regardless of whether the root and clay surfaces are so close that contact exchange, as postulated by Jenny and Overstreet (1939) can take place, the amount obtained from the immediate contact would be small and insufficient to make the root functional. The significant source of nutrients to the root surface comes from movement or diffusion into the film of water between the root surface and the soil surface." Bray's conclusion did not specify allowances for the renewal of ions on the clay exchange site by contact exchange with other clay material, even if he did consider this in his computations. However, Brown (1953) had just completed an experiment that showed that ion transfer without liquid film media was non-existent under the conditions he imposed. He had converted part of a soil sample to H-clay and enclosed it in a permeable membrane. This was then buried in the natural portion of soil so that ion exchange could take place between the two samples. With soil water contents similar to those where plant roots thrive, ion exchange was rapid. However, when the water content was reduced to near wilting point, the quantity that exchanged also decreased toward zero. This indicated that the solution was necessary for transfer. Brown (1953) ascribed the transfer to "migration" and "diffusion". Thus, Brown's statements, like Bray's, favored diffusion over contact exchange. At about this same time, Husted and Low (1954) published results which also indicated that ion movement was dependent on the solution phase, and derived a solution for soil ion transfer which followed Fick's diffusion laws. Perhaps the most convincing data to dispel the contact exchange theory was provided by Olsen and Peech (1960) who measured plant uptake at Rb^+ and Ca^{++} from both the suspension and equilibrium dialyzate. Although they varied the relative concentrations in the phases to extremes, the rate of Rb^+ and Ca^{++} uptake from both phases was the same.

A different process that has been envisioned as also contributing to ion uptake is initiated by the acidifying action of plant roots. It was postulated that the solution activity near the root was enhanced above that measured in soil extracts. For example, as the roots excrete CO_2, H_2CO_3 may be formed, Or if H^+ ions are excreted to preserve electrical neutrality (in case more cations are absorbed than anions), the soil solution pH would decrease. A pH decrease would provide consequential activity differences. From Donnan equilibria it can be calculated that a pH decrease of one unit would increase the solution potassium by a factor $\sqrt{10}$, while the calcium would increase by a factor of $\sqrt[3]{10}$. Nye (1968) has argued that perhaps just the reverse situation may exist. He states "It is widely believed that roots make nutrients more available by rendering their environment more acid." By using the data of Cunningham (1964), where 62 common plant species were studied, he reasoned that, on the average, more anions than cations were taken up from the soil - when counting nitrogen uptake as NO_3^- rather than NH_4^+. Nye speculated from these data that roots excrete HCO_3^- (not H^+), which tends to raise the pH. As an indication of this, he pointed out that it is normal for plants growing in nutrient media to increase the pH value when the nitrogen is applied as NO_3^-. Because of the difficulties encountered in measuring actual pH changes near root, speculation only has dominated. Therefore, it must be concluded that this type of exploration is inconclusive and more specific evidence is needed.

Coupled with this need is also a need for determining more about the exact nature of the several complexing agents that a plant may excrete. To study the effects, Elgawhary et al (1970b) used a simulated root made of porous ceramic tubing which they embedded in the soil. Complexing materials were mixed with water and passed through this "root" which acted as a sink for ions. EDTA, at 10^{-3} M concentration, increased zinc uptake by a factor of 17 over water alone. Other materials increased zinc uptake less, but were still highly effective. As to the actual materials excreted by plant roots, Rovira (1962) was able to isolate only small amounts of chelating anions as citrate and lactate from wheat roots. Thus it was concluded by Hale et al (1971), because of lack of conclusive evidence, that the implications in mineral nutrition of plants are unknown.

From the previous literature cited herein it has been pointed out that mechanisms such as contact exchange, acidifying action of roots, or their complexing exudates have failed to explain the large differences between soil solution concentration and plant uptake by mass flow. Evidence pointing toward diffusion is more conclusive, as will be shown.

The first work in soil ion diffusion did not relate to the plant root role in the process. Emphasis was placed on diffusion of fertilizer materials once they had been added to the soil, or to the theoretical basis of soil diffusion itself. Initial workers in these studies included Chernov (1939), Brown (1954), Husted and Low (1954), Klute and Letey (1958) and Marshall (1958). However, in the early 1960's Bouldin (1961) and Olsen et al (1962) initially proposed the importance of diffusion for transporting ions to plant roots. In their publications it was pointed out that the root must reduce the solution concentration of ions at the root-soil boundary and they solved mathematical models indicating the extent. A quite convincing portrayal of the root sink - diffusive flow mechanism was provided about this same time by Barber (1962) with autoradiographs. He used a technique of growing plants in soils labeled with a radioactive isotope. X-ray film was placed close to the active roots so that the developed film would depict the isotope distribution about them. Using this method, Barber labeled a soil with a small amount of Rb-86. The resulting autoradiographs showed that there was depletion of this material in the root vicinity associated with plant uptake. As time of uptake progressed, the soil zone of depletion widened. To try to ensure that the depletion was not associated with a soil water gradient in the root area, the plants were watered daily. In another portion of this general study he applied excess (to plant uptake) Sr-90 to an agar root media, grew plants, and added Hoagland's solution as a source of nutrients. In this system the isotope initially collected around the roots by mass flow. After the roots were carefully pulled out of the agar the Sr-90 diffused away from the previous area of concentration. Therefore, it was evidenced that a root was capable of inducing a concentration gradient, either by reducing or by increasing the near-root ion concentration.

From then, diffusion became accepted as an important mechanism for plant nutrition, and the initial soil diffusion studies took on new importance as they helped to depict the basic process.

As yet, this discussion has been devoted to the way that soil diffusion became established rather than to the theoretical development of the process itself. As diffusion of ions in soil encompasses a broad field, there will be emphasis placed on the scope of the hypothesis and experimental work to be given herein.

Where ion or matter transport results from Brownian motion it is termed diffusion. Brownian motion is random, so if a concentration gradient initially exists the motion results in reducing the gradient which in turn results in a net transfer of matter to the region of initially lower concentration. To some, the actual net transfer should exist before the term diffusion may be implied. Even so, many soils experiments have invoked the initial condition that one zone of a soil contained labeled material added while the adjacent zone had an equal amount of nonlabeled material. The transfer of labeled and nonlabeled material into each other's zone has been studied and is termed diffusion, although there was no net transfer of the general ion.

Fick's first law describes the diffusion process for a steady state condition, and as amended for a soil anion is

$$J = -DI\Theta(dC/dx) \qquad (1)$$

where

J = the flux of substance crossing a soil unit area perpendicular to flow direction per time, (meq, grams . . .) (cm^{-2}) (sec^{-1})

Θ = the volumetric soil water content (dimensionless)

C = soil solution concentration (meg, grams . . .) (cm^{-3})

x = space variable (cm)

D = diffusion coefficient (cm^2) (sec^{-1})

I = impedence factor, due to soil particles interfering with aqueous diffusion (dimensionless)

There is some ambiguity regarding terms in the literature. Concentration has sometimes been used to denote the amount per volume of soil, in effect combining C and Θ. As just shown, C will always refer to solution content. By use of the denoted terms combined with D in equation (1), J will refer to a unit area of soil. "I" includes a combination of impedence factors which are tortuosity, reduced fluidity and electrostatic repulsion for anions (or, in the case of cations, negative adsorption). These three factors that provide the overall impedence term are (in theory) multiplied by each other to determine the impedence value. However, in practice it has been necessary to measure total impedence, then separate values of the contributing factors - usually by assuming values of at least one of the factors. The values of "I" (except possibly for H^+) will be less than 1 (which is the value of an aqueous solution alone where $\Theta = 1$). The values of D are literature values for dilute aqueous solutions. It may be noted that some publications have referred to a diffusion coefficient for soils (or D_e as an effective diffusion coefficient) which was a combination of (D)(I) or (D)(I)(Θ) in comparison to equation (1).

The use of a tortuosity factor, acknowledged from the oil industry literature by Porter et al (1960), incorporates the increased path length an ion must travel to reach its final destination with the reduced path area in which to travel. As can be shown by the model they propose, these two factors are related. Therefore, the tortuosity factor they describe is $(L/L_e)^2$. L stands for the effective distance an ion travels while L_e denotes the total distance it travels in its tortuous path. This factor is dependent on water content, solution fiscosity and ionic-clay interactions. Further, these other factors are not independent of each other. For example, reducing the water content increases the average solution viscosity (as the solution is more viscous near surfaces) and causes diffusion to take place in regions closer to clay particles where they become subject to electrical forces. Since an anion is repelled away from the clay charge, it does not experience as much influence from increased viscosity as a cation, but it does experience the effective pathway reduction to a greater extent. With chloride, which is not appreciably adsorbed, Porter et al (1960) found that the product of the tortuosity times reduced fluidity times electrostatic repulsion was linearly related to volumetric water content. The product term had values extrapolating to 0 when Θ was reduced to near 15 atmospheres. Rowell et al (1967) obtained very similar results to those of Porter et al and denoted the similarity in their writings by plotting both sets of data on one graph.

A functional relationship that was derived by Kemper and van Schaik (1966) is

$$DI\Theta = Dae^{b\Theta} \qquad (2)$$

where "a" and "b" are empirical constants with "a" being related to the surface area of the soil studied. Olsen and Kemper (1968) later concluded that, for the overall work done, there was reasonable agreement when "b" was equal to 10 and "a" ranged from 0.005 to 0.001 for sandy loam to clay soils.

When phosphorus diffusion was measured under several water contents, Mahtab et al (1971) found a fairly linear relationship between water content and impedence values as others had with chloride. However, Olsen et al (1965) and also Rowell et al (1967) found more curvature in the form of a hyperbolic function. Olsen et al attributed the difference between phosphate and chloride to adsorption of the phosphate. That is, as the solution phosphate is adsorbed at lowered water contents, its total solution concentration per volume of soil becomes less. In comparison, the total chloride concentration per volume remained the same.

Low (1962) has reported that water takes on "quasi-crystalline" properties at close proximities to clay surfaces. These reduced mobility effects were measured by Kemper et al (1964) and the fluidity found to be 0.05 (as compared to 1 for normal water) in the first layer of a Ca-clay and 0.03 on a Na-clay. The mobility increased rapidly by the third water layer but was still affected at 40Å from the clay.

For cations, Bear (1964) depicts that the distribution of ions from a clay surface follows the proposal of Stern in 1923 for a double layer. The distribution is relative to the ionic dimension of the ion, in addition to the following the earlier proposals of Gouy and Chapman, and Helmholtz. Adjacent to the clay a layer of cations (Stern layer) is concentrated and there they rarely exchange positions. Next to the Stern layer a less tightly held and concentrated layer exists where the cations are termed exchangeable. Away from this layer is the bulk solution. In comparison to the steady state equation given for anions (equation 1), Olsen and Kemper (1968) show that with cations there is a contribution from solution, and

$$J_{(\text{from solution})} = - (DI\Theta C/RT)\ d\bar{\mu}/dx \qquad (3)$$

where

R = the gas constant

T = absolute temperature

$d\bar{\mu}/dx$ = the driving force, where $\bar{\mu} = \mu_o + RT \ln a + zF\psi$, and a is activity, z is valance, F is Faraday, and ψ is the phase electric potential.

Other notation is the same as used for equation (1).

The soil suspension driving force, $d\bar{\mu}/dx$, has been controversial. While it has been argued that the gradient in the chemical potential (called the da/dx theory) depicts the driving force, Khasawneh (1971), in review, states that the more recent body of evidence supports the $d\bar{\mu}/dx$ (electrochemical potential) theory as argued by Frere and Axley (1964), Lagerwerff (1960) and Olsen (1968).

With cations, Rowell et al (1967) and Patel et al (1963) found nearly the same hyperbolic curve relating impedance factors to volumetric water content as was found by most workers with phosphorus.

The relative contribution to diffusion within the adsorbed phase has been considered to be minor for strontium and sodium by Rowell et al (1967) minor for sodium by Mott and Nye (1968) and minor for calcium by van Schaik et al (1966). These latter authors found that sodium was largely regulated by diffusion in the adsorbed phase on a Na-clay. Ellis et al (1969), from using equations they developed, concluded that Mott and Nye's (1968) findings coincided with their development. Conversely, Elgawhary et al (1972) and Bole and Barber (1971), with plant uptake studies with calcium and strontium, concluded that with diffusion of these ions, they were the portion balanced by negative clay charges. By using the expression developed by Ellis et al (1969), Phillips et al (1972) proposed that when only a small fraction of the soil cation exchange capacity is filled with an ion in question, it will tend to diffuse primarily in the adsorbed phase. Thus they calculated that copper and presumably manganese and zinc will diffuse in the adsorbed phase.

As transient conditions are more common in soils than steady state, equations for these will be given. Some simplification will be made to cope with problems found in less than ideal situations, as in soils, but no more than is usually found in the literature. For example, Low (1962) has discussed that both co-diffusion (also termed salt diffusion) and counter-diffusion are assumed to be operative in soil-plant systems. Co-diffusion is the process whereby, in order to maintain electrical neutrality, an anion and cation move in the same direction. For counter-diffusion, electrical neutrality is maintained by ions of like charge traveling in opposite directions. The general equation for transient condition diffusion (Fick's second law) can be derived by use of Fick's first law for an anion and the equation for continuity

$$\partial C/\partial t = DI(\partial^2 C/\partial x^2) \tag{4}$$

Another way of expressing this is by multiplying by Θ, and

$$\partial M/\partial t = D\Theta I(\partial^2 C/\partial x^2) \tag{5}$$

where M is the quantity diffusing per unit volume of soil. Gardner (1965) has given a useful analytical solution for equation (5) for planar diffusion in a semi-infinite system. They were derived by assuming that the initial concentration in the soil is uniform, but after time zero the boundary is maintained at a new concentration, or

$$C = C_o,\ t = 0,\ x \geq 0 \tag{6}$$

$$C = C_r,\ t > 0,\ x = 0 \tag{7}$$

where C_o is the original soil solution concentration, and C_r is the boundary (as root or other sink) concentration. Then, subject to these conditions

$$(C-C_r)/C_o-C_r) = \text{erf}\ [x/(2)(DIt)^{1/2}] \tag{8}$$

which depicts the solution concentration with varying t and x. The rate of diffusion into the sink is

$$DI(dC/dx)_{x=o} = (C_o-C_r)\ DI/(\pi DIt)^{1/2} \tag{9}$$

Integration to show the quantity of material diffused per unit area until time = t shows

$$M_t = 2(C_o - C_r)\ (DI\Theta t)^{1/2}/\Pi^{1/2} \qquad (10)$$

where M_t = the quantity per unit surface area of soil per time. Equation (10) has been used by Nye and co-workers (1966b) for diffusion of both cations and anions, and a version of it was used by Warnche and Barber (1972).

In these equations the diffusion coefficient, D, was taken to be constant. It is known to vary with concentration, but not appreciably until concentrations become larger than are normally found in soil solutions. For example, Kemper and van Schaik state that a constant diffusion coefficient "will be sufficiently accurate for most practical applications". If only two ions were involved in a diffusion process in soil (for co-diffusion or counter-diffusion) a weighting method to obtain a mutual diffusion coefficient could be used as shown by Low (1962). Although this method cannot be applied to more complex systems where the exact actions of the many ions are unknown, it does provide insight into the general nature of the diffusion process. The equation is:

$$D_{12} = D_1 D_2\ (z_1 C_1 + z_2 C_2)\ /\ (D_1 z_1 C_1 + D_2 z_2 C_2) \qquad (11)$$

when D_{12} is the mutual diffusion coefficient, C is the ion concentration, z is the valence of the ion, and the subscripts 1 and 2 refer to the two respective ions. From this equation it may be seen that the value of D_{12} is between D_1 and D_2, and that the ion present in low concentration will largely control D_{12}. Nye (1966a) has proposed that in diffusion to a zero sink, the appropriate average diffusion coefficient is the self-diffusion coefficient, such as would be obtained from measuring the rate that a labeled ion diffuses counter to an identical unlabeled ion. Further, he believed that ions present in small concentrations may be assumed to be moving independently with their own diffusion coefficients, being little affected by other macrocomponents in the system.

A method of determining the contribution from adsorbed ions to diffusive flux, where they enter into a simultaneous reversible reaction with the solution phase, was first proposed by Olsen et al (1962) in 1962. The solid plus solution phase contribution for this reaction comes from the differential equation

$$(\partial C/\partial t)\Theta + (\partial S/\partial t) = DI\Theta(\partial^2 C/\partial x^2) \qquad (12)$$

where S is the quantity of ion per unit volume of soil entering into the diffusion process. If the isotherm between adsorbed and solution phase is linear

$$S = R\Theta C + \text{constant} \qquad (13)$$

where R is the ratio of ions in the adsorbed phase to those in the solution phase, per unit volume of soil. A new equation may be written by combining equations (12) and (13)

$$\partial C/\partial t = [DI/(R+1)](\partial^2 C/\partial x^2) \qquad (14)$$

The (R+1) term depicts the slope of the isotherm for the ratio of the (adsorbed + solution phase) to the solution, only, phase. It is what

Olsen et al (1962) termed a "capacity factor". In heat flow equations, $D/(R+1)$ is analogous to thermal diffusivity. When including the capacity factor (R+1), equations (8) (9) and (10) become, respectively

$$C-C_r/C_o-C_r = \mathrm{erf}\ \{ [x(R+1)^{1/2}]/\ 2(DIt)^{1/2} \} \quad (15)$$

$$DI(dC/dx)_{x=o} = (C_o-C_r)\ DI/[(\pi DIt)/(R+1)]^{1/2} \quad (16)$$

$$M_t = 2(C_o-C_r)[DI\Theta t\ (R+1)]^{1/2}/\pi^{1/2} \quad (17)$$

It may be noted that, from the adsorbed pool, the contribution to the diffusion process is enhanced by the capacity factor over that of not having the adsorbed material - but only when relating C as the solution concentration as done here. In the literature of Nye and co-workers (1966b) and others who take the concentration term to equal the total diffusible concentration per unit volume of soil, they use terms that depict that the diffusion process is reduced by the adsorption of ions. Gardner (1972) has derived the equations of Nye et al in terms used herein and shown them to be identical, and varying only in how individuals prefer to work with them.

When the adsorption isotherm is not linear, as shown in equation (13), finite difference methods are necessary to solve the contribution of both sorbed and solution phases. This aspect, then, becomes an important consideration. Olsen et al (1962) found the amount of P that underwent isotopic dilution with P-32 in a 24-hour reaction was linear throughout the important range of concentration. Therefore, the capacity factor (slope of R+1) was a constant. As more fertilizer P was added the slope of (R+1) decreased taking the form of a Freundlich isotherm. Also, it was thought that the slope of the isotherm would be more variable for acid soils with their greater anion adsorption capacity. Nye (1966) has indicated that the appropriate measure of the capacity factor is a straight line passing from the point ($x=C_o$, y = total diffusible concentration), to the origin in the case that the isotherm displays some curvature. With boron, as with phosphorus, the isotherm has been found to be linear over low concentrations by Bigger and Fireman (1960), Hingston (1964), Okazaki and Chao (1968, and Sulaiman and Kay (1972), but following a Freundlich or Langmuir isotherm at higher concentrations. These authors have not agreed on adsorption and desorption characteristics. But this might be expected when considering that boron may, in addition to being sorbed or forming complexes, enter into the clay lattice or precipitate with sesquioxides, as was found by Sims and Bingham (1967, 1968).

With cations, Vaidyanathan et al (1968) found certain soils had fairly linear sorption isotherms for K. Brewster and Tinker (1970) found that most of the K isotherm was linear, but similar to Beckett's findings (1964), there were mineral sorption sites particular to K only which were operative at a very low K status. Thus, a larger ratio of K is sorbed at low concentrations as compared to the ratio found at intermediate or higher total concentrations. From Brewster and Tinker's experiment (1970) Na and Mg had linear isotherms. They state, though, that as Ca is the major soil ion, the aspect of increasing the Ca sorbed phase with increased solution phase concentration would not be possible, except with very limited solution changes. Zinc was found to have a linear isotherm by Elgawhary et al (1970a). With iron, O'Connor et al (1971) found that the slope of the isotherm increased with one month's time (from 1000 to 5000), and therefore instead of terming the slope a "capacity factor", stated that it should be used as a "correction factor". The increase in the slope was associated with gradual precipitation of added iron as amorphous iron oxides.

Nye (1966) pointed out that, to avoid hysteresis problems, the isotherms should be determined under the same conditions as diffusion is to occur, indicating that if diffusion to a sink were to be studied, a desorption isotherm would be preferred to an adsorption isotherm. The procedures used in desorbing soil materials have usually consisted of sequentially extracting portions of the ions and measuring them together with newly obtained equilibrium soil solution concentration. Conversely, Bar-Yosef et al (1972) pointed out that the hysteresis phenomena in the adsorption-desorption process with phosphorus arises during desorption from drastically reducing the P concentration. Because of this, there is dissolution of silica and an altering of the available P adsorption sites on the clay. Thus, with these opposing views and questionable understanding of hysteresis, it appears that conclusions at present would be premature.

As an overall consideration about the buffer capacity term, when it is obtained from an isotherm it is an approximation, varying in exactness of application among soils, and with ion type and concentration within a soil. Even with these drawbacks, however, this factor quantity has provided considerable needed resolution of quantitative diffusion process.

In regard to other factors contributing to diffusion regulation, Olsen and Kemper (1968) have stated "While the osmotic movement and electrical potential increased by salt gradients are intriguing, they change the salt diffusion coefficients only slightly ..." Therefore, these items will not be detailed here. Ion-pair formation is still another factor that deserves mention, but falls into this same category.

Ion exchange resins have been used in diffusion studies because of their ability to reduce a soil ion concentration at a soil-resin interface. Vaidyanathan and Nye (1966), used both cation and anion exchange resins in paper strips as sinks for planar diffusion studies and outline methods of determining accumulative flux. They did not compute a capacity factor, but obtained overall potentials for soils to contribute to diffusive flux. This technique was also used by Warncke and Barber (1972) in zinc-soil interaction studies with equal success. Vaidyanathan and Nye (1970), in later studies, rejected the use of an anion exchange resin paper for measuring P diffusion as they assumed that diffusion through the paper was rate limiting. Their next approach (1971) to measuring P diffusion was by evaluating impedence factors together with the capacity factor as had been proposed by Olsen et al (1962) previously.

In conclusion, much work has gone into determining how to measure soil diffusion and interpreting the basic process, both from soil and from plant-soil aspects. As is normally encountered in plant and soil research, systems have not been ideal and also much measurement has had to be done by indirect methods. As yet, application of diffusive mechanisms for determining soil fertility status and plant contribution have been relatively unutilized except in isolated instances.

Hypotheses

It was hypothesized that by measuring planar diffusive flux from a soil to an exchange resin sink the results could be used to depict the soil's fertility status, especially in regard to those nutrients that are transported to a plant root by this method. Specifically, those aspects that could be estimated by this method include the following:

1. The original (before reduction by sink uptake) soil solution concentration. Also, the concentration after time = t and distance = x from the adsorbing sink.
2. The soil adsorbed (and other state) ion concentration that contributed to diffusive flux by equilibria, calculated from the model for an instantaneous reversible reaction having a linear adsorption isotherm.
3. The estimation of the slope of a linear adsorption isotherm (buffer capacity) calculated to go to the origin from 1. and 2., above.
4. The impedence value for an indifferent ion (Cl) for any soil under consideration.
5. From these first four (above) quantities, the calculated quantities of a fertilizer that need to be added to a soil to have it provide a flux rate equal to plant needs.

It will be shown in the "Theoretical Considerations" section how the development of equations (15), (16) and (17) (shown in the literature review portion of the "Introduction" section) can be developed to determine these various aspects. While it may be noted that the integrated (over time) planar flux has been previously measured by Vaidyanathan and Nye (1966) and others, the separation of any of the components shown above has not been previously accomplished using diffusion theory.

EXPERIMENTAL METHODS AND MATERIALS

Theoretical Development

A major portion of the basic studies in soil diffusion have been to resolve how fundamental principals of diffusion apply to a soil system. Therefore, the literature review section contains the general established theory relating to this study. Proceeding from this general established theory, a development will be given to show how the components that contribute to diffusive movement (soil solution concentration, soil adsorbed concentration, capacity factor, etc.) can be separated to characterize a soil.

The quantity of soil ion flow by diffusion in a unidirectional system to a constant sink over a time period has been given previously

$$M_t = 2(C_o - C_r)\,[DI\theta t\,(R + 1)]^{1/2}/\pi^{1/2} \qquad (17)$$

In equation (17), the (R + 1) term is the slope of an adsorption isotherm, and is assumed to be linear. It describes the amount of change in total diffusible ion concentration (solution plus adsorbed phase) per amount of change in solution concentration when a condition is imposed to cause this change. Mathematically

$$(R + 1) = (\Delta C_o + \Delta C_s)/\Delta C_o \qquad (18)$$

where C_s is the sorbed (and/or other unspecified) phase. If a fertilizer or other material is added to a soil, and if the material remains in diffusible form, then this quantity becomes

$(\Delta C_o + \Delta C_s)$. The quantity of diffusive movement over a time period may be rewritten for an unfertilized soil and also for a fertilized soil using the terms in the right side of equation (18), and equation (17) becomes

$$M_{tu} \doteq 2(C_o - C_r)(DI\theta t)^{1/2}[(\Delta C_o + \Delta C_s)/\Delta C_o]^{1/2}/\pi^{1/2} \quad (19)$$

where M_{tu} represents the unfertilized condition. Where fertilizer has been added, the new solution concentration becomes $C_o + \Delta C_o$, and

$$M_{tf} = 2(C_o + \Delta C_o - C_r)(DI\theta t)^{1/2}[(\Delta C_o + \Delta C_s)/\Delta C_o]^{1/2}/\pi^{1/2} \quad (20)$$

using M_{tf} to represent the fertilized condition.

The term ΔC_o can be solved in terms of C_o by dividing equation (19) by equation (20)

$$M_{tu}/M_{tf} = (C_o - C_r)/(C_o + \Delta C_o - C_r) \quad (21)$$

Also, simplification may be made by having C_r go to 0 (as was found to be the case in experiments done) and

$$M_{tu}/M_{tf} = C_o/(C_o + \Delta C_o) \quad (22)$$

Perhaps it will add clarity, before solving for $(C_o + \Delta C_o)$ in terms of C_o, to introduce a factor "z". Let z be a quantity such that $z\,C_o = C_o + \Delta C_o$. Then equation (22) may be written as

$$M_{tu}/M_{tf} = C_o/(C_o + \Delta C_o) = 1/z \quad (23)$$

or

$$z = M_{tf}/M_{tu} \tag{24}$$

and reverting back to terms used before introducing z,

$$\Delta C_o = [(M_{tf}/M_{tu}) - 1]C_o \tag{25}$$

If the quantity of fertilizer added to a diffusion system is termed "K" , and which equals $\Delta C_o + \Delta C_s$ (where the total added may contribute to diffusion), and using terms just defined

$$M_{tu} = 2C_o(DI\theta t)^{1/2}(KM_{tu})^{1/2}/[C_o(M_{tf}-M_{tu})\pi]^{1/2} \tag{26}$$

By squaring both sides of equation (26) and solving

$$C_o = (M_{tu})(M_{tf}-M_{tu})(\pi)/4DI\theta tK \tag{27}$$

Also, from equations (25) and (27)

$$\Delta C_o = [(M_{tf}/M_{tu}) - 1](M_{tu})(M_{tf}-M_{tu})(\pi)/4DI\theta tK \tag{28}$$

or

$$\Delta C_o = (M_{tf}-M_{tu})^2(\pi)/4DI\theta tK \tag{29}$$

Following this development, (R + 1) may be easily denoted from realizing it is equal to $K/\Delta C_o$. Substituting the value of ΔC_o from equation (29) into this expression

$$(R + 1) = 4K^2DI\theta t/(M_{tf}-M_{tu})^2\pi \tag{30}$$

To solve for C_s, the same analogy will be used as is when determining labile soil ions

$$\Delta C_o/\Delta C_s = C_o/C_s \tag{31}$$

or, on rearranging

$$C_s = (C_o)(\Delta C_s)/\Delta C_o \tag{32}$$

and also

$$\Delta C_s = K - \Delta C_o \qquad (33)$$

and

$$C_s = (C_o)(K - \Delta C_o)/\Delta C_o \qquad (34)$$

The terms in the right hand side of equation (34) have been found previously so that

$$C_s = M_{tu}\,[(K)/(M_{tf} - M_{tu}) - (M_{tf} - M_{tu})(\pi)/4DI\theta tK] \qquad (35)$$

The use of the analogy in equation (31) depicts that as the sorbed phase of an ion approaches zero, the solution phase must also, and with a linear relationship. Therefore, (R + 1) from this relationship is merely $(C_o + C_s)/C_o$.

From these equations, the values in equation (17) may be solved, providing that total ions transferred to a sink from a fertilized and unfertilized soil are measured. In addition, volumetric water content (θ), and time must be measured. Diffusion coefficients from dilute aqueous solution experiments may be used. For Cl^-, K^+, and orthophosphate ions there has been repeated agreement in soils literature, with D being, respectively; 1.82, 1.98, and 0.5×10^{-5} cm^2/sec. The impedance value may be solved by adding an ion as chloride, which is not adsorbed by the clay and becomes ΔC_o. From equation (29)

$$I = (M_{tf} - M_{tu})^2 (\pi)/4D\theta tK^2 \qquad (36)$$

The term "labile" usually associated with the amount of soil ion exchanging with its isotope, has been used here to also indicate the total diffusible amount.

Soils Used and General Chemical and Physical Analysis

Twenty one soil samples were gathered from the United States, and represented a wide range of characteristics. They were dried for 3 days in a forced air drier at 60° C and stored for future plant uptake, chemical and physical analysis, and ion diffusion tests.

To determine their general characteristics, routine tests were done initially by usual routine methods as found in many textbooks. These included textural analysis by the hydrometer method, organic matter content by the Walkley-Black (without external heat) method, exchangeable Ca, Mg, K and Na (extracted with 1N NH_4OAc), cation exchange capacity, and available phosphorus by Olsen's $NaHCO_3$ test (with color development in ascorbic acid) (1965). Soil pH measurement was done by mixing 0.01 N $CaCl_2$ and soil in a 2:1 ratio, and placing the pH meter glass electrode in the soil suspension and the calomel electrode in the supernatant liquid. Also, a 1N NaOAc extract was made to determine exchangeable Ca and Mg on the calcareous soils, as evidenced by their pH value and also by the sum of Ca + Mg + K + Na from the NH_4OAc extract exceeding the cation exchange capacity. The 1N NaOAc extraction procedure was identical, except for extractant, to the 1N NH_4OAc extracting procedure.

The results of these determinations are given in Table 1.

Table 1 - Results of soil physical and chemical determinations on soils used in experiments.

Soil/Origin	Clay	pH	CEC	Exchangeable cations Ca	Mg	K	Na	P	OM
	%		meq/100g					ppm	%
Amsterdam si l - MT	26	7.5	26	16	3.0	1.5	T	20	2.1
Astoria c l - OR	33	4.1	56	0.2	0.5	0.4	0.3	9	11.2
Camas Creek si l - ID	12	5.8	18	9	1.4	0.4	0.1	15	2.1
Dayton si c l - OR	36	5.4	25	9	1.4	0.9	T	110	3.4
Door l - IL	23	5.1	18	4	2.4	0.2	T	14	3.2
Drummer si c l - IN	35	6.6	29	12	6.0	1.1	T	54	4.7
Frankfort-Bryce c - IN	45	7.2	35	14	7.2	1.0	T	102	3.7
Jory si l - OR	23	5.6	26	5	1.3	0.8	T	16	3.4
Lloyd c - AL	45	5.1	17	1.5	0.7	0.1	T	4	0.4
Minidoka s l - ID	7	7.5	7	5	1.6	1.0	T	13	1.3
Portneuf si l - ID	24	7.6	25	16	6.3	1.1	0.2	43	1.3
Portneuf subsoil si l - ID	16	7.7	18	14	5.2	0.7	0.3	17	0.9
Sagemoor s l - WA	12	7.7	13	13	2.2	0.6	0.3	11	0.6
Stanton's Crossing s l - ID	7	7.5	14	12	2.0	0.1	0.1	8	1.9
Tetonia si l - ID	20	7.6	21	15	2.5	1.6	0.1	11	1.4
Tracy s l - IL	18	4.1	12	0.8	0.2	0.1	T	24	2.4
Wahluke l - WA	9	7.4	12	8	2.0	0.3	0.2	34	0.7
Whitney l - CA	21	6.7	21	13	3.6	0.8	0.3	54	3.4
Williams l - MT	28	6.3	24	8	5.4	1.0	T	22	2.0
Willamette si c l - OR	30	4.6	28	5	2.0	0.3	T	7	2.8
Winchester l s - WA	4	7.5	8	4.2	1.9	0.7	0.1	3	0.3

To estimate labile P, the method initially proposed by Amer et al (1955) and which was also compared by Olsen (1970) was used. For this test 1 g of the three rates of the spiked soil that were used to estimate labile K were placed in a 125-ml Erlenmeyer flask. To this 1 g of "Amberlite 1RA-410" anion resin, which had been previously purified in a column regeneration process with 1N HCl, air dried and retained on a 32-mesh sieve, was added. The samples were then placed under partial vacuum to degas the resin, stoppered and placed on a hand shaker for 24 hours. After this shaking period, the resin-soil-water sample was poured into a 60-mesh sieve. To obtain complete transfer of soil and resin, the Erlenmeyer was partially refilled with additional distilled water and again poured into the sieve. The soil was washed through the sieve with a jet of distilled water, which left only the resin. To collect the resin for extraction, a piece of fine mesh nylon fabric was fastened very loosely over the top of a graduate cylinder with a rubber band so that the resin could be rinsed out of the sieve with distilled water into the hollow formed by the nylon fabric. After transfer, the nylon fabric holding the resin was tied into a bag. To prepare to extract, the bagged resin was positioned at the bottom of a 30-ml separatory funnel (which had the top previously cut off), and was held tightly in place by a teflon-coated stirring rod which in turn was attached to a stretched rubber band. Extraction of the resin was done with 50 ml of 1 N H_2SO_4 at the rate of 1 drop per second into a volumetric flask. Phosphorus content was determined by ammonium molybdate color development in ascorbic acid.

The soil solution concentration of K and P (associated with the labile concentration just described) was determined at the same spiking rates from extracts of near saturated paste on soil samples undergoing diffusion tests. The method of preparing the pastes is included in the section describing diffusion tests. Concentration of K in the extracts was determined with a flame photometer. Phosphorus was determined on the extracts by ammonium molybdate color development in ascorbic acid where there was sufficient concentration for this test. An extraction of ammonium phosphomolybdate into isobutyl alcohol was made on extracts having insufficient concentration for the ascorbic acid method.

Chemical Determination of Solution and Sorbed Concentration and Capacity Factors for Phosphorus and Potassium

The dried soil samples were initially moistened with water to have 15 percent water by weight. They were then stored in plastic lined containers at four degrees centigrade for six weeks. To determine if water loss had occurred after the refrigeration period, the samples had water content determined and allowed for spiking with fertilizer to be done on a dry weight basis. A neutral solution containing 4.32 g KCl, 1.45 g KH_2PO_4 and 2.89 g $K_2HPO_4 \cdot 3H_2O$ per liter was added at rates of 0, 10, and 20 ml per 100 g soil (which had previously passed through a 100 mesh sieve). The soil water content was then increased to produce a saturated paste and the soil was mixed and air dried a total of four times during a two-day period. To estimate labile K, the method of Graham and Kampbell (1968) was used, where 1.0 g of soil and 24 ml of 0.01 M $CaCl_2$ were added to a centrifuge tube. The mixture was stoppered and placed on a shaker having 120 excursions per minute for one-half hour. Then the sample was centrifuged and the supernatant liquid collected in a 250 ml plastic bottle. Seven more portions of $CaCl_2$ were sequentially added, shaken and centrifuged as before and the resulting extract added to the plastic bottle. The collected volume was brought to 200 ml by adding additional $CaCl_2$ solution. Potassium content of the extract was determined by flame spectroscopy.

Determination of Solution and Sorbed Concentration, Buffer Capacity And Impedance Values by Diffusion

For these determinations, soil was used from the same bulk containers having the soil water and refrigeration pretreatment as for the chemical determination of phosphorus, potassium and capacity factors. Also, the same spiking solution and rate was applied to a 400 g (dry weight basis) sample. These samples were then mixed with distilled water to produce a paste that was slightly less wet than a saturated paste. (The reason for this deviation from a normal saturated paste was to ensure that the solid portion of the samples would not shrink away from the resin sink during the diffusion period, which would have produced poor soil-resin sink contact.) The wetted soil was then placed in a sealed plastic bag, the bag was placed in a round capped jar, and the jar placed on a slowly revolving rock tumbler for 24 hours. In this manner the bag rolled in the jar and the soil was mixed with no separation of liquid from solid phase, which had been a problem with other mixing methods attempted. After this mixing a portion of the soil solution was extracted under suction in a Buchner funnel and the extracts saved for determining soil solution concentration -- as mentioned in the section on "Chemical Determination of Solution and Sorbed Concentration and Capacity Factors for Phosphorus and Potassium". The other portion of soil was used to fill the diffusion cell, shown in Figure 1. In addition to measuring the quantity of water added to the soil for the diffusion

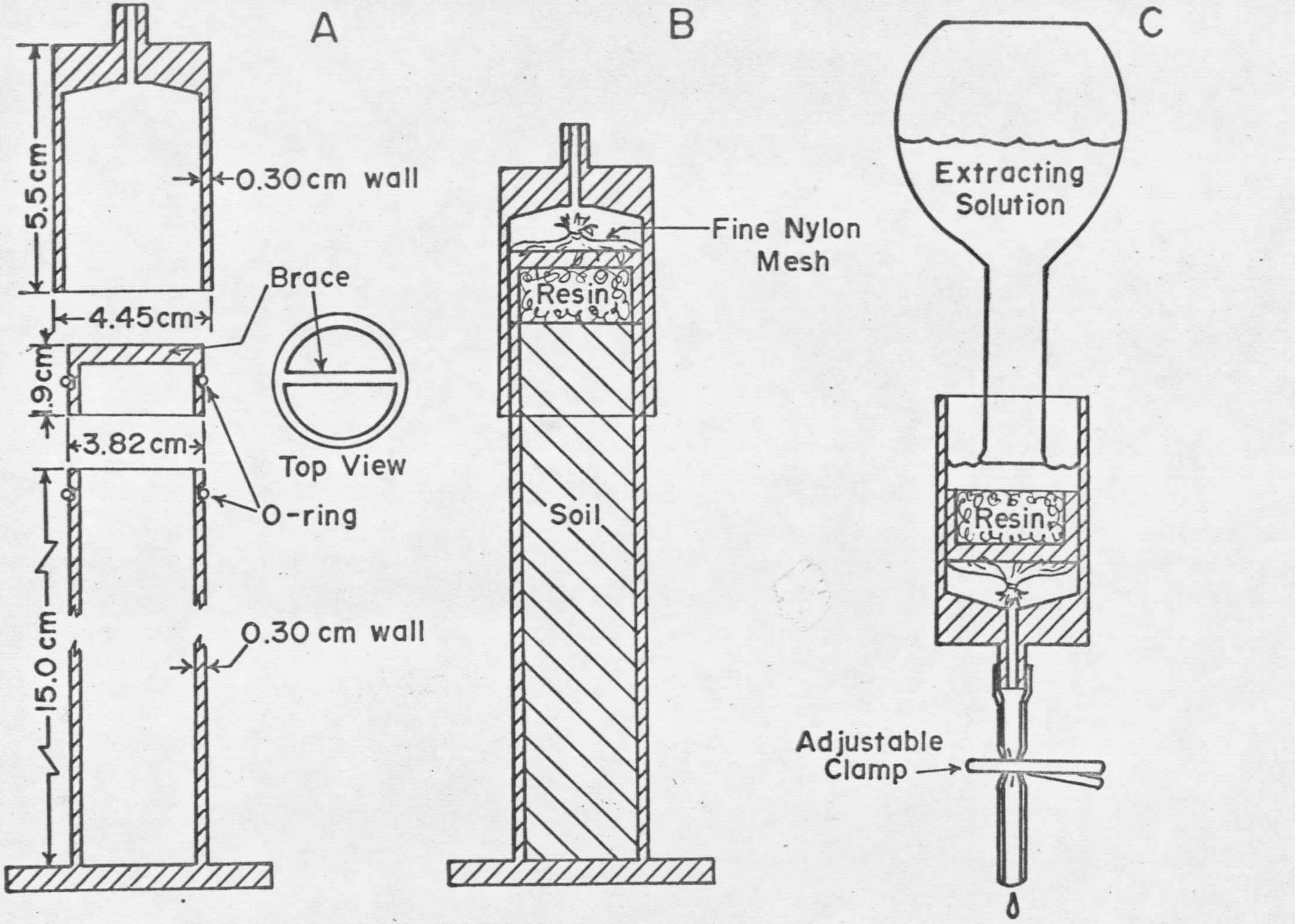

Figure 1. Diffusion cell showing: A-Dimensions (model shown could have soil column height reduced to one-half); B-Cell in operation; C-Method of extracting resin. A wooden match can be inserted through cap holder to push out resin after extraction.

test, the soil filled cell (of known volume and tare weight) was weighed. From this, P_v (percent by volume) was calculated from estimating that the specific gravity of the mineral portion was 2.65 and

$$P_v' = [\text{ml soil} - (\text{ml soil} - \text{g wet soil})/1.65](\text{ml soil}/100) \quad (37)$$

Using this same information to calculate P_w (percent by weight)

$$P_w = 100\,[2.65\,(\text{ml soil} - \text{wet soil})]/2.65\,(\text{g wet soil} - \text{ml soil}) \quad (38)$$

and bulk density was computed from

$$BD = P_v/P_w \quad (39)$$

Two replications with the three spiking rates for each soil were done. When filling the cells, a vibrating hair clipper was touched to the side of the cell which facilitated getting the soil packed without air bubbles. The exposed soil at the top of the cell was struck off with a spatula to produce a smooth glistening surface, and the resin sink (degassed and previously stored in water) was placed in contact and was capped as shown in part B of Figure 1. After diffusion of ions was allowed to take place for 24 hours, the cap with resin sink was removed, and the soil adhering to the nylon mesh was rinsed away with a jet of distilled water. Extraction was done with 100 ml of 1 $\underline{N}$ H_2SO_4 as shown in part C of Figure 1.

The resin used in the sink was a neutral mixture of Amberlite 1R-120 H (medium porosity), a strongly acidic resin and Amberlite 1RA-410 OH (medium porosity), a strongly basic resin. Before use, the resins were sized. The 1R-120 H resin was purified with 1 $\underline{N}$ H_2SO_4 while the basic 1R-410 resin was converted from the Cl^- to OH^- type by

1 N NaOH in standard resin column technique. To determine the proportion of each resin to add to the mixture, enough of each were added to produce a neutral pH when a sample was placed in a ten percent NaCl solution.

Potassium content of the extract was determined by flame emission, phosphorus by ammonium molybdate color development in ascorbic acid, and chlorine by a potentiometric method. This method involved titrating a standard 0.002 N KCl solution in 1 N H_2SO_4 (resin extraction solution) with 0.005 N $AgNO_3$ and determining the relative millivolt reading (set at zero before titrating) with each increment addition of the $AgNO_3$. A Ag reference and Ag-Ag-Cl electrode were used. The inflection point of the resulting graph agreed with the calculated end point and the unknowns were titrated to this millivolt end point with the $AgNO_3$ solution.

Determination of Plant Uptake from Soils

The Neubauer seedling method as described by Vandecaveye (1948) was followed closely, using three replications of each soil and sand checks. Barley (Hordeum distichon var Piroline) was grown for 17 days in a growth chamber with full light (500-600 microeinsteins/m^2/sec within the 400-700 nm wavelength range) for 16 hours at 24°C and with an eight-hour nighttime of 18° C. Then the entire plant was harvested, weighed and ground in a Udy cyclone mill. The TCA extraction procedure for phosphorus and potassium, as outlined by Leggett and Westermann (1973), was used. Potassium content of the extract was determined by flame photometer, while phosphorus was determined by ammonium molybdate color development in ascorbic acid.

Also, the short term method of DeMent, Stanford and Bradford (1959) was used with 40 barley seedlings grown. Two replications of "minus K" and also two replications of "minus P" treatments were grown per soil and also three sand checks. The roots and tops were ground, extracted, and K and P content measured in the same method as the Neubauer tests.

RESULTS AND INTERPRETATIONS

Impedance Values from Chloride Diffusion

The quantity of Cl that diffused to the resin, using the cell shown in Figure 1, was measured. Impedance values (which denote the relative quantity of diffusive flow in soil solution as compared to an aqueous solution of similar concentration) were calculated from equation (36) to average 0.28 for the various soils used. The standard deviation was 0.11, and the range was from 0.10 to 0.46. These values found were in general agreement with those that Porter et al (1960) obtained from Cl diffusion.

Precision of this measurement was such that the average deviation of a single soil sample value from the mean of replicates (for the same soil) was 3.8 percent. From comparing the impedance values of the various soils to their bulk density (within the diffusion cell), texture, and organic matter content, there were no apparent relationships. The soil with the lowest impedance value (0.10) was Astoria clay loam. It was an extremely "fluffy" soil and had a bulk density of only 0.76 while undergoing diffusion.

To compute the theoretical Cl distribution within a soil undergoing diffusion, equation (8) may be used. For illustrative purposes, the results are shown in Figure 2 for the Dayton soil after 24 hours. This soil had an average impedance value. As may be noted from Figure 2, diffusion reduced the initial Cl concentration (C_o) for a 2-cm soil distance from the resin sink during the period. The average quantity of Cl adsorbed in 24 hours by the resin sink was 4.3 percent of the

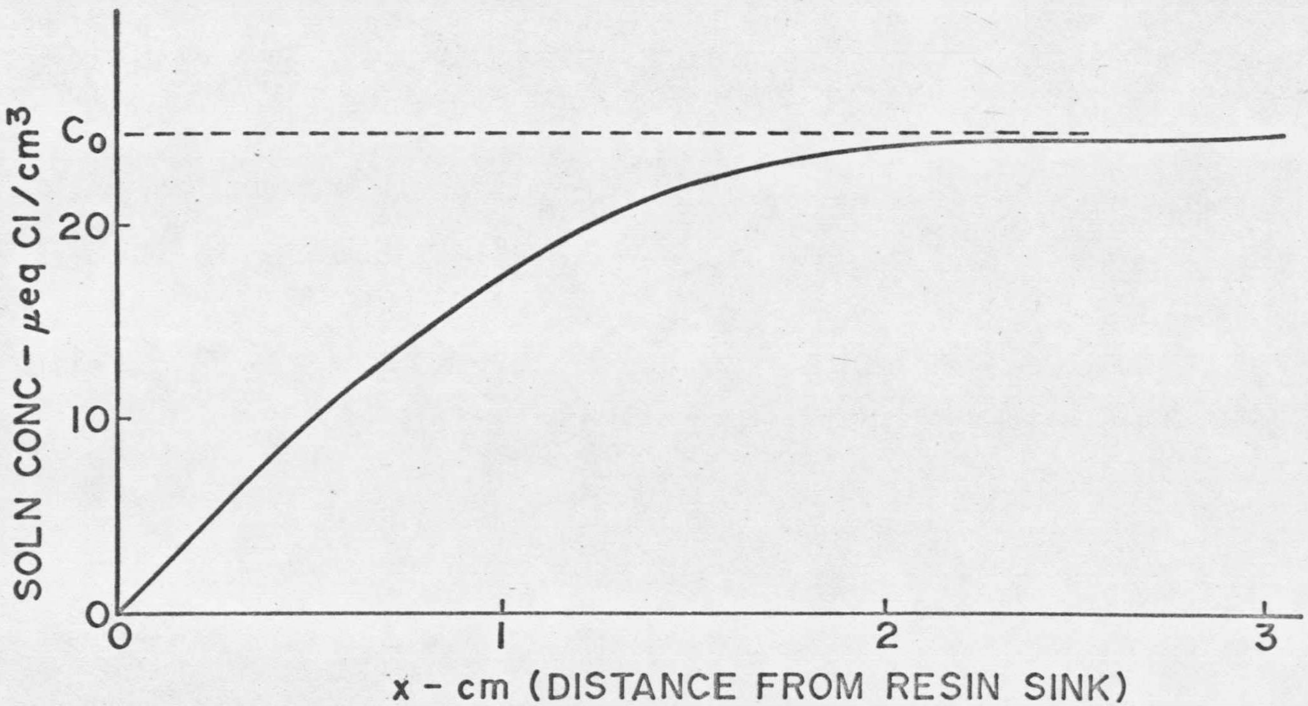

Figure 2. Computed solution concentration of chloride as related to distance from sink, after diffusing one day. A zero sink is assumed here. C_o was calculated from the Cl spiking done.

amount added to the soil in the spiking solution. It may also be visually noted that the area of reduced concentration in Figure 2, as compared to the total area for a 15-cm high cell, agrees with the 4.3 percent of Cl adsorbed.

Diffusion and Chemically Determined Soil Potassium

The repeated 0.01 M $CaCl_2$ extraction of soil K, as proposed by Graham and Kampbell (1968) was used as an estimate of labile K. It had been shown by the authors to very closely predict K-42 isotope measured labile K. From comparing the results of the $CaCl_2$ extract to the 1N NH_4OAc extract for exchangeable K (Table 1), it was noted that the $CaCl_2$ extract provided somewhat larger values. These averaged 0.84 meq K/100g from the $CaCl_2$ extract and 0.71 meq K/100g soil from the NH_4OAc extract. Similar differences were reported by Graham and Kampbell (1968), and thus the use of their procedure seemed justified. The results of this test are shown in Table 2, and may be compared to diffusion-based estimates of labile K. The diffusion data depicting labile K were obtained from measuring flux of K and Cl to the resin sink during a measured time together with the values needed to solve equations (27) and (35) for C_o and C_s, respectively - as mentioned in the "Methods and Materials" section.

Although three rates of spiking (0, 10, and 20 mls spiking solution per 100 g soil) were used, only the results from the 0 and 10 ml rate were used for inclusion in Table 2. Also, values of M_{tu} and M_{tf} these spiking rates are included with other data in Table 3. It was

Table 2 - Comparisons between chemical determinations and diffusion determinations of labile K, ($C_s + C_o$), and solution K, (C_o).

Soil	Chemical Methods		Diffusion Methods	
	Labile K *	C_o †	Labile K ‡	C_o ‡
	$\mu eq/cm^3$	$\mu eq/cm^3$	$\mu eq/cm^3$	$\mu eq/cm^3$
Amsterdam	17.5	0.41	23.7	0.33
Astoria	1.4	.06	4.8	.03
Camas Creek	8.5	.12	8.7	.14
Dayton	7.8	.47	12.4	.67
Door	1.3	.10	4.8	.13
Drummer	10.2	.54	12.0	.56
Frankfort-Bryce	13.1	.46	20.4	.46
Jory	10.2	.34	7.6	.63
Lloyd	7.4	.11	1.8	.14
Minidoka	25.5	1.82	12.3	3.60
Portneuf	16.9	.28	12.7	.17
Portneuf subsoil	10.1	.19	11.8	.25
Sagemoor	12.9	.17	7.4	.23
Stanton's Crossing	5.7	.04	12.6	.07
Tetonia	22.8	.39	24.1	.43
Tracy	3.8	.54	2.0	.36
Wahluke	5.7	.12	5.8	.05
Whitney	15.2	.76	15.0	.75
Williams	18.6	.34	14.4	.33
Willamette	2.6	.06	4.5	.05
Winchester	21.8	.33	11.6	.41

* From Graham - Kampbell method

† From soil saturation extract

‡ Computed after measuring K flux to resin sink.

thought that the capacity factor (R+1) might be reduced at higher spiking rates because, with a limited quantity of exchange sites on the clays, the new equilibrium between sorbed and solution phase would tend to maintain a greater share of K in solution. From recomputing from the higher together with the zero spiking rate (as two rates are needed for one determination), it was found that the new average C_s values were reduced to 83 percent of the old values. Likewise, there was an identical increase in the new average C_o values (as mathematically would be expected). Figure 3 illustrates the C_s values, as determined from the zero plus the 10 ml spiking rate versus those determined from the zero plus the 20 ml spiking rate. Beckett (1964) has established that (R+1) values decrease with higher concentrations of K added, and so the result here might be expected.

The variation about the treatment mean for K determinations of the resin sink extract (M_{tu}, M_{tf}) averaged only 2.9 percent. Thus the procedure appeared to be sufficiently simple and without inherent sources of experimental error for acceptable precision when used to determine K diffusion. The similarity of values shown in Table 2 obtained from chemical extraction of soil itself versus diffusion uptake was an exciting surprise, in spite of the original hypothesis suggesting that a diffusion mechanism could be used to measure solution and adsorbed ion concentration (C_o and C_s).

The use of equation (30) may be arranged so that

$$K = (M_{tf} - M_{tu})\,\pi^{1/2} / (R+1)^{1/2} / (4DI\theta t)^{1/2} \qquad (40)$$

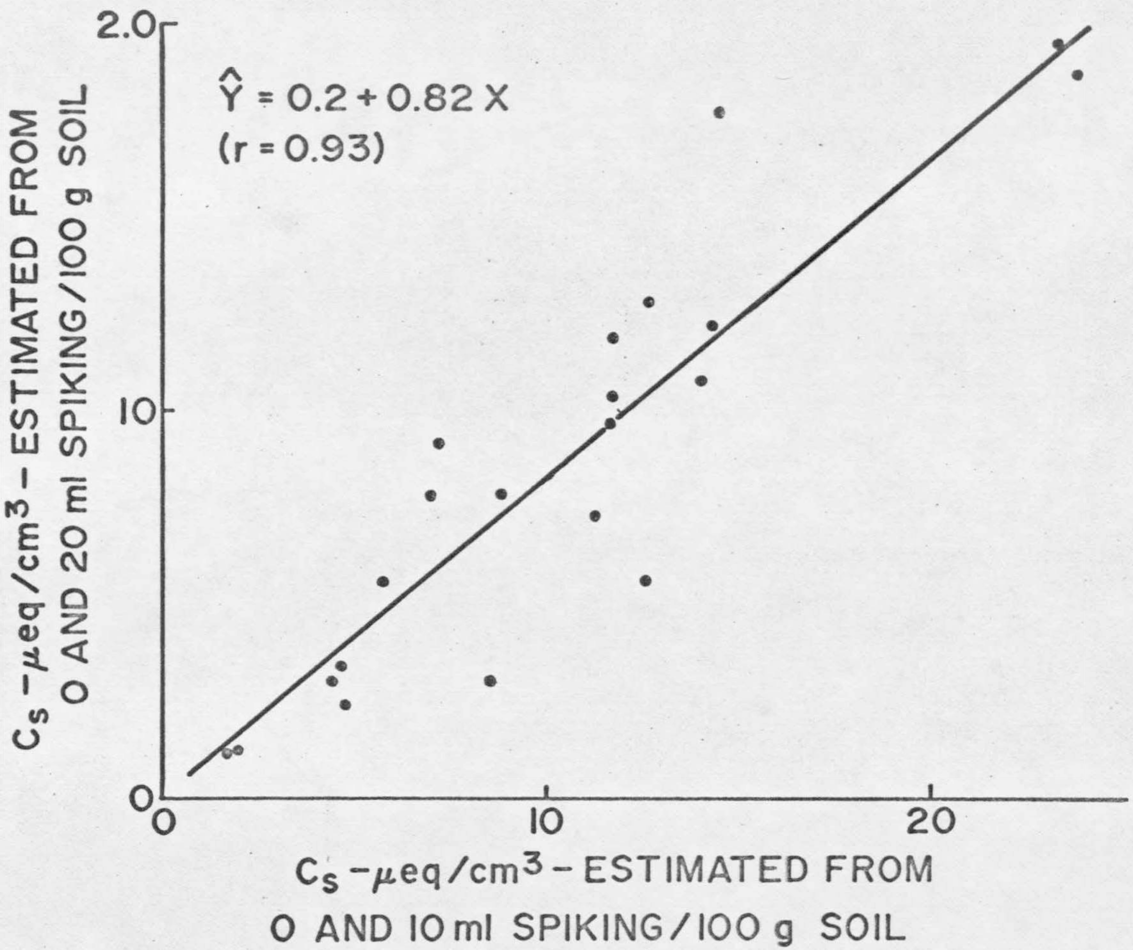

Figure 3. Adsorbed potassium concentration (C_s) for soils. Comparison is made between two spiking rates to calculate C_s.

and K predicts the quantity of spiking needed to increase the accumulative flux of a nonspiked soil (M_{tu}) to a new value (M_{tf}). In order to maintain notation, K_k will denote spiking with potassium and K_p will denote phosphorus spiking. In the case where fertilizer recommendations are needed K_k would equal the quantity needed. A preliminary check was made to determine the validity of the use of the diffusion experiments to determine needed K_k values. This involved computing K_k needed to obtain the M_{tf} found from the low spiking rate (10 ml spiking solution added per 100 g soil), or where K_k was already known. To do this, the values of (R+1) and I were used from the results of the diffusion cells having the high spiking rate together with the nonspiked soil. These results are shown in Table 3. In this Table, the average computed K was 90 percent of actual K used to obtain M_{tf}. It is recognized that these values were obtained entirely from the diffusion experiments. Therefore, while it does not supply proof of the utility of the method, it does make a comparison from the data that could have disproven its utility. The relative efficiency of K_k toward increasing flux can be compared for various soils by use of this method, which varies largely from the portion of K_k going into solution versus being adsorbed.

Plant Potassium Uptake Compared to Chemical and Diffusion Tests

The results from the DeMent-Stanford short-term test (1959) were somewhat different than the Neubauer test. Several simple linear correlations were made between plant uptake quantities by these two

Table 3 - Computed quantities of K_k spiking needed to obtain M_{tf} (accumulative flux per day) versus quantity of K_k actually supplied to obtain M_{tf}.

Soil	M_{tf}*	M_{tu}*	Computed K_k†	Actual K_k Supplied
	$\mu eq/cm^2/day$		$\mu eq/cm^3$	
Amsterdam	2.88	1.93	11.6	9.7
Astoria	0.66	0.27	7.1	4.6
Camas Creek	1.84	0.75	12.8	6.2
Dayton	3.21	1.68	11.3	10.0
Door	2.06	0.54	13.3	10.0
Drummer	3.68	2.05	9.6	12.9
Frankfort-Bryce	2.36	1.55	10.6	9.4
Jory	2.03	0.81	11.6	13.6
Lloyd	1.54	0.19	13.0	10.9
Minidoka	7.43	3.48	13.9	14.0
Portneuf	1.88	0.96	12.2	12.4
Portneuf subsoil	2.37	1.14	12.9	10.6
Sagemoor	2.35	0.80	14.5	18.6
Stanton's Crossing	0.96	0.45	14.1	6.5
Tetonia	3.21	2.08	13.0	10.4
Tracy	2.48	0.33	13.0	13.0
Wahluke	1.05	0.33	12.8	12.6
Whitney	3.70	2.07	11.8	10.2
Williams	2.12	1.11	13.1	13.4
Willamette	1.01	0.28	12.0	13.2
Winchester	2.29	1.00	15.0	10.1

* Measured values from 0 and 10 ml spiking rate/100 g soil.

† Value computed from results of 0 and 20 ml spiking rate/100 g soil.

methods versus chemical and diffusion tests. The squared correlation coefficient values (r^2) are given in Table 4. In the DeMent-Stanford method, plants are first partially grown in a sand-nutrient solution lacking K. Then the K-depleted plants are transferred so their roots grow in soil for only 6 days. In comparison, the Neubauer method allows seedling plants to grow in limited soil for 18 days and completely exhaust the K supply. Therefore, the DeMent-Stanford method measures an immediately available supply while the Neubauer method tends to combine this with the reserve amounts. As seen, the Neubauer method values and the soil exchangeable K content were fairly well correlated ($r^2 = .81$). The greater soil extraction done by Graham-Kampbell's method, as compared to exchangeable K, resulted in much reduced values ($r^2 = .39$). Correlation between the diffusion method and Neubauer's values ($r^2 = .54$) were intermediate to the correlations just described. By theory, the diffusion method should reflect ion movement from an infinite source. In contrast, the barley plants in the Neubauer pots are expected to almost completely exploit the available K source. Thus, the poor correlation between the diffusion method and Neubauer's method might be anticipated.

Results from the diffusion method had better correlation with the DeMent-Stanford cropping experiment ($r^2 = .88$) than any of the chemical evaluation made. Thus the diffusion method appeared to be valuable for depicting short-term uptake by plants.

By diffusion theory, ion diffusion to a sink from solution should

Table 4 - Results of simple linear correlation relating plant uptake of potassium to chemical and diffusion tests.

Independent variable	Dependent variable	$r^2 \times 100$
Exchangeable K	Neubauer total K uptake	81
Graham-Kampbell "labile K"	" " "	39
Diffusion M_{tu}	" " "	54
Exchangeable K	DeMent-Stanford plant K (%)	62
Graham-Kampbell "labile K"	" " "	41
Diffusion M_{tu}	" " "	88
Soil solution extract K	" " "	54
Soil solution extract K X (capacity factor)$^{1/2}$ *	" " "	63
Soil solution extract K X (capacity factor)$^{1/2}$ †	" " "	43

* Capacity factor computed as: Graham-Kampbell "labile K"/soil solution extract K

† Capacity factor computed as: (exchangeable K + soil solution extract K)/soil solution extract K

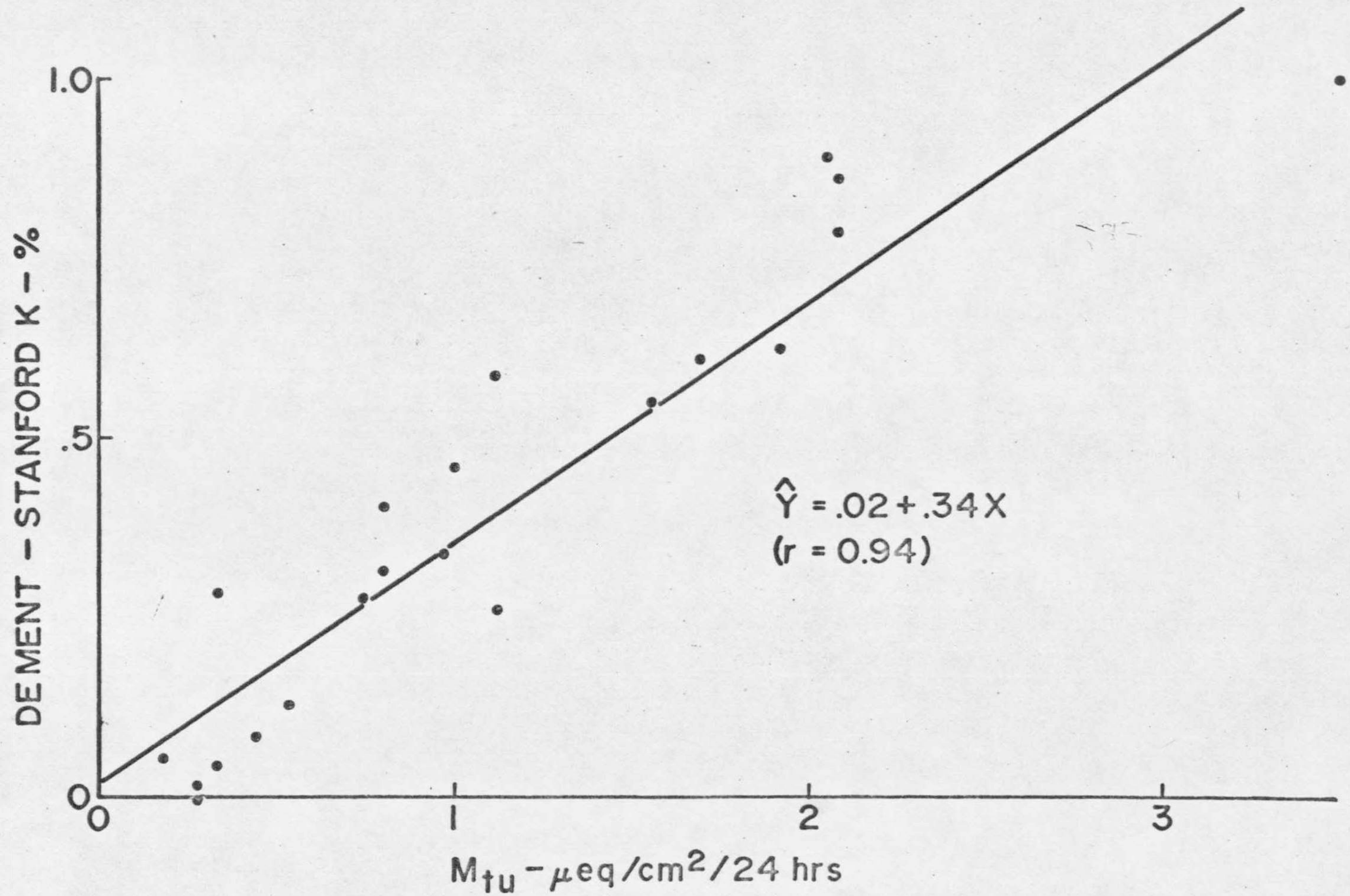

Figure 4. Relationship between plant potassium content and one-day accumulative diffusive flux.

be enhanced by the square root of the capacity factor. Therefore, capacity factors were estimated from chemical data, multiplied by the solution concentration, and the resulting product values correlated with DeMent-Stanford values. The resulting correlation coefficients (Table 4) were about the same as the correlation coefficient obtained by comparing solution concentration alone to the DeMent-Stanford results. Therefore, no benefit was found by utilizing this concept when the capacity factor was taken from the chemical methods outlined at the bottom of Table 4.

The reduction in solution K content next to a new root in a soil can be determined from equation (15). It was found that most of the soils would have the solution concentration reduced to a degree to about 0.4 cm at the end of a day and about double this in three days. In this calculation it was assumed that the plant root geometry was that of an infinite cylinder. Equation (15) is the first term of a series solution for a cylinder, and thus an approximation. To know the percent of C_o reduced, C_r would also need to be known -- the figure of 0.4 cm denotes the effective soil solution volume about the root in regard to potassium.

Diffusion and Chemically Determined Soil Phosphorus

Results of available phosphorus determinations by Olsen's $NaHCO_3$ method were given in Table 1. These data point to the large variation in the soil's P. Extreme values were 3 and 110 ppm P. The test of Amer et al (1955) with anion exchange resin to estimate labile P was noted to be related to Olsen's test (r = 0.97, when eliminating one obviously bad point) where the resin extracted about two times as much soil phosphorus as $NaHCO_3$. Soil solution extracts of unspiked Astoria, Door, Lloyd and Stanton's Crossing soils could not be determined with suitable reliability as they contained less than .02 ppm P, as did Lloyd even at the low spiking rate. Other soils had solution extracts containing as much as 2.8 ppm P.

By having the estimate of labile P, which has been denoted as $(C_s + C_o)$, and by knowing the solution concentration, (C_o), further estimates of the capacity factor, (R+1), were computed. In the first computation (R+1) was let equal $(C_o + C_s)/C_o$ - which was also used as a first approximation in the diffusion experiment with P.

Five soils in the diffusion experiment did not show definite increased (or sometimes even positive) diffusive flux from increased rates of P spiking. The average variation from the treatment mean value averaged 8.6 percent for all soils. Because of this variation and erratic diffusive response for the five soils in particular, their values of C_o, C_r and (R+1) are not included in the diffusion data. For the other soils, comparison are shown in Table 5. The values in this table were taken from the non-spiked soils and the low spiking rate. Using these, the r^2 value relating chemically determined C_o to diffusion C_o was 0.66. The r^2 values relating chemically determined $(C_s + C_o)$ and (R+1) to diffusion methds were 0.33 and 0.25, respectively.

Other methods of approximating (R+1) from diffusion were tried, but correlations were not as good as those just shown.

Table 5 - Comparisons between chemical determinations and diffusion determinations of labile P, (C_s+C_o), solution P, (C_o), and (R+1).

Soil	Chemical methods			Diffusion methods		
	Labile P *	C_o †	(R+1)	Labile P ‡	C_o ‡	(R+1) ‡
	—— $\mu eq/cm^3$ ——			—— $\mu eq/cm^3$ ——		
Amsterdam	39	.06	650	218	2.6	84
Camas Creek	62	.10	620	478	.38	13
Door	67	.03	2140	389	.15	2590
Drummer	134	.16	830	415	1.24	330
Frankfort-Bryce	219	.30	730	528	2.2	240
Jory	36	.06	620	117	.13	900
Minidoka	61	.27	230	54	7.6	7
Portneuf subsoil	39	.21	190	98	1.4	70
Sagemoor	39	.13	308	125	1.74	72
Stanton's Crossing	20	.04	460	316	.10	3160
Tracy	62	.08	760	203	.04	5120
Wahluke	68	.40	170	62	.96	65
Whitney	150	1.39	110	223	10.4	21
Williams	58	.20	280	273	1.58	170
Winchester	60	.12	510	57	2.8	20

* From method of Amer et al (1955)

† From saturation extract

‡ Computed after measuring P flux to resin sink

A reason believed partly responsible for the deviation in diffusion results from chemical results (if assuming the chemical determinations to be more correct) was the lack of linearity in the adsorption isotherms. From chemical data the calculated slopes for solution concentrations between: (1) 0 to C_o, (2) C_o to $C_{\text{low spiking rate}}$, and (3) $C_{\text{low spiking rate}}$ to $C_{\text{high spiking rate}}$ are shown in Table 6. The method of computing (1) was the same as was used in Table 5. For computing (2) and (3), $(\Delta C_{\text{sorbed}} + \Delta C_{\text{solution}})/\Delta C_{\text{solution}}$ figures were used. It is readily apparent that Freundlich-like adsorption isotherms are being adhered to. This type of isotherm has been associated with acid soils by Olsen and Kemper (1968). Fox and Kamprath (1970), from acid soils, have plotted the solution concentration on a log scale versus the adsorbed concentration on a linear scale and obtained straight lines. The constant values Olsen and Watanabe (1970) found were from calcareous soils. Also, adding too much phosphorus spiking solution could be expected to make the isotherm flatten in that area of the curve. However, if fertilizer application rate figures are to be determined from diffusion data, it seems logical that the diffusion experiments should be done at, at least, these rates. The problem of correctly solving C_o, C_s, and (R+1) values, where curvature exists, could be resolved if there were analytical solutions -- or even approximations. Without these, finite difference methods need to be used in conjunction with a computer.

Table 6 - Slope of phosphorus adsorption isotherm from chemical determinations as depicted in text.

Soil	Slope (R+1) Between Solution Concentrations		
	O to C_o	C_o to $C_{\text{low spiking}}$	$C_{\text{low spiking}}$ to $C_{\text{high spiking}}$
Amsterdam	560	23	- 470
Camas Creek	620	168	18
Door	2140	520	194
Drummer	830	188	199
Frankfort-Bryce	730	22	18
Minidoka	230	11	37
Portneuf subsoil	190	302	47
Sagemoor	308	60	142
Stanton's Crossing	460	942	75
Tracy	760	547	--
Wahluke	170	16	--
Whitney	110	14	2.7
Williams	200	35	29
Winchester	510	25	--