



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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Abstract:

A mathematical derivation from diffusion theory was applied to soil diffusive flow to an exchange resin sink. The measured flux was used to estimate some factors influencing soil fertility. These included initial (before diffusive flow) solution phosphorus and potassium concentration, adsorbed concentration, buffer capacity, soil impedance values, soil solution concentration changes with time of diffusion, and quantity of fertilizer needed to bring about predetermined flux rates. At least two diffusion measurements were needed for each soil. One was needed from an unspiked portion (no fertilizer or chloride added) and one from a spiked portion.

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, especially for potassium.

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ABSTRACT

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INTRODUCTION

Literature Review

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

$$J = -D\theta(dC/dx) \quad (1)$$

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 = impedance 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 impedance 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 impedance term are (in theory) multiplied by each other to determine the impedance value. However, in practice it has been necessary to measure total impedance, 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 $(D)(I)(\theta)$ 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 viscosity 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

$$D_{I\theta} = D_{ae} b^{\theta} \quad (2)$$

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 impedance 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 40\AA 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,

