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MOVEMENT OF SOLUTES IN SOILS

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MOVEMENT OF SOLUTES IN SOILS

A summary of lectures given by Donald R. Nielsen

Early Laboratory Studies - When a fluid containing a tracer in solution is displaced from a porous medium by the same fluid without a tracer, this miscible displacement results in a tracer concentration distribution which depends upon microscopic flow velocities, tracer diffusion rates, and other chemical and physical processes. Studies of miscible displacement provide not only a means of determining microscopic flow velocities in soils, but should give a physical explanation of phenomena occurring in leaching of soils, ion exchange and adsorption chromatography, movement of fertilizers, and similar processes.

The flow of water through soil is often times considered as bulk movement which can be described by Darcy's law. This description becomes inadequate for the purpose of defining movement of transient dissolved solutes and their chemical and physical processes. It is of interest to measure the ionic or molecular tracer concentration distribution moving through a soil-water system so that the mechanisms of both tracer and water movement be more clearly understood. The distance a tracer will travel through bulk soil is determined by the tortuosity of the total path length it follows. Owing to the magnitudes of convection, diffusion and other processes which occur in different pore sequences, the paths of each ion will not be the same and the resulting tracer distribution will clearly give a good deal of information about the behavior of the water flowing through various soils.

An apparatus was specially designed such that stationary flow conditions and water content of the media could be maintained when tracer-free water was replaced by water containing a dissolved tracer. It was desired that no mixing of the two waters occurred initially at the boundary between them. At the same time the contribution of flow associated with the the boundary between soil and soil container had to be eliminated. Also, samples of effluent to be analyzed for tracer concentrations had to be collected without disturbing stationary flow conditions. A cross-sectional sketch of the apparatus is given in Fig. 1. Samples of air-dry soil screened through a 2-mm sieve were uniformly packed in the 30-cm long lucite tubes. The water content and the flux density were controlled using hanging water columns and negative air pressure imposed on fritted glass bead porous plates shown on each end of the horizontal column. The use of fritted glass bead plates offers the advantage over other porous materials of having a negligible exchange capacity, large capillary conductivity and an exceedingly narrow pore size distribution.

The water in the small reservoir behind the inflow plate could be rapidly changed from one containing a tracer to tracer-free water or the reverse by the use of leveling bottles. Burettes graduated to 0.2 ml were connected in the system to measure the volumes of water which entered the column. The X's in the figure are necessary on-off valves. The vacuum arrangement allowed samples of effluent to be collected as close as possible to the end of the soil column thereby eliminating further dispersion of solutes outside the sample. During the time samples were not being collected, water flow was maintained by means of suction obtained from hanging water columns at the same suction as the vacuum arrangement. The necessary valves for this operation are indicated on the effluent side of the soil column. Miscible displacements of tracer and tracer-free waters were made using the above mentioned porous materials at different average flow velocities and different water contents.

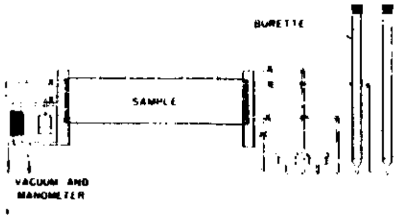


Figure 1. Schematic cross-section of apparatus used for collecting samples of effluent from soil columns maintained at constant water content and average flow velocity.

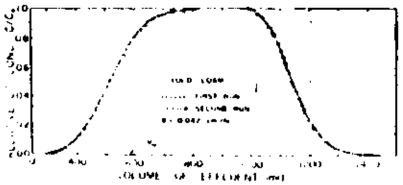
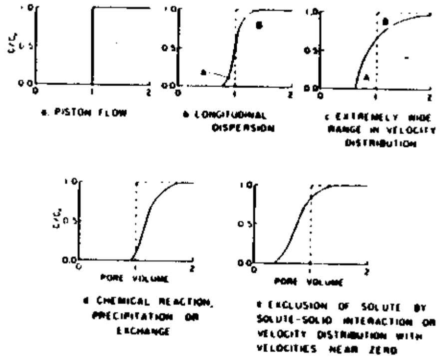


Figure 2. Relative chloride concentration C/C_o of effluent from Yolo loam. A 620-ml slug of chloride tracer water was preceded and followed by tracer-free water in a soil column having a volumetric water capacity V_w of 588 ml.

The curves shown in the next several figures are the result of measuring chloride tracer concentration of effluent from the media. Consider Fig. 2 for Yolo loam in which a 620-ml slug of water containing chloride tracer of concentration C_o is preceded and is followed by tracer-free water. If piston flow had occurred (i.e., no spreading of the tracer front) the Cl^- distribution or breakthrough curves would be represented by the broken vertical lines. If no diffusion occurs in a medium having rather large microscopic flow velocities narrow in their distribution, a skewed sigmoid breakthrough curve will pass through $C/C_o = 0.5$ at V_w (volumetric water capacity of column) and the areas above and below this point will be equal. If the flow velocity is everywhere zero and only diffusion takes place at a tracer front within the medium, the resulting symmetrical sigmoid Cl^- distribution curves will pass through $C/C_o = 0.5$ at the original position of the tracer front. The curve in Fig. 2 is skewed and sigmoid but does not pass through $C/C_o = 0.5$ at V_w. The general translation of the experimental breakthrough curve to the left of $C/C_o = 0.5$ at V_w is not expected after considering the foregoing remarks. This shift is caused by a significant fraction of the total pore volume not contributing to the volume of effluent measured, a fact which will be more fully dealt with later. The congruent nature of the experimental data for the first and second runs indicates the precision of the method and that soil swelling or shrinkage was negligible during the experiment, a time lapse of nearly 3 months.

Without considering the physical and chemical mechanisms involved in miscible displacement, much can be learned from a general description of continuous flow systems as shown by Danckwerts (1953). Let the volume of any porous material or vessel occupied by a fluid be V_o (cm^3) and the rate of inflow and outflow of fluid is q (cm^3 per hour). If suddenly, the incoming fluid is identified by a solute of concentration C_o, the fraction of this solute in the effluent at time t (hour) will be C/C_o.

Plots of C/C_o vs pore volume (qt/V_o), commonly called breakthrough curves, are descriptive of the relative times taken for the displacing fluid to flow through the medium or for the solutes in the displacing fluid to come in chemical equilibrium with the soil. It should be noted that this definition of pore volume is not restricted to saturated water contents but is applicable to all water contents. Furthermore, it refers to a relative volume of effluent which should not be confused with the accepted definition of pore volume of a soil defined as the ratio of total volume of voids including water to total bulk volume of soil. Any experimentally measured breakthrough curve may be considered one or a combination of any of the five curves shown in Fig. 3.



a. PISTON FLOW

b. LONGITUDINAL DISPERSION

c. EXTREMELY WIDE RANGE IN VELOCITY DISTRIBUTION

d. CHEMICAL REACTION, PRECIPITATION OR EXCHANGE

e. EXCLUSION OF SOLUTE BY SOLUTE-SOLID INTERACTION OR VELOCITY DISTRIBUTION WITH VELOCITIES NEAR ZERO

Figure 3. Types of breakthrough curves for miscible displacement. C/C_o is the relative concentration of the invading fluid measured in the effluent. Pore volume is the ratio of the volume of effluent to the volume of fluid in the sample.

For Figs. 3a, b, and c, it has been assumed that the solute spreads as a result of velocity distribution and molecular diffusion only, i.e., there is no interaction between the solute, solvent and solid. In these cases it is useful to observe that

$$\frac{q}{V_o}\int_0^\infty (1 - C/C_o)\,dt = 1 \qquad [1]$$

regardless of the shape of the curve. Physically, this simply states that the original fluid occupied exactly one pore volume or that the quantity of solute within the column that will eventually reach a chemical equilibrium with that in the influent and effluent is C_oV_o. It is also helpful for future discussions to recognize that the area under the breakthrough curve up to one pore volume equals the area above the curve for all times greater than one pore volume, regardless of the shape of the curve. Although this can be concluded from inspection, it is a direct result of Eq. [1]:

$$\frac{q}{V_o}\int_0^{V_o/q} C/C_o \, dt = \frac{q}{V_o}\int_{V_o/q}^{\infty} (1 - C/C_o) \, dt \qquad [2]$$

Danckwerts quantitatively defined holdback H as the left hand integral of Eq. [2]. When no interaction exists between solute and solid, H varies from 0 for piston flow to values < 1 for the other cases.

Piston flow (Fig. 3a) would rarely, if ever occur in soils. There exists for a single capillary tube of constant radius, only a narrow range of flow velocities at which this type flow is even approached. Because soils do not have pore sequences of constant radii the probability that their breakthrough curves would be piston type is almost nil. A column of 200µ diameter glass beads yielded a curve more nearly approaching piston flow than any other material used (Fig. 4).

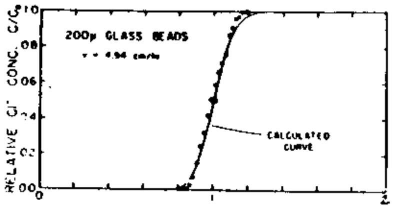


Figure 4. Chloride breakthrough curve measured for 200µ glass beads.

A breakthrough curve obtained from a saturated Oakley sand (Fig. 5) is characteristic of the longitudinal dispersion described by Fig. 3b. Evidence for lack of solute-solid interaction in this soil is obtained by noticing that the areas described by Eq. [2] are nearly equal.

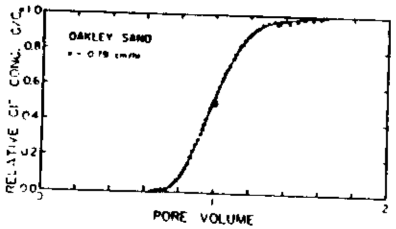


Figure 5. Chloride breakthrough curve measured for Oakley sand.

A soil composed of equal-sized aggregates with no smaller or larger particles possesses an extremely wide range in pore velocity distribution which is bimodal at saturation. The curve in Fig. 6 for Aiken clay loam aggregates between 1- and 2-mm diameter provides a good example of that type of mixing illustrated in Fig. 1c. Although the shape of this curve is different than those in previous figures, it is significant to notice the areas of Eq. [2] are certainly comparable.

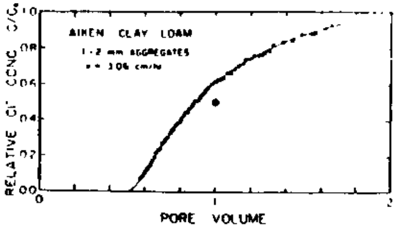


Figure 6. Chloride breakthrough curve measured for 1- to 2-mm aggregates of Aiken clay loam.

The curves presented in Figs. 4, 5, and 6 exhibit increasing holdback equal to 0.0255, 0.0664, and 0.151, respectively. The concept of holdback is a useful qualitative description whenever an interaction between solute, solvent or solid is a minimum. It is especially useful to indicate the large amount of water not easily displaced from unsaturated soils. Values of holdback for unsaturated conditions have been measured to be 3 to 4 times greater than that when the soil was saturated.

Whenever the displacing fluid or its solutes are retained within the column by any chemical or physical process, the breakthrough curve will be translated to the right as shown in Fig. 3d. However, the shape of the curve is not determined by these retaining processes alone, but how these processes are coupled with the microscopic velocity distribution and other processes which translate the curve to the left. An example of a breakthrough curve being translated to the right as a result of adsorption and exchange is given in Fig. 7 where tritiated water displaced nontritiated water from a saturated sample of Yolo loamy sand θ = 0.393. Under these conditions, it is easily seen that the areas described in Eq. [2] are not equal.

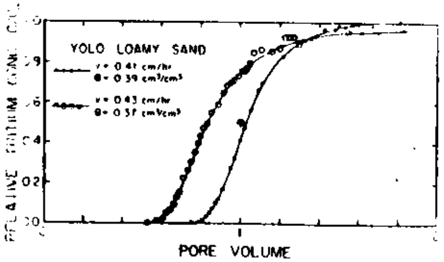


Figure 7. Tritium breakthrough curves measured for Yolo loamy sand at two water contents θ.

Any process within the soil causing an increase of solute concentration or an incomplete mixing throughout the entire soil solution will yield a breakthrough curve translated to the left as shown in Fig. 3e. In the case of anions measured to distinguish the displacing fluid, their repulsion away from the negatively charged clay surfaces would translate the breakthrough curve to the left. The same would occur if mixing were not complete owing to nearly stagnant pores. Solution of slightly soluble salts already present in the sample would of course, translate the curve to the left. A breakthrough curve of tritium for Yolo loamy sand, the same soil given in Fig. 7 but unsaturated to 0.372 cm^3 per cm^3 water content, is an example of incomplete mixing in nearly stagnant pores of an unsaturated soil. Even though exchange takes place which would tend to shift the curve to the right, the effect of the stagnant pores is evident.

Figure 8 presents three chloride breakthrough curves from the 390μ glass beads initially saturated with Na_2SO_4 solution. For the greatest velocity of 56.7 cm per hour, which is well within the limits of laminar flow, the chloride breakthorugh is abrupt, resembling that of piston displacement (Fig. 3a). At a velocity of 0.395 cm per hour, the chloride appears nearly 0.4 pore volume before that of the previous curve and requires 0.2 pore volume more effluent to reach $C/C_o = 1$. Breakthrough curves for intermediate velocities appeared between the plotted curves. At the least velocity of 0.122 cm per hour the chloride appears before 0.2 pore volume has been displaced with its curve having the least slope of those presented. Nearly 3 pore volumes are required to reach $C/C_o = 1$. For each velocity a distinctly separate chloride curve is measured. The greater the velocity, the more abrupt the breakthrough. The velocities used in this investigation are those common to agricultural soils with the velocity of 56.7 cm per hour well above the average velocity measured in saturated field soils.

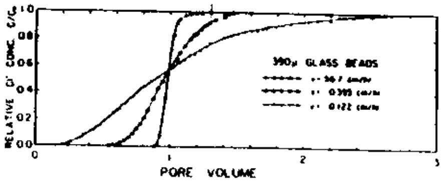


Figure 8. Chloride breakthrough curves from 390μ glass beads for three flow velocities.

Measured breakthrough curves for the greatest and least velocities for both chloride and tritium are given in Fig. 9. At the greatest velocity, the curves are nearly identical. At the least velocity the curves are slightly rotated from each other as would be expected for substances having different diffusion coefficients. For all velocities, no translation occurred between pairs of chloride and tritium curves, thus assuring the glass beads were inert.

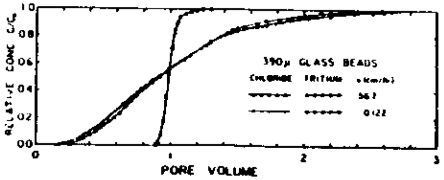


Figure 9. Chloride and tritium breakthrough curves from 390μ glass beads measured at velocities of 56.7 and 0.122 cm per hour.

Breakthrough curves obtained from unsaturated soils yield more information regarding microscopic flow than those from saturated soils. They also provide a more complete description of flow occurring in saturated soils. Figure 10 shows breakthrough curves obtained for equal flow velocities from Oakley sand at three water contents. The drier the soil, the greater is the volume of effluent required to reach a maximum $C/C_o = 1$. Desaturation eliminates larger flow channels and increases the volume of water within the sample which does not readily move. These almost stagnant water zones act as sinks to ionic diffusion.

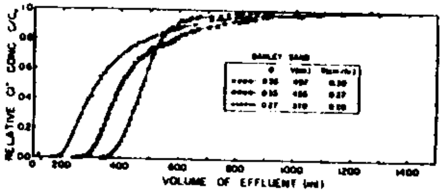


Figure 10. Breakthrough curves for Oakley sand at three different water contents. The average flow velocities were of equal order of magnitude at 0.3 cm per hour.

Oakley sand, saturated with Ca^{2+}, was packed into an apparatus which allowed accurate control of water content during steady-state flow conditions in both saturated and unsaturated soil. The soil columns were 30 cm in length. Before introducing the $MgCl_2$ solutions, steady-state flow conditions were established in the columns using either 0.05N or 0.1N Ca acetate solution. The 0.05N acetate solution was followed by 0.05N $MgCl_2$ solution and 0.1N acetate by 0.1N chloride solution. Samples of effluent were collected and analyzed for Cl^- and Mg^{2+}.

Breakthrough curves for 0.1N $MgCl_2$ displacing 0.1N Ca acetate at fluxes of 1.77 and 0.194 cm per hour are presented in Fig. 11. The pore volume of each column is given by the bullseye and the total number of milliequivalents to be exchanged is 85.7 and 84.4 for the large and small fluxes, respectively. The Cl BTC for both columns indicate the manner in which the penetrating solution is dispersed as it passes through the soil. Had piston flow occurred, the BTC would be represented by a vertical line through the bullseye. The two columns are essentially Cl^- systems after 550 ml has passed through. For the larger flux the Cl^- curve breaks sharply initially in contrast to the smaller flux. The latter appears after 250 ml (0.58 pore volume) compared with 325 ml (0.78 pore volume) for the large flux. This initial appearance of Cl^- in the effluent and the flatter curve in general at the smaller flux illustrates the important contribution of diffusion to the transport of the salt.

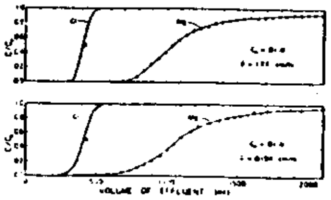


Figure 11. Breakthrough curves for Cl- and Mg^{2+} ion during the displacement of 0.1N Ca acetate by 0.1N $MgCl_2$ at two fluxes in Ca-saturated Oakley sand under saturated conditions.

Unsaturating the soil results in a disproportionate shifting of the breakthrough curve for chloride to the left of one pore volume and drastic modification of the shape of the curve. In the present study two columns were unsaturated and the BTC investigated for fluxes of 0.192 and 0.188 cm per hour at normalities of 0.1 and 0.05, respectively. The water contents of these columns were approximately 7% less than the saturated columns. The shifting and shapes of the Cl^- curves as illustrated in Fig. 12 are similar to those illustrated in Fig. 3e.

The initial breakthrough for 0.1N and 0.05N occurred after 0.84 and 1.31 pore volumes, respectively. For the saturated cases at the same flux these were 0.86 and 1.11 pore volumes. Unsaturating the soil has not produced an initial shift in the cation breakthrough comparable to the chloride. The shapes of the curves for unsaturated soil are noticeably different than those for saturated soil. It takes less than twice as much 0.05N solution to reach the same C/C_0 ratio as 0.1N solution. Further consideration of this latter point may be worthwhile. It would appear in most cases that less total me. of salt are required to reach the same level of Mg^{2+} saturation in the column when the solution is applied at a concentration of 0.05N compared to 0.1N. Such a conclusion is based on the fact that it required less than twice as much 0.05N solution to reach the same C/C_0 ratio. The underlying assumption is that reaching a given C/C_0 ratio in the effluent implies the same average ratio in the soil, i.e., what appears in the effluent can be accurately related to conditions in the soil. Such an assumption may not be valid.

Complete equilibrium may exist at all times between the solution present in the pore and the adjacent exchange sites. In a smaller pore, the displacing solution will not have penetrated as far as in the larger pore but here also equilibrium can prevail. Hence, after the solution has penetrated some distance into the column, and a cross section of the column examined, it is possible to have various soil grains at various stages of exchange but also in equilibrium with the solution in their respective pores. The shape of the BTC will not only depend then upon the characteristics of the exchange isotherm but will reflect the mixing which has occurred by microscopic flow velocity, ionic diffusion and the interaction of these three processes.

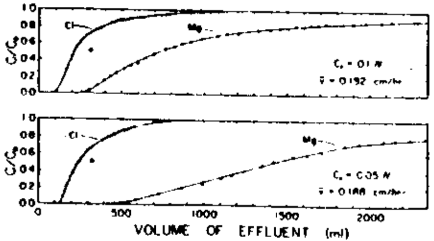


Figure 12. Breakthrough curves for Cl^- and Mg^{2+} ion during displacement of 0.1N and 0.05N Ca acetate solution from Ca-saturated Oakley sand by 0.1N and 0.05N $MgCl_2$ solution at two fluxes under unsaturated conditions. θ is the water content.

Five lengths (30, 60, 90, 120, and 150 cm) of sandstone columns having 5-cm square cross-sections were used in a miscible displacement apparatus. Initially, the columns were thoroughly leached with 0.01N $CaSO_4$. This solution was displaced from the column by 75 ml of 0.1N $CaCl_2$ with 0.01 mc per liter tritium added followed by the original $CaSO_4$ solution. Thus, in all experiments, it was the mixing of a 75-ml slug of tritiated $CaCl_2$ solution during displacement that was measured and interpreted to describe the nature of the sandstone.

The experimentally measured chloride concentration distributions of the effluent from the 5 lengths of sandstone for a displacement velocity of 5.64 cm per hour are given in Fig. 13. It is evident from these curves that the greater the displacement the greater is the dispersion or spreading of chloride. A maximum relative chloride concentration of 0.9 is measured

for a 30-cm displacement while that for 150 cm is only 0.45. A symmetric chloride distribution within the sandstone is responsible for the shapes of the elution curves. Each curve is not symmetric owing to the time-dependent sampling at a constant distance.

For a velocity of 5.64 cm per hour the tritium distributions in the effluent from the 30, 90, and 150 sandstone columns are similar to those of chloride (Fig. 14). The chloride curves appear to be translated to the left by a volume directly proportional to the column length. This behavior suggests an interaction between the chloride ion or tritiated water and the grains of the sandstone. At this velocity it has been shown that chloride and tritium curves are not measurably different when no interaction occurs.

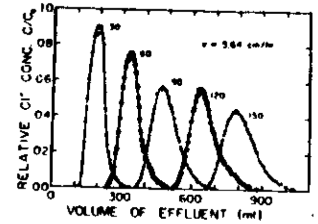


Figure 13. Relative chloride concentration distributions from 5 lengths of saturated sandstone for a displacement velocity of 5.64 cm per hour. The number by each curve represents the sandstone length in cm.

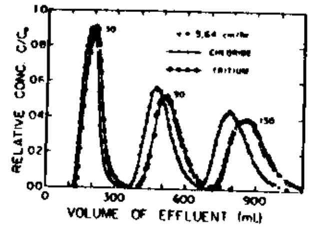


Figure 14. Relative chloride and tritium concentration distribution from the 30, 90, and 150 cm long saturated sandstone columns for a velocity of 5.64 cm per hour.

Practical Field Implications of Early Laboratory Studies – The coupled manner in which dissolved substances move with a fluid flowing through a porous material is intimately associated with soil salinity, the quality of water stored in groundwater recharge reservoirs, and effluents in filter beds. The manner of movement is as important as these associated factors in present-day problems of increasing the efficiencies of fertilizer and pesticide application while decreasing the hazard of contaminating the groundwater with objectionable residues. Studies of these and similar problems have been made with sundry objectives in mind.

Soil studies have emphasised the premise that when water moves, solutes also move. This premise has focused attention on the quantities of water needed to pass a solute completely through a soil or to a particular depth. Formulas for the leaching of soluble salines have often been based upon quantity of water leaving the soil. Similarly, formulas used to calculate the quantity of a chemical additive to a soil are usually material balance equations based upon initial and desired quantities of chemical and water in a given depth of soil.

With the use of such simple assumptions, investigations of leaching or adding chemical amendments to soils often neglected examination of how solute movement is related to water movement. Little thought has been given to merely displacing the salts into a more favorable distribution within the profile without actually leaching and decreasing the total salts present. Nor have studies been made of the possibility of obtaining a desired concentration of a chemical additive at a particular depth while simultaneously keeping additive concentration at a minimal value at other depths. Instead, investigations aimed to increase the effectiveness of the treatment merely by increasing the uniformity of the areal application and by applying depths of water based upon the soil storage capacity.

A level, 1-acre site of Panoche clay loam was divided into 0.01-acre plots delineated by plastic levees. The plots were statistically arranged such that the treatments were randomized with 5 complete blocks. On the surface of each plot chemically pure KCl was applied uniformly at a rate of 93 pounds per plot. The way this applied salt was leached and redistributed through the profile was observed for three methods of water application: (1) the soil surface continuously ponded with water; (2) the soil surface intermittently ponded with repeated applications of 6 inches of water; and (3) the soil surface intermittently ponded with repeated applications of 2 inches of water. For the intermittent treatments, water was applied to the plots whenever the soil water pressure at the 1-foot depth reached -150 mb (corresponding to a volumetric water content of 30.4%).

Porous ceramic cups were used to take samples of the soil solution from each plot at the previously mentioned depths in proximity to the tensiometers. The soil solution was extracted through the cups by applying a vacuum greater than that of the soil water pressure. This method allows samples to be taken repeatedly at all depths without destroying the site with soil sample removal. It also offers a means of sampling the soil solution when the soil is ponded with water or when the soil is so wet that soil removal is almost impossible because of contamination from one depth to another.

The chloride concentration of the soil solution was analyzed by titration. Samples were extracted every hour at each depth during water application and at greater time intervals during drainage periods of the intermittently ponded treatments. At least 3500 samples were extracted and analyzed for each treament.

The three methods of water application yielded three distinctly different soil water regimes within the profile. These regimes may be observed in Figs. 15 and 16. In Fig. 15 the broken line merging into the unbroken line (30- to 6-inch depth) represents the water content distribution if the soil profile were saturated with water. These values range from 0.41 cm^3/cm^3 at the 12-inch depth to 0.51 cm^3/cm^3 at the 4-foot depth. After the soil had wetted to a maximum value during the continuously ponded treatment, the soil water content was either equal to the saturated value or no more than 0.01 cm^3/cm^3 from saturation at all soil depths. The continuous, unbroken line adjacent to the broken line in Fig. 15 shows the water content during continuous ponding. That the soil should remain slightly below saturation between the 6- to 36-inch depths was expected based on in situ hydraulic conductivity measurements.

The shaded area in Fig. 15 represents the values through which the water content fluctuated during the 6-inch intermittently ponded treatment. The left-hand boundary of the area represents the soil water content distribution after one week of drainage from a previous 6-inch application. The soil water contents never fell below these minimum values. The right-hand boundary represents the maximum values attained during the percolation of the 6-inch water application. These maximum values are nearly equal to values measured for the continuously ponded treatment. As the water moved through the upper 36-inch portion of the profile, the water contents increased about 0.09 cm^3/cm^3 over the minimum values. At the greater depths, the increase was somewhat less pronounced, approximately 0.06 cm^3/cm^3. A comparison of the soil water contents manifested during the 6-inch intermittently ponded treatment with contents from the continuously ponded treatment reveals that the soil ponded intermittently was about 0.04 cm^3/cm^3 drier even though its maximum values approached the continuously ponded values.

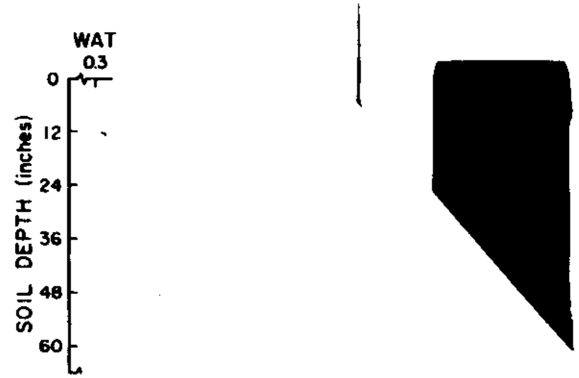


Figure 15. Soil water content
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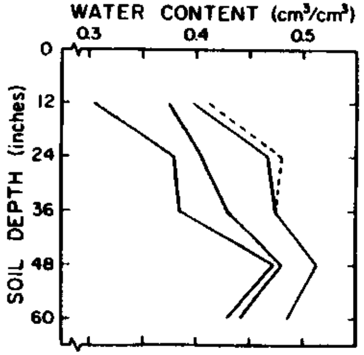

Figure 16. Soil water content distributions within Panoche clay loam during continuously ponded and intermittently ponded conditions. The broken line represents water saturation; the unbroken line represents the water content distribution during continuously ponded conditions. The shaded area represents the range of water contents during infiltration of 2-inch water applications and the subsequent drainage period before the next 2-inch application.

The soil water contents measured during the continously ponded treatment and soil water contents of saturation are repeated in Fig. 16 in comparison with contents measured during the 2-inch intermittently ponded treatment. As the 2-inch water application infiltrated and passed through the soil profile, the average soil water content was about 0.06 cm^3/cm^3 less than the average content during the continuously ponded treatment and 0.02 cm^3/cm^3 less than average content during the 6-inch intermittently ponded treatment. Furthermore, the maximum water content values for the 2-inch treatment were considerably less then maximum values of the other two treatments. These maximum values were about 0.04 cm^3/cm^3 less than the saturated soil water content values.

Figure 17 shows chloride concentration values determined from the 6-inch intermittently ponded treatment. The total time required to complete this treatment was 1050 hours, 6 times longer than the continuously ponded treatment.

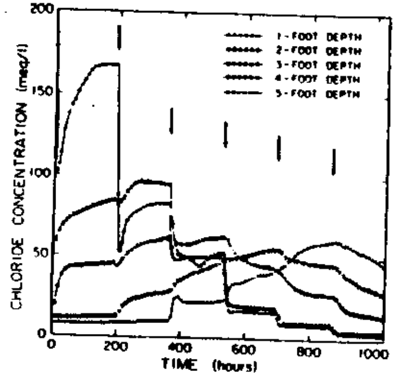

Figure 17. Concentration of chloride in the soil solution vs time for Panoche clay loam intermittently ponded with 6 inches of water. Zero time represents the time when the first 6-inch irrigation was initiated. The vertical arrows represent other times when additional 6-inch applications were initiated.

In Fig. 18 and the following two figures, the chloride concentrations are plotted vs soil depth, the parameter of each curve being the total quantity of water penetrating the soil surface at the time of measurement. In observing the chloride concentration profiles during leaching and drainage, it is helpful to consider the chloride distribution within the profile as well as the depth of maximum concentration. With the entry of 4 inches of water, the chloride collects in the upper 2 feet of the soil profile and changes very little with the addition of 2 more inches. In fact, at the 1-foot depth the concentration remained unchanged at 186 meq/l. After 12 inches have penetrated the surface, the concentration increases at the greater depths with a maximum of 93 meq/l persisting at the 1-foot depth. It is notable that with progressive leaching the maximum concentration in the profile is reduced and the chloride distribution is extended throughout the profile. A comparison of the chloride concentrations at the greater depths, after 24, 30, and 36 inches of water had penetrated the soil, reveals that substantial redistribution of the chloride under continuous ponding is not attained. After 40 inches of water had entered the surface (not given in Fig. 18) the chloride concentrations at 1, 2, 3, 4, and 5 feet were 4, 5, 21, 40, and 47 meq/l, respectively.

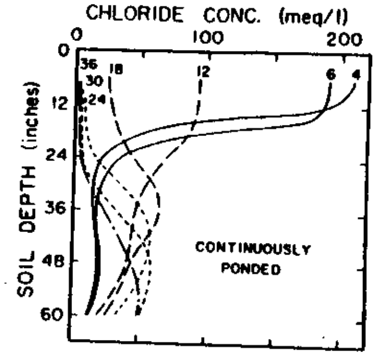

Figure 18. Chloride concentration of the soil solution vs profile depth of Panoche clay loam intermittently ponded with water. The number near each curve signifies the total inches of water that entered the soil surface at the time of measurement.

The curves given in Fig. 19 represent the chloride distributions from intermittently applying 2 inches of water. When the soil was leached with 4 inches of water, followed 11 days later by 2 inches of water, the concentrations were changed from 70, 84, and 34 meq/l at the 1-, 2-, and 3-foot depths to 100, 104, and 60 meq/l, respectively. In contrast, continuous ponding produced little change from 4 to 6 inches of applied water. After intermittent leaching with 12 inches of water, a major part of the chloride was removed from the surface 18 inches and redistributed primarily within the 2- to 4-foot depth with a maximum concentration of 115 meq/l at 3 feet; For the same amount of water applied continuously, the maximum concentration within the profile persisted at the 1-foot depth.

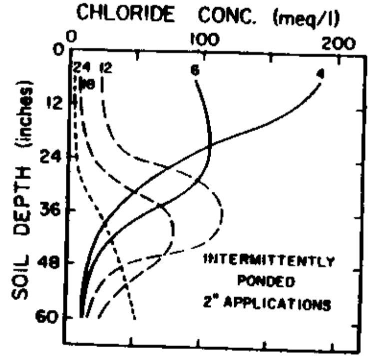

Figure 19. Chloride concentration of the soil solution vs profile depth of Panoche clay loam continuously ponded with 2 inches of water. The number by each curve signifies the total inches of water that entered the soil surface at the time of measurement.

The chloride concentrations in the upper 36 inches, after 24 inches of water had been intermittently applied (Fig. 19), were less than one-half those obtained under ponded conditions. Furthermore, for the intermittent treatment, the maximum concentration was deeper than 5 feet. The maximum concentration of the continuously ponded treatment was at 4 feet. In fact, intermittent ponding of 24 inches of water produced a chloride distribution comparable with 36 inches under continuous ponding. The chloride concentrations after 28 inches of intermittent leaching (not given in Fig. 19) were 4, 4, 9, 23, and 60 meq/l at the 1-, 2-, 3-, 4-, and 5-foot depths, respectively.

The chloride profiles given in Fig. 20 are derived from data plotted in Fig. 17. These chloride distributions were effected by intermittently ponding the soil with 6 inches of water, an intermediate treatment between the two extremes of continuous ponding and 2-inch intermittent ponding. To some extent the results indicate a combination of the two extremes. The chloride distribution after the initial 6-inch application was almost identical to distribution after the initial 4-inch application given in Fig. 19. On the other hand, after 18 and 24 inches of water had penetrated the soil surface, the chloride distributions of the 6-inch intermittently ponded treatment more nearly resembled chloride distributions of the continuously ponded treatment. The concentrations near the soil surface are noticeably higher than concentrations for the other two treatments, undoubtedly owing to the high evaporating conditions prevailing during the 6-inch intermittently ponded treatment, especially during the later stages of leaching. After 36 inches of water had entered the soil, the chloride concentrations of the 6-inch treatment of the greater depths were less than concentrations of the chloride profiles between the two intermittently ponded treatments reveals that 24 inches of water applied in 2-inch increments produced lower chloride concentrations than did 30 inches of water applied in 6-inch increments.

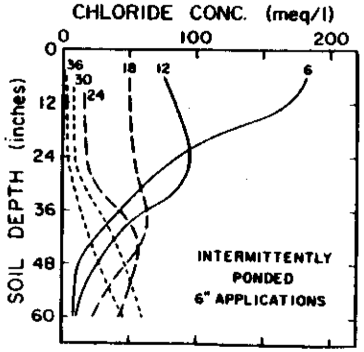

Figure 20. Chloride concentration of the soil solution vs profile depth of Panoche clay loam intermittently ponded with 6 inches of water. The number by each curve signifies the total inches of water that entered the soil surface at the time of measurement.

This experiment has revealed that the manner in which chloride is displaced from the surface of Panoche clay loam is a result of a dynamic process that can be altered or controlled with the method of water application. The markedly different behavior of the chloride concentration distributions within the soil was characterized by two facts: (1) the amount of chloride displaced from a given depth was not uniquely related to the volume of displacing water; and (2) the maximum chloride concentration attained at any depth could be either less than or greater than the concentration above or below that depth. Related to these findings was the measurement of greater maximum concentrations and narrower chloride distributions within the profiles ponded intermittently. Undoubtedly this behavior is related to the water content distributions and flow velocities occurring during leaching.

Suppose that a uniform concentration of a soluble salt or chemical soil additive were desired throughout the soil profile. After applying the salt to the soil surface, the best means of attaining such a distribution would be to leach the soil under a continuously ponded condition or intermittently with 6-inch applications. In Fig. 18 approximately 15 inches of water causes a nearly uniform chloride distribution throughout 4 feet of the 5-foot profile, with an average chloride concentration of 60 meq/l. A similar result was achieved with a concentration of 50 meq/l, using a total of 18 inches of water applied in 6-inch increments (Fig. 20).

Suppose on the other hand that the establishment of a narrow distribution of solute within the soil profile is required. Such a distribution may be desirable when dealing with the placement of fertilizer to specific soil depths relative to the crop rooting characteristics. In Fig. 19 a narrow distribution of chloride was meaured after 12-18 inches of water added in 2-inch increments had penetrated the soil. It is also apparent that this water application treatment yielded the greatest maximum concentrations, particularly to 4 feet. This knowledge is useful in maximizing the depth to which a minimum lethal concentration can be introduced without unnecessarily contaminating greater soil depths.

In areas where water is limited or expensive, or where high groundwater table levels exist, it is desirable to leach a soil in the most efficient manner possible. Of the three treatments, intermittently ponding the soil with 2-inch increments of water was markedly more efficient in leaching the applied chloride from the profile. The concentrations of chloride in the upper 3 feet after 24 inches of water were applied intermittently were less than one-half of chloride concentrations obtained under ponded conditions (Figs. 18 and 20). In fact, intermittent ponding of 24 inches of water produced results comparable with continuous ponding of 36 inches. A saving of one-third the quantity of water (e.g., 2 acre-feet per acre vs 3 acre-feet per acre) to obtain the same leaching represents a significant reduction in water use. Where drainage is a limiting factor, this reduction could significantly reduce water table problems. On the other hand, it should be recognized that intermittent ponding requires much more time than continuous ponding to allow the same quantity of water to enter the soil.

<u>Theoretical Considerations of Solute Movement in Soil</u> - The flux of a soil solute J_s ($gcm^{-2}day^{-1}$) is described by

$$J_s = -\theta D \frac{dc}{dz} + J_w c \qquad [3]$$

where c is the concentration in the soil water (g/cm^3) and D the apparent diffusion coefficient. Equation [3] is fraught with difficulties inasmuch as inside a soil, both c and J_w are spatial averages over an ensemble of soil pores. Experimentally, each remains somewhat ambiguous, with their values depending on the method of measurement and the size of the ensemble that is sampled. Hence, neither their product nor the gradient dc/dz in Eq. [3] is unique. Further difficulties stem from the fact that soil particle surfaces have a net charge density that influences the distribution of solutes within each soil pore, which in turn is modified further by the soil water content and the soil water flux. Because of these and related difficulties, the parameter D in Eq. [3] has been the subject of numerous investigations and, in general, has a unique value only in relation to a particular set of conditions.

Because soil solute movement rarely exists in the steady-state condition, many descriptions of solute behavior are obtained from solutions of the following equation:

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \theta c}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial J_w c}{\partial z} + \phi \qquad [4]$$

where ρ is the soil bulk density (g/cm^3), s the solute associated with the soil particles [g/(g soil)], and ϕ is an irreversible source or sink of solute (g cm^{-3}day^{-1}). Recent literature shows that much has been learned about the affects of diffusion, convection, adsorption and other processes on solute transport and retention in soils. Numerous conceptual-mathematical models have been developed in attempts to describe the one-dimensional transport of solutes in laboratory columns as well as in field soils. van Genuchten and Alves (1982) have recently summarized numerous analytical solutions of the above equation. The following is a selected set of laboratory and field studies illustrating present-day understanding and technology.

<u>Laboratory Studies of Nitrogen Transformation During Leaching</u> - The kinetics of microbial transformations of N has been discussed by McLaren (1969a, 1969b, and 1971). Under steady-state conditions, the transformations are generally considered to be zero- or first-order rate reactions for relatively large or small concentrations, respectively. For zero-order reactions, the value of ϕ_i would be invariant. For more dilute solutions and/or where oxygen or carbon supplies are limited, the net rates of oxidation of ammonium c_1, oxidation of nitrite c_2, and reduction of nitrate c_3 would be,

$$\phi_1 = - k_1 c_1 \qquad [5]$$

$$\phi_2 = k_1 c_1 - k_2 c_2 \qquad [6]$$

$$\phi_3 = k_2 c_2 - k_3 c_3 \qquad [7]$$

respectively. Many factors such as microbial growth kinetics, temperature, pH, and the supply of oxygen and carbon as well as a host of other environmental parameters are implicitly included in the rate coefficient k_i. Here the various factors are lumped together into one apparent rate coefficient for each reaction.

Equation [4] written for processes of nitrification and denitrification becomes

$$\frac{\partial c_1}{\partial t} = \frac{D}{1+R}\left[\frac{\partial^2 c_1}{\partial x^2}\right] - \frac{v}{1+R}\left[\frac{\partial c_1}{\partial x}\right] - \left[\frac{k_1}{1+R}\right] c_1 \qquad [8]$$

$$\frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} - k_2 c_2 + k_1 c_1 \qquad [9]$$

$$\frac{\partial c_3}{\partial t} = D\frac{\partial^2 c_3}{\partial x^2} - v\frac{\partial c_3}{\partial x} - k_3 c_3 + k_2 c_2 \qquad [10]$$

where the exchange reaction of NH_4^+ - N with the soil is included in the 1 + R term assuming R to be a constant and equal to the ratio of adsorbed to solution ions, and c_i is the mass of NH_4^+ - N, NO_2^- - N, or NO_3^- - N per unit volume of soil solution (mg liter^{-1}). It is assumed that the values of the apparent diffusion coefficients D for the three ions are identical.

Owing to the complexity of both the mathematical and experimental problem, the treatment here is initially restricted to steady-state conditions, as well as assuming that the value of c_2 (NO_2^-) approaches zero as is commonly found in many field soils. Thus, Eq. [8] through [10] become

$$D\frac{d^2 c_1}{dx^2} - v\frac{dc_1}{dx} = k_1 c_1 \qquad [11]$$

and

$$D\frac{d^2 c_3}{dx^2} - v\frac{dc_3}{dx} + k_1 c_1 = k_3 c_3 . \qquad [12]$$

If D, v, and $c_i(x)$ are measured, the first and second derivatives of c_1 are known and k_1 can be obtained from a plot of the left side of Eq. [11] vs c_1. If ϕ is a first-order rate reaction, the slope of such a plot is equal to k_1. In the case of a zero-order reaction, the slope would be identically zero with the left side of Eq. [11] equal to the zero-order rate constant. Similarly, the value of the rate coefficient for denitrification k_3 can be found by plotting the left side of Eq. [12] vs c_3.

In addition to NH_4^+ - N and NO_3^- - N in the soil solution, the diffusion of nitrogen gases in the soil atmosphere resulting from denitrification can be examined. For nonsteady conditions, the concentration of the given gas is given by

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + F(x,t) \qquad [13]$$

where F(x,t) is a source (production) term if it is positive in sign and a sink (consumption) term if negative. If neither source nor sink terms exist, F(x,t) is zero. For Eq. [13] to be valid, the gas must not be adsorbed appreciably on the soil particles, and transport must occur by diffusion only. Under steady-state conditions, c and F vary only with depth, and if D is known, the second derivative of the measured concentration distribution yields values of

$$F(x) = - D(\partial^2 c/\partial x^2). \qquad [14]$$

A plot of F(x) vs depth shows the zone of gas production or consumption.

Hanford sandy loam, California soil was passed through a 0.6-cm square screen and packed into a 15.2 by 13.2 by 100-cm acrylic plastic column to an average density equivalent to an oven-dry value of 1.51 g cm^{-3}.

Fritted glass tubular cups (5 by 0.6 cm) were placed at 5-cm intervals. Nylon tubing (1.0 mm I.D.) was placed along side each cup, with one end wrapped in glass wool to prevent plugging with soil particles. The other end of nylon tube was inserted through rubber serum stoppers into 3-cm long flexible tubes, both ends of which were closed with rubber serum stoppers. The porous cups and spaghetti tubing provided a means of extracting soil solution and atmosphere without disturbing the soil. The soil water pressure was measured at five depths by means of the porous cups connected with flexible tubing to mercury manometers. The three intermediate manometers were connected to extraction cups after the soil moisture characteristic data was obtained. A perastaltic pump was used to deliver the applied solution through seven evenly spaced nylon tubes (1 mm I.D.) to the soil surface. Water dropped from a height of 1 cm above the soil surface at a rate of 16 ± 0.5 ml $hour^{-1}$. One-cm^3 soil atmosphere sample was taken with a syringe needle inserted through the rubber serum stoppers into the nylon tubes. Analyses were made for CO_2, O_2, N_2, and $^{15}N/^{14}N$ ratio with the mass spectrometer, and N_2 determined with a gas chromatograph. The soil column, maintained at 20 ± 0.5C was leached with 0.01N $CaSO_4$ throughout the experiment. The average pore-water velocity was 6.0 cm day^{-11} with an average final water content of 0.32 cm^3cm^{-3}. The initial treatment consisted of enriching the influent with 50 ppm NH_4^+-N, labeled with 8.65 atom percent excess ^{15}N, until a steady state was obtained. After an intervening set of secondary treatments not to be reported here, the first treatment was repeated in an attempt to reproduce the conditions and results obtained initially. The two steady-state experiments are called A and B, respectively.

Steady-state conditions within the column for the continuous application of the NH_4Cl solution occurred at 39 and 41 days for experiments A and B, respectively. Steady-state conditions were ascertained by examination of the NO_3^--N concentration distribution within the soil as well as that in the soil effluent. The use of constant values for k_1 and k_3 assuming a first-order reaction gave excellent predictions of the vertical distribtuion of NH_4^+ and NO_3^- as seen in Fig. 21a and 21b.

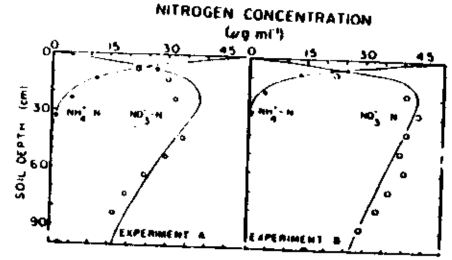

Fig. 21. Theoretical (Eq. [10]) and measured distributions of NH_4^+-N and NO_3^--N with soil depth for experiment A (Fig. A) and experiment B (Fig. B).

A plot of the left side of Eq. [11] for measured values of D and v vs c_1 is given in Fig. 22 for both experiments. The average slopes of the plot give k_1 values of 0.76 and

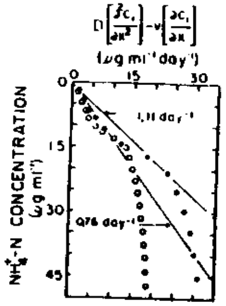

Fig. 22. The left side of Eq. [11] vs the concentration of NH_4^+-N in the soil solution. Open and solid circles designate measured values for experiments A and B, respectively. The straight lines represent the average slopes, k_1.

1.11 day^{-1} for experiments A and B, respectively. At concentrations greater than about 20µg ml^{-1}, the left side of Eq. [11] is approximately constant - indicating a zero-order reaction for the greater concentrations. Values of the denitrification rate coefficient k_3 obtained in a similar manner with Eq. [12] for soil depths from 40- to 80-cm were 0.075 and 0.040 day^{-1} for experiments A and B, respectively.

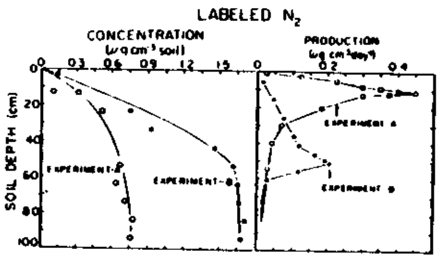

Fig. 23. Labeled N_2 concentration (Fig. A) and production rate stemming from Eq. [14] (Fig. B) vs soil depth.

In the above experiment, steady-state conditions prevailed as regards both solute and water content values, i.e., they did not vary with time and hence, the more simple Eqs. [11] and [12] were used to analyze the experimental results. A second example is that of following the transport and transformation of urea, NH_4^+ and NO_3^- under steady-state water content but transient solute concentration conditions. It is assumed that the enzymatic hydrolysis of urea c_1, the microbial oxidation of ammonium c_2, and the microbial reduction of nitrate c_3 seem to obey first-order rather than zero or other order reaction kinetics. Using this assumption, the following equations were used to describe the behavior of urea, ammonium, and nitrate in the soil solution of a laboratory column of Tyndall silty clay:

$$(1 + R_1)\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} - k_1 c_1 \qquad [15]$$

$$(1 + R_2)\frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} + k_1 c_1 - k_2 c_2 \qquad [16]$$

$$\frac{\partial c_3}{\partial t} = D\frac{\partial^2 c_3}{\partial x^2} - v\frac{\partial c_3}{\partial x} + k_2 c_2 - k_3 c_3 \qquad [17]$$

where R_1 and R_2 are the distribution coefficients for urea and ammonium assuming a reversible, instantaneous linear relation between the solution phase concentration and that in the sorbed phase, and k_1, k_2, and k_3 are the rate constants describing the processes of urea hydrolysis, ammonium oxidation, and nitrate reduction, respectively.

A controlled pressure chamber was utilized to simultaneously apply suction to the bottom of the column and collect effluent samples. The use of a constant head buret at the influent end of the column established a unit hydraulic gradient which minimized water content differences within the soil. Steady-state conditions of unsaturated water flow in the vertical direction were established in each column at a water content of approximately 60% of saturation using 0.01N $CaSO_4$. Simultaneously, steady-state gas flow was established in the horizontal direction. Once these conditions prevailed (after approximately 5 days for a 15-cm column, 10 days for a 30-cm column), a 100-ml pulse of 0.01N $CaSO_4$ containing urea enriched with ^{15}N and 10^{-2} ml ^3H_2O was leached through the column followed once again with 0.01N $CaSO_4$. Effluent samples were collected and analyzed for ^3H_2O and urea, NH_4^+, NO_2^-, and NO_3^-. The columns were sampled upon the termination of leaching and the distribution of urea, NH_4^+, NO_2^-, and NO_3^- within the column determined.

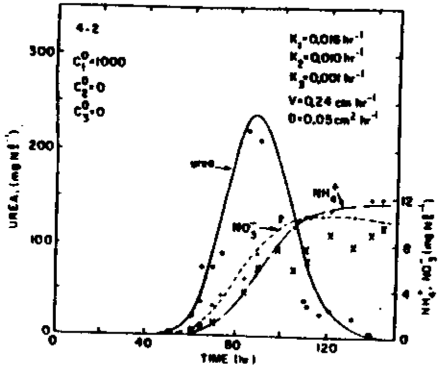

Fig. 24. The experimentally measured effluent concentrations of urea, NH_4^+, and NO_3^- determined after the application of a pulse urea-N with the theoretical curves stemming from Eq. [15] [16], and [17].

The use of isotopically labeled N plus the analysis of both the solution and gaseous phases of the soil with time and depth provides a means for identifying and quantifying sources and sinks. Some modifications and additional measurements that may prove helpful include: analysis of the soil atmosphere and soil solution at smaller depth increments near the soil surface; the sampling of the soil atmosphere at a sufficiently slow rate so as to minimize contamination of the sample from air above the column and/or from large distances within the column; analyzing the soil solution for various dissolved gases and organic C; microbial biomass estimations; and gaseous diffusion coefficients as a function of soil air porosity.

Relative Flow Rates of Salt and Water in Soil - Many miscible displacement experiments have shown that a readily soluble salt moves at a different rate through soil than the water in which it is dissolved. For example, when a $CaCl_2$ solution containing ^{36}Cl and ^3H is passed through some soils, the ^{36}Cl appears earlier in the effluent than the ^3H. Qualitatively, this behavior can be explained by anion repulsion or negative adsorption of salt by the negatively charged soil particle surfaces. Krupp et al. (1972) developed a model for describing the mixing of two miscible solutions in a soil in which the Gouy theory for ion distribtuion in soil pores is combined with convective-diffusion Eq. [4]. It was shown that the exclusion volume for isotope and the separation volume for ^{36}Cl and ^3H increased as flow velocity decreased and these changes were related to the total ion concentration, the thickness of the diffuse double layer, and the zones of mobile and immobile solution.

Owing to uncertainty about understanding the actual shapes and sizes of aggregates, whether packed in a column or in the field, a more practical approach has been to assume that solute transfer between the mobile and stagnant water regions can be modeled as a simple first-order exchange process [Coats and Smith, 1964; Raats, 1973; van Genuchten and Wierenga, 1976]. Convective-diffusive solute transport is again limited to the mobile water regions, whereas diffusive mass transfer between the mobile and stagnant water regions is assumed to be proportional to he concentration difference between the two soil water phases.

The presence of immobile or stagnant water in the system can be attributed to the physical configuration of the aggregates; the nonequilibrium situation, if present, is therefore an apparent physical phenomenon [van Genuchten, 1981]. In order to verify the assumption of physical nonequilibrium and to investigate the tendencies of model parameters with variation in experimental conditions, a series of miscible displacement experiments were carried out using an aggregated Oxisol as the porous medium and ^{36}Cl and ^3H_2O as the solute tracers. The experiments were carried out with different aggregate sizes and run at different flow rates.

The Ione soil from the Eocene formation of California classified as an Oxisol is strongly aggregated, has a pH of 3.7, a CEC of 2 meq/100 g soil, a Fe_2O_3 content of 6.5%, a zero point of charge (ZPC) at pH 3.6, and has kaolinite as the predominant clay mineral.

The procedure followed to adjust the soil to a pH of 7 and the separation of the calcium saturated soil into aggregate fractions of 0.5-1.0, 1-2, and 2-4.7 mm has been described by Nkedi-Kizza (1979). Each aggregate fraction was packed into acrylic plastic cylinders, 5 cm long and 7.6 cm in diameter. Miscible displacement techniques, similar to those described by Nkedi-Kizza were employed to measure effluent BTC's for three tracers (^{36}Cl, ^3H_2O, and ^{45}Ca) applied simultaneously in one pulse. The BTC's were obtained using 0.001, 0.01, or 0.1 N $CaCl_2$ solutions adjusted to a pH of 7. The electrolyte solutions were spiked with three radioactive tracers, each giving about 5 nCi/ml. The small velocity displacements were carried out first at a concentration of 0.1 N $CaCl_2$ and then followed by 0.01 N and 0.001 N, respectively; the larger flow velocity experiments were run subsequently in a similar order of solution concentrations. All columns had similar bulk densities ρ and saturated water contents θ.

Equation [4] implies that all the soil-water freely participates in the convective-dispersive solute transport process and that all adsorption sites are readily accessible to the solute. In the model developed by van Genuchten and Wierenga (1976) the soil-water phase was partitioned into mobile and immobile regions. Convective-dispersive solute transport was limited to the mobile soil-water region. Solute transfer between the immobile and mobile soil-water regions was assumed to be diffusion-controlled. Solute adsorption-desorption in both regions was considered instantaneous; at equilibrium the relationship between adsorbed and solution concentration was described by a Freundlich equation.

Based on the above conceptualization of the system, the solute transport model may be restated as follows:

$$\beta R \frac{\partial C_1}{\partial T} + (1 - \beta)R \frac{\partial C_2}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial x^2} - \frac{\partial C_1}{\partial x} \qquad [18]$$

$$(1 - \beta)R \frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \qquad [19]$$

where

$$T = \frac{vt}{L} = \frac{v_m t \phi}{L} \qquad P = \frac{v_m L}{D} \qquad v_m = \frac{q}{\theta_m}$$

$$x = \frac{z}{L} \qquad \omega = \frac{\alpha L}{v_m \theta_m} = \frac{\alpha L}{q}$$

$$\phi = \frac{\theta_m}{\theta} \qquad \theta = \theta_m + \theta_{im} \qquad R_m = 1 + \frac{\rho f K_D}{\theta_m} \qquad R = 1 + \frac{\rho K_D}{\theta}$$

$$C_1 = \frac{C_m}{C_0} \qquad C_2 = \frac{C_{im}}{C_0} \qquad \beta = \frac{\theta_m + \rho f K_D}{\theta + \rho K_D} = \frac{\theta_m R_m}{R\theta} = \frac{\phi R_m}{R}$$

The fraction of immobile water (1 - ϕ) surfaces (shown in Fig. 25) illustrate the interaction between aggregate size, flux, and solution concentration on the estimated ϕ. The immobile water (1 - ϕ) seemed to increase with aggregate size and flux for displacements run with 0.001 N or 0.01 N $CaCl_2$ (Figs. 25a, and 25b). However, for displacements run with 0.1 N $CaCl_2$, the immobile water parameter is not sensitive to aggregate size and flux (Fig. 25c). The mobile water content ϕ for a given soil column and solution concentration estimated from BTC's is actually an apparent ϕ, since it varies with flux. Increasing aggregate size at a given pore water velocity increases the diffusion path length, causing incomplete mixing between solutes in the mobile and immobile water regions. This, in turn, causes the solutes to appear early in the effluent. Similarly, a large pore water velocity provides a short residence time available for diffusive mass transfer of solutes into and out of the immobile water regions and yields an early breakthrough of the solute. Therefore, both large aggregates and high pore water velocities would result in large immobile water, if estimated from BTC's (Fig. 25). The effect of solution concentration on ϕ could be attributed to changes that might occur in the proportion of macro- and micropores between aggregates as the solution concentration is varied from 0.1 N to 0.001 N $CaCl_2$. This decrease in concentration would increase the thickness of the electrical double layers such that some macropores in the system become micropores. This would result in an increase in (1 - ϕ). For displacements obtained with the greatest concentration of $CaCl_2$, the estimated ϕ appears to be independent of both particle size and flux.

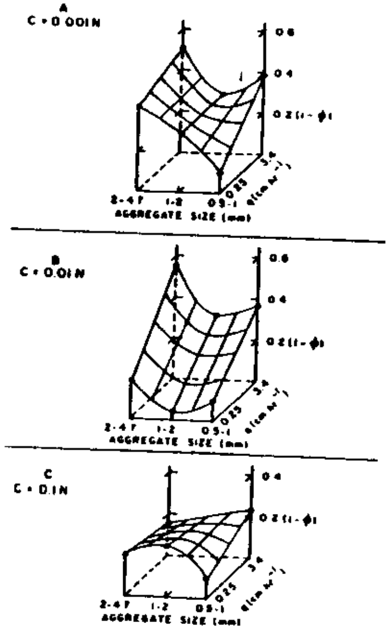

Fig. 25. Immobile water (1 - ϕ) as a function of aggregate size and flux. (a) Immobile water for displacements run with 0.001 N $CaCl_2$. (b) Immobile water for displacements run with 0.0 N $CaCl_2$. (c) Immobile water for displacements run with 0.1 N $CaCl_2$.

Equations [18] and [19] describe all the experimental data well. This particular study revealed that the mobile water fraction ϕ estimated from BTC's is not a constant but a function of aggregate size, pore water velocity, and solution concentration. For small aggregates and for small pore water velocity experiments, ϕ estimated from BTC's was essentially equal to one. A decrease in concentration showed a decrease in ϕ. The mobile water generally decreased also with an increase in both aggregate size and flux. The mobile water was calculated for both ^3H_2O and ^{36}Cl was similar. The diffusive mass transfer coefficient α in this study was a function of aggregate size, pore water velocity, and concentration. The variation of these two parameters ϕ and α with changes in experimental condition (e.g., flux and aggregate size) point out that although Eqs. [18] and [19] are the best available to describe solute transport through aggregated porous media, the model is and always will be an approximation of the physical system if parameters are estimated from BTC's.

Solute Movement in the Field - Solute movement occurs in soils during leaching, crop irrigation, reclamation of soils, and other similar processes. This movement determines the presence or absence of beneficial or detrimental solutes in the soil profile and the quality of water draining from a given area. Many laboratory studies have been undertaken to describe the chemical and physical processes which occur during solute movement. However, the application of laboratory results to actual field situations has been only partially successful because of poorly defined boundary conditions in the field and variability in soil properties with respect to depth and time. Recent results have exemplified the magnitude and degree of variation of solute movement in a field soil. Since it is frequently necessary to predict the volume and quality of water draining from large land areas, knowledge of the spatial variability of solute concentrations and pore-water velocities in these areas is essential. The purpose of this study was to determine the rates of movement of chloride measured at several locations within a field being leached and to compare these rates with those computed from the rate at which water was applied to the field. An analysis is presented of the variation in pore-water velocities and apparent diffusion coefficients observed between locations and depths within the field.

For the steady state water flow conditions of this experiment, which were used to displace a solution of chloride initially applied to the soil surface, the following equation is appropriate:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \qquad [20]$$

where C is the concentration (milliequivalents per liter) of either chloride or nitrate in the soil solution, D is the apparent diffusion coefficient (square centimeters per day), v is the average pore water velocity (centimeters per day), x is the soil depth (centimeters), and t is time (days). We assume that the chloride does not react chemically with the soil and that they are not subject to microbial transformation or assimilation. The value of D depends upon the value of v, the functional relation depending upon the particular pore geometry and the magnitude of v.

For times $0 < t \leq t_1$ the soil was leached steadily with water having a concentration C_0. For times $t < 0$ and $t > t_1$ the soil was leached with water having a concentration C_t. Initial and boundary conditions appropriate for the solution of [20] in view of the large pore water velocities manifested experimentally are

$$\begin{array}{lll} C = C_i & x > 0 & t = 0 \\ C = C_0 & x = 0 & 0 < t \leq t_1 \\ C = C_i & x = 0 & t > t_1 \end{array}$$

Values of v can be estimated directly from the ratio of the steady-state flux of water at the soil surface during infiltration v_0 (centimeters per day) and the average soil water content $\bar{\theta}$ (cubic centimeters per cubic centimeter) or can be estimated from the rate at which the solute is displaced through the soil profile. These estimates of v are designated v_w and v_s, respectively. For the latter an initial estimate can be obtained by the time that it takes to displace the pulse of solute a given distance. Hence v_s is approximated by

$$v_s = x(t_m - 0.5\ t_1)^{-1} \qquad [21]$$

where x is the soil depth at which the maximum value of $(C-C_i)/(C_0-C_i)$ is observed at time t_m. The value of D and the final estimate of v_s are obtained by matching, with the aid of a computer, values of the relative concentration measured at specific soil depths as a function of time with those described by the solution of Eq. [20].

Details of most of the experimental procedure have been given before [Nielsen et al., 1973]. In that publication the spatial variability of a natural soil based on values of hydraulic conductivity measured at six depths in 20 plots randomly located within a 150-ha agricultural field was analyzed. Briefly, twenty 6.5-m-square plots were randomly established over a 150-ha field in which two tensiometers and two soil suction probes were placed in the center of each plot at depths of 30.5, 61.0, 91.4, 121.9, 152.4, and 182.9 cm to follow soil water pressure and solute concentration of the soil solution. Each plot was initially ponded with water until steady-state water content and flow conditions were established throughout the 182.9-cm profile as indicated by the tensiometers.

After steady-state water flow conditions prevailed, 7.5 cm of water containing 219 and 123 meq/l^{-1} of Cl^- and NO_3^-, respectively, were leached through the soil surface. After this solution (C_0 = 219 and 123 meq/l^{-1}) had infiltrated the soil, the soil surface was continuously ponded once again with the original water ($C = C_i$).

Samples of soil solution were extracted from each soil suction probe prior to the addition of the solute-enriched water C_0 and were also extracted once every hour during the day and night in order to measure and delineate carefully the chloride and nitrate concentration distributions as functions of both depth and time.

It can be seen in Fig. 26 where 359 estimates of v_s have been placed in class lengths of 10 cm per day, that the frequency distribution is log-normal having a mode, median, and mean of 4.3, 20.3, and 44.2 cm per day, respectively.

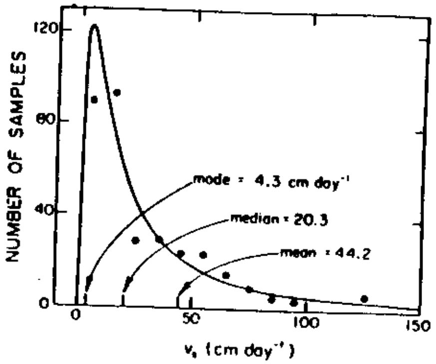

Fig. 26. Frequency distribution of values of the pore water velocity v_s for a class length of 10 cm d^{-1}.

Values of D are similarly log-normally distributed, as illustrated in Fig. 27, with a mode of 4.0, a median of 85.1, and a mean of 367.6 cm^2 per day.

Concentration distributions as a function of soil depth calculated by using the mode, median, and mean values of (D, v) are shown in Fig. 28 for a 7.5-cm pulse of chloride or nitrate solution (C_0) infiltrated and leached to the 90- and 180-cm depths. Relative maximum concentrations for those depths calculated with mode and median values are much too large in comparison with those calculated with the mean values. Moreover, since the mode and median values are less than the mean velocity, the time required for the displacement is substantially overestimated when the former values are used. From a practical viewpoint, it

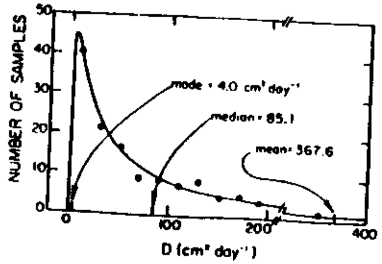

Fig. 27. Frequency distribution of values of the apparent diffusion coefficient D for a class length of 2 cm^{2}d^{-1}.

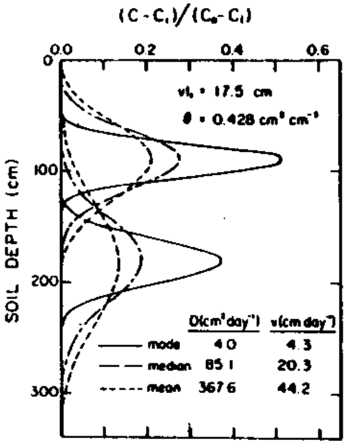

Fig. 28. Concentration distributions calculated with the solution of Eq. [20] for a 7.5-cm pulse of solute C_0 for mode, median, and mean values of D and v.

would be expected that concentration profiles similar to those calculated for the modes would be frequently observed, while indeed, less-pronounced profiles similar to those for the mean and exhibiting even greater dispersion would also be observed and would be displaced relatively quickly through the soil. It should also be pointed out that these extremes in solute leaching can be observed at equal or different depths within a relatively small area.

The results of this study inform us that substantial errors can be made in estimating the flux or the amount of solute passing, for example, below the root zone of a crop by multiplying average values of the flux of water by average values of the concentration of the soil solution. Both average values depend ultimately upon the pore water velocity distribution and its attendant horizontal and vertical spatial variability within the field soil profile. Hence we expect point measurements such as the discharge from drainage tiles, solution samples from suction probes and piezometer wells, and excavated soil samples to provide good indications of relative changes in the amount of solute being transported but not quantitative estimates sufficiently precise to ascertain the amounts of fertilizers or other solutes leached beyond the recall of roots. Only in case of a thorough analysis of the frequency distribution of such measurements would quantitative results be assured.

Next, let us consider different methods to average field observations of the two parameters v and D in the convective-diffusion equation. We explore ramifications of soil variability on averaging salt distributions in the soil profile and on the rate and cumulative amounts of solutes leached from the profile.

In the above experiment, it was found that values of v were log normally distributed with the mean and standard deviation of $\ln v = 3.01$ and 1.25, respectively. Similarly, measurements of D (cm^2/day) were found to be apparently log normally distributed with ln D having a

mean of 4.42 and a standard deviation of 1.74. It was also determined that D was approximately related to v by this equation:

$$D = 0.6 + 2.93\, v^{1.11} \qquad [22]$$

with a correlation coefficient of 0.8. It was further observed that the soil water content θ (cm^3/cm^3) was normally distributed with a mean of 0.428 and a standard deviation of 0.0042. This leads to the expectation that anywhere within the (x, y) plane of the field, a wide valety of solute distributions described by the solution of Eq. [20] will be manifested for the extremely wide ranges of both v and D. Figure 29 shows solute distributions stemming from the leaching of a pulse of salt water for several combinations of v and D. For a pulse leached at an intermediate value of $v(v_0)$ as shown in Fig. 29A and 29 B, the solute is leached with minimal dispersion for the small value of $D(< D_0)$. For the large value of D, the maximum value of c/c_0 is only 0.2 compared with 1.0 for the small value less than D_0. The pulses dispersed at the intermediate value of $D(D_0)$ shown in Fig. 29C and 29D are leached to depths that reflect the magnitude of v at the particular location in the (x, y) plane. For the small velocity less than v_0, the pulse is leached to the shallower depth. The areas under each of the four curves (Figs. 29A-29D) are identical because the simulations were made for equal values of vt_1 regardless of the value of v. Figures 29E and 29F are based upon equal values of t_1, and hence the areas under the curves are proportional to the particular value of v.

The curves shown in Fig. 29 as well as countless others, are each potentially observable in a field or even in a relatively small experimental plot. Suppose only those shown in Fig. 29 had indeed been measured. Had they been measured by sampling at 10-cm intervals, the curves shown in the figure could have been delineated. Had they been sampled at 30-cm intervals, only curve 29B and possibly 29F could have been ascertained. Had the six sites of data been averaged to obtain an "average" profile, the curve in Fig. 30 would have been calculated for the 10-cm interval observations, while the solid circles would represent the 30-cm interval observations.

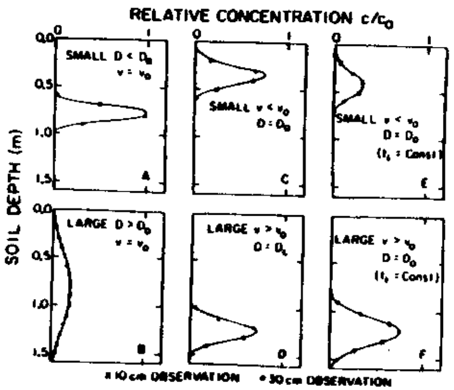

Fig. 29. Relative solute concentration vs soil depth simulated for values of v and D less than, equal to, and greater than values of v_0 and D_0, respectively. For A-D, equal amounts of salt are added; for E and F, intake time is the same with salt added proportional to v.

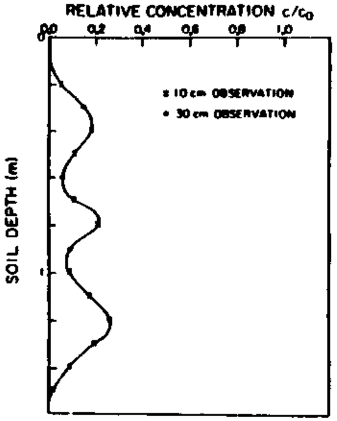

Fig. 30. Average relative solute concentration vs soil depth calculated from the six curves given in Fig. 29.

How is an appropriate average solute concentration profile obtained? In the absence of any information regarding the scale of observation of solute concentrations measured in field soils, we shall assume that v, D, θ, and c are random variables characterized by their relative frequency distributions, and that across a field in the (x, y) plane, their frequency distributions are statistically stationary. Two kinds of solute concentration distributions are of interest. The first is that solute distribution expected at any location within the field at a given time of leaching, and the second is that distribution at a given time obtained by averaging solute distributions from many locations within the field. The former is important because it is commensurate with that solute distribution associated with a single crop plant or a small neighborhood of plants. The latter, which is not necessarily manifested in the root zone of any plant or small neighborhood of plants, is important because it is the indication of an entire field in terms of solute retention and mass emission of solutes below the root zone as a result of leaching.

The solute concentration distribution $c(z, t)$ expected at any location (x, y) within the field may be calculated with the solution of Eq. [20] using values of v and D from their relative frequency distributions considered independently or jointly. The average solute concentration distribution $\bar{c}(z, t)$ expected for the entire field may be calculated from

$$\bar{c}(z, t) = \int_0^{c_0} c\, f(c|z, t)dc, \qquad [23]$$

where $f(c\ z, t)$ is the relative frequency distribution of $c(z, t)$. We shall compute $\bar{c}$ without the simplified parameterization used in Eq. [23], but by Monte Carlo simulation using the measured frequency distributions of D, v, and θ. The step-wise procedure was to:

1) Draw a random value from the normal distribution with mean zero and standard deviation 1;
2) Find random values of $\ln D$ and/or $\ln v$ and θ from their respective statistical distributions given in Table 1 by the equation $y = \beta\sigma + \mu$ where β is the value with mean zero and standard deviation 1, and y is the random value with mean μ and standard deviation, σ;
3) Calculate a random value of c/c_0 from the solution of Eq. [20] using the above values of D, v, and θ for each z and t;
4) Repeat steps 1 through 3 above 2,000 times and calculate the mean value of c/c_0 for each z and t.

Under normal experimental conditions in the field, we would expect too few observations to discern the relative frequency distribution of D, v, or θ, much less the dependence of D upon v. Case I is the solute distribution calculated from mean values of the parameters in a deterministic manner. The calculation describes the average distribution of c/c_0 for any particular location (x, y) in the field. Case II assumes that sufficient observations have been made to allow deterministic evaluation of v and θ with D assumed to be log normally distributed. Case III neglects the spreading of the solute owing to apparent diffusion ($D = 0$). Case IV is that of Case III with the impact of apparent diffusion included. For Case V it is assumed that insufficient observations have been made to ascertain the functional relation between D and v, and hence, their values have been chosen independently. Lastly, Case VI accounts for the spreading of the solute with random values of v associated with Eq. [22]. For each of the above cases, simulations were made for $(t_1 > t)$, corresponding to the continuous leaching of a soil with water having a concentration c_0 (step input) and for $(t_1 > t)$ corresponding to a pulse of solute being leached through the soil profile with solute-free water (pulse input).

Average solute concentration simulated for Cases I and II for $(t_1 > t = 2$ days) and $(t = 2;\ t_1 = 0.4)$ are given in Fig. 31A and 31B, respectively. The curves for Case I, the simplest solution based on average values of v, θ, and D, manifest the sigmoidal and Gaussian $(t = 2,\ t_1 = 50)$ shapes for the step $(t_1 > t = 2)$ and pulse $(t = 2,\ t_1 = 0.4)$ inputs, respectively, commonly measured in laboratory soil columns. The curves for Case II, although

Table 1. Choices of apparent diffusion coefficient, D, water-filled porosity, θ, and pore water velocity, v, for Monte Carlo simulations of mean solute distribution and fluxes.

Case	v	θ	D
	cm/day	cm^3/cm^3	cm^2/day
I	Constant (44.3)	Constant (0.428)	Constant (378)
II	Constant (44.3)	Constant (0.428)	Variable§
III	Variable*	Variable‡	0
IV	Variable	Variable	Constant (378), Variable§
V	Variable	Variable	(independent of v)
VI	Variable	Variable	$0.6 + 2.93v^{1.11}$

* $\ln v \cong N(3.01, 1.25^2)$.

‡ $\theta \cong N(0.428, 0.0442^2)$.

§ $\ln D \cong N(4.42, 1.74^2)$.

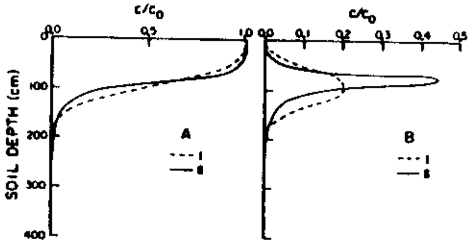

Fig. 31. Relative solute concentration vs soil depth simulated for Cases I and II for a step input of solute (A) and a pulse input of solute (B) for $t = 2$ and $t_1 = 0.4$ days.

the same shapes and occurring at relatively the same soil depths, are more abrupt than those of Case I. Those of Case II were simulated using average values of v and θ with the Monte Carlo procedure for D from its log-normal distribution. Inasmuch as the distribution of D is skewed with a high probability of many values much smaller than the mean, taking as many as 2,000 values of D still gave less spreading of the solute than that of Case I.

The average concentration distributions simulated from the relative frequency distributions of v and θ (Cases III through VI) are considerably different from those of constant v and θ presented above having sigmoidal and Gaussian shapes. For Cases III-VI, the concentration distributions tend to be hyperbolic with no sharply defined solute front or depth to which the solute has been leached. For these latter cases, the spreading of solute averaged across the field is dominated by variations in pore water velocity and not that associated with variations in the apparent diffusion coefficient. This latter statement is supported by comparing the average concentration distributions in Fig. 32 simulated for Cases III ($D = 0$) and IV ($D = 378$). Although the curves for Case IV clearly manifest the impact of the additional mixing associated with the mean value of D, they closely resemble those for Case III for both the step and pulse inputs. When the average concentration is simulated from the relative frequency distribution of D independent of that of v (Case V), the mixing is less than that for Case IV using the mean value of D. When D is related to the pore-water velocity v, the concentration distributions are nearly identical to those for $D = 0$. Compare curves for Case III with those for Case VI. Experimentally measured values of the solute concentration obtained by Biggar and Nielsen (1976) are given by the solid circles in Fig. 31B. (Standard deviation of measured values at 30-cm increments were 0.132, 0.127, 0.153, 0.103, 0.081, and 0.033.) Considering the large magnitudes of the standard deviation of those observations, any one of the simulated distributions in Fig. 31B successfully describes the measured values.

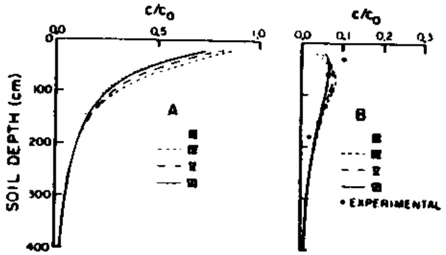

Fig. 32. Relative solute concentration vs soil depth simulated for Cases III through IV for a step input of solute (A) and a pulse input of solute (B) for $t = 2$ and $t_1 = 0.4$ days.

With sufficient observations of the soil-water parameters available to estimate their relative frequency distributions, the leaching of an entire field may be estimated but not necessarily that of a specific site. We expect future field experiments will allow the determination of the scales of observation of v, D, c, and θ. With spatial autocorrelation of those observations known, a simulation or an observation of a solute distribution in the field could then be associated with a small site or known domain in the vicinity of the point (x, y). Without those scales, the extent of the field; or the fraction of the root zone of a single or group of plants characterized by a single observation is not known. With the scales known, the size of the site or domain characterized would allow an additional basis for ascertaining the number of observations to be taken.

To monitor the average solute concentration within a field or to estimate the mass emission of salt leached below the root zone implicitly requires a knowledge of the relative frequency distribution of the pore-water velocity as well as its mean value in order to ascertain when and how often to sample at that depth.

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