

포장에서 물리적 진행과정에 의해  
영향을 받은 물질과 수분의 이동성

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**Mobility of Water and Solute Influenced  
by PHYSICAL PROCESSES in field Soils**

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**ABSTRACT**

The self-diffusion coefficients of chloride and tritiated water ranged from  $4.8 \times 10^{-7}$  to  $7.2 \times 10^{-7}$   $\text{cm}^2/\text{sec}$  and  $5.5 \times 10^{-5}$  to  $1.6 \times 10^{-4}$   $\text{cm}^2/\text{sec}$  for three different depths of soil constituents at about 50 % water content by volume, respectively. Mobility of solute and water was conducted under steady-state flow conditions in a field soil consisting of 70 cm of clay to silty clay over a medium sand. A steady-state water flow conditions was maintained by applying irrigation water at a constant flux of 2cm per day. The water labeled with chloride and tritium was leached into the plot during the steady-state condition for 87 days.

The positions of tritium and chloride as a function of soil depth and the time was measured by extracting samples of the soil solution with suction probes. Extremes in solute displacement occurred at equal and different depths within the plot. An analysis of these measurements indicated the observations of the pore-water velocity and the apparent diffusion coefficient were log normally disturbed. Twenty-four soil suction probes, used to identify the rate at which a solute was displaced in the soil, will yield an estimate of the mean pore-water velocity of this soils within a range of approximately 5% of its true value providing the effects of potential solute-soil interaction are taken into account.

**Key word:** diffusion coefficient, mobility, pore water velocity

## 요 약 문

실험실 내에서 부피비로 약 50% 내외의 수분함량을 가진 3개의 서로 다른 깊이의 토양에서 염소와 중수의 확산계수는  $4.8 \times 10^{-7}$  부터  $7.2 \times 10^{-7} \text{ cm}^2/\text{sec}$  와  $5.5 \times 10^{-5}$  부터  $1.6 \times 10^{-4} \text{ cm}^2/\text{sec}$  였다. 한편, 물과 물질의 이동성에 대한 연구는 중간사로 구성된 토양층 위에 위치하는 점토로부터 미사질 양토에 속하는 약 70cm 깊이의 토양에서 실시되었고, 87일간의 실험기간동안 리터당 15.2ml의 염소와 0.6bq의 중수로 처리된 물을 일정한 유량(2cm/일)으로 관개하였다.

토양의 깊이와 시간에 따른 염소와 중수의 변동위치는 suction probe에 채취된 토양수를 가지고 측정하였는데 실험지 안에서 서로 다른 깊이 또는 동일 위치에서 염소와 중수가 발견되었다. 이러한 실험의 결과로부터 추정컨대 토양수의 유속과 표면확산 계수가 염소와 중수의 분포에 직접적인 영향을 미쳤고 24개의 suction probe에서의 결과는 실질적 물질과 토양의 상호작용의 효과를 나타내는 순수치의 25% 내외에서 평가치를 추정할 수 있었다.

**찾는말:** 확산계수, 이동성, 공극수유속, 염소, 중수

## INTRODUCTION

In order to better manage our lands we need the ability to accurately measure and predict the movement and fate of applied chemicals which occur in soils. The rate at which these chemicals move with percolating water from the soil surface to groundwater is particularly important for determining their potential to pollute the soil and groundwater environment. The mass transport of water and solute in soils takes place through a complex three-dimensional inter-connected network of pores or voids of nonuniform sizes and shapes. Dullien (1979) has grouped pore structure models into two broad categories: (i) those that are based on the arrangement of soil (or solid) particles, which in most cases are assumed to be spherical in shape but of different sizes and (ii) those that are based on shapes, sizes, and arrangements of pores that contain water and

solutes, a continuum approach rather than a geometric approach is generally used to describe mathematically water and solute transport in soils. The continuum approach (macroscopic scale) is adequate for the practitioner interested only in a phenomenological description of water and solute transport processes in soils. The continuum approach fails, however, to provide the insight required in many instances to explain observations that depend on the properties of the pores and the behavior of water and solutes at a molecular scale. Attempts have been made to explain the transport of water and solutes at a microscopic scale, but these approaches have not been completely satisfactory, primarily because physical and chemical measurements within the individual soil pores or voids are not feasible.<sup>9)</sup>

Many laboratory studies have been undertaken to describe the chemical and physical processes that 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. The purpose of this study was to determine the rates of movement of chloride and tritium measured at several locations within a field plot being leached at a constant infiltration rate and to compare these rates with those computed from the rate at which water was applied to the plot. An analysis is presented of the variation in pore-water velocities and apparent diffusion coefficients observed between location and depths within the plot area.

**THEORETICAL**

Fick's law<sup>3)</sup> for steady state diffusion is given as

$$(\Delta Q / \Delta t) = D * A(\Delta C / \Delta x) \dots \dots \dots (1)$$

w

here Q is an amount(g)

t is time(seconds)

D is the diffusivity or diffusion coefficient  
(cm<sup>2</sup>/sec)

A is the cross-sectional area across which the flow takes place(cm<sup>2</sup>)

C is the concentration(g/cm<sup>3</sup>)

x is the distance in the direction of the net movement of ions(cm)

When diffusion takes place through water in a porous system, several geometric and interaction factors must be considered. A steady-state diffusion experiment is difficult to set up, particularly at higher moisture tensions.

Transient diffusion systems can more readily be set up at these moisture tensions. Consequently, Fick's second law<sup>3)</sup>,

$$\partial C / \partial x = De(\partial^2 C / \partial x^2) \dots \dots \dots (2)$$

where De is the effective diffusivity; C' is the concentration of ions per unit volume of soil. In applying equation (2) to the diffusion of ions in soils, it was assumed that: (a) De is independent of concentrations; (b) no chemical or biological reactions takes place to interfere with the diffusion process; and (c) if adsorption of the ions occurs at some point, equal quantities of the same ions are liberated at that point.

If two soil samples of equal cross-sectional area and infinite in length are brought into contact for time t, a solution of equation (2) applicable to this problem is

$$C' = (Co' / 2) \operatorname{erfc} (x / (2(De * t)^{1/2})) \dots \dots \dots (3)$$

with the boundary conditions at t = 0

$$C' = Co' \text{ for } -\infty < x < 0,$$

and

$$C' = 0 \text{ for } 0 < x < \infty$$

In this procedure the total quantity of ions diffused is the most readily measured.

Equation describing the concentration of a solute in a porous medium during displacement and leaching have been derived and evaluated by many researchers. For steady-state flow conditions the following equation may be used to describe solute movement:

$$\partial C / \partial x = (D \partial^2 C / \partial x^2) - v(\partial C / \partial x) \dots \dots (4)$$

where C is the concentration(meq/liter) in the soil solution. D is the apparent diffusion

coefficient ( $\text{cm}^2$  per day) representing both hydrodynamic dispersion as well as molecular diffusion.  $v$  is the average pore-water velocity (cm per day).  $x$  is the soil depth (cm) measured positively downward, and  $t$  is time (days). Initially there was some chloride present in the soil solution, but no measurable tritium. Leaching solution, enriched with chloride and tritium, was applied at a constant rate over the soil surface. Assuming a semi-infinite, uniform soil profile input of solute, the boundary and initial condition are:

$$\lim_{x \rightarrow 0^+} (vC - D \frac{\partial C}{\partial x}) = vC_0 \dots 0 < t < t_1 \dots (4a)$$

$$\lim_{x \rightarrow 0^+} (vC - D \frac{\partial C}{\partial x}) = 0 \dots t \geq 0 \dots (4b)$$

$$C = C_i \dots x > 0, t > 0 \dots (4c)$$

$$\lim_{x \rightarrow \infty} (C(x, t)) = C_i \dots (4d)$$

may be estimated by matching values of the relative concentration measured specific depths as a function of time, with those determined from the solution of Lindstrom et al. For layered soils, values for  $D$  and  $v$  may be estimated by matching observed concentration-time distribution at specific soil depths with those obtained with a numerical model (van Genuchten and Wirenga, 1974) which allows for depth dependent values of  $D$ ,  $\theta$ , and  $v$ . Soil variability manifested horizontally: thus only values of  $D$  and  $v$  obtained by the solution given by Lindstrom et al. are presented.

## MATERIALS AND METHODS

The experiment was conducted on an  $8 \times 8$  m plot at the Pendleton Experimental Research

Center at Clemson University, South Carolina. For the analysis of soil physical and chemical properties and diffusion experiment, soil samples, collected from the each layer of soil depths, were air-dried and ground to pass the 2-mm sieve. Diffusion of chloride and tritiated water through soil were measured in diffusion cells under laboratory conditions using the methods of Phillips and Ellis. The diffusion system consisted of a half cell containing soil treated the labeled chemicals in contacted with a half-cells with untreated soil. After a given time the half-cell were separated and the labeled chemical content determined in each half-cell.

For the transport experiment, the plot was separated from the surrounding soil with polyethylene plastic extending to a depth of 75 cm below the soil surface. To ensure a uniform steady-state infiltration flux of 2 cm per day, trickle lines were installed 30 cm apart with emitters placed on the lines at 30 cm intervals resulting in a 30-cm square grid system. Irrigation water was supplied to the trickle lines through two header lines which were connected to a positive displacement pump. Both the trickle lines and the pump were calibrated before installation. During the part of the leaching experiment this water was labeled with chloride and tritium by adding  $\text{CaCl}_2$  and tritiated water to the irrigation water in a large tank outside the plot, resulting in an average chloride concentration of 15.12 meq per liter and an average tritium activity of  $0.6 \mu\text{Ci}$  per liter. the soil was initially leached for 42 days with unlabeled water to equilibrate chloride concentrations of the soil and irrigation water and to attain steady-state flow conditions in the

soil profile. Leaching with labeled irrigation water took place for 36 days followed by 51 days of leaching with unlabeled water.

The soil within the plot consisted of 15 cm of clay over 50~60cm of silty clay over a variable amount of silty loam. The silty loam changed rather abruptly into a medium to fine sand. Three sampling sites were established within the plot. At site 1, suction probes with porous cups (2.5 cm diameter and 5 cm long) were installed at 15.0, 37.5, 49.0, 66.0, 72.5, 90.5, 119.0, and 151.5 cm depth. Suction depth at site 2 were 31.5, 36.5, 48.9, 63.5, 75.9, 92.5, 119.0, and 146.5 cm. At site 3, suction probes were installed at 19.0, 33.5, 46.0, 63.5, 77.5, 91.0, 119.5, and 149.5 cm depths. Soil solution samples were extracted 24 locations (3 sites by 8 soil depths) intermittently before, during, and after the addition of the labeled water in order to measure the chloride and tritium concentration distributions as functions of soil depth and time. Triplicate tensiometers were installed in the center of the plot at depths of 30, 60, 90, 120, and 150 cm below the soil surface. Two neutron access tubes were installed close to the tensiometers. Neutron probe and tensiometer readings were taken throughout the experiment to verify that steady-state soil water conditions prevailed within the profile during the course of the experiment. Chloride and tritium concentrations in the soil solution samples were determined on a Buchler-Cotlove Chloridometer and a Packard Tri-Carb Liquid Scintillation Counter, respectively.

## RESULTS AND DISCUSSION

The distribution of soil water content with

depth measured during steady-state infiltration of 2 cm per day is presented in Fig. 1. The hydraulic gradients and the values of the hydraulic conductivity calculated between successive depths from tensiometer at assuming a flux of 2 cm per day are also shown in Fig. 1. Hydraulic gradient values for uniform soil under steady-state conditions are generally very near unity. The large deviations from unity, particularly between the 45- and 90-cm depths, demonstrate clearly the non-uniform character of this soil profile.

After soil solution samples were withdrawn from each suction probes and analyzed for chloride and tritium, the relative concentration values  $(C-C_i)/(C_0-C_i)$  were plotted as a function of time of leaching for all twenty four probes. The variability of solute movement within the field plot is implied in Fig. 2a, 2b, and 2c. These graphs, representative of other data from this experiment (R. M. van der Pol), clearly

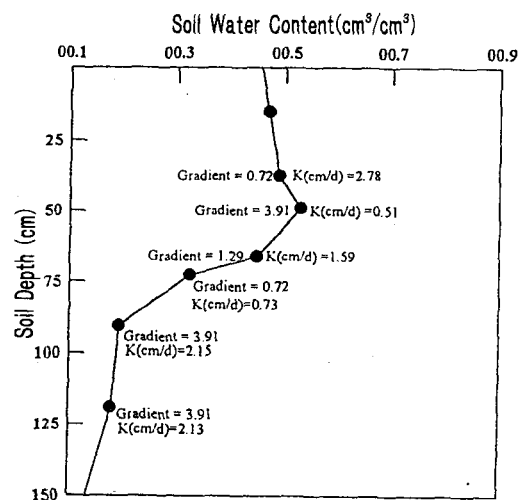


Figure 1. Distributions of soil water content (neutron measurement), hydraulic gradient(tensiometer), and hydraulic conductivity  $K$  (calculated) during steady-state infiltration flux of water(2 cm per day).

show the variation in chloride and tritium movement between depth and location. For example, the chloride distribution curves given in Fig. 2a and 2c appear at approximately the same time. Had the soil been uniform, the chloride distribution for the 63.5 cm depth should have appeared later than that for the 33.5 cm depth(Fig. 2b) is delayed considerably (about 16 days), compared to those for the 33.5- and 63.5-cm depths. In addition to the above variations, it should be noted that the chloride and tritium distribution curves are separated from each other (Fig. 2). This separation, to be

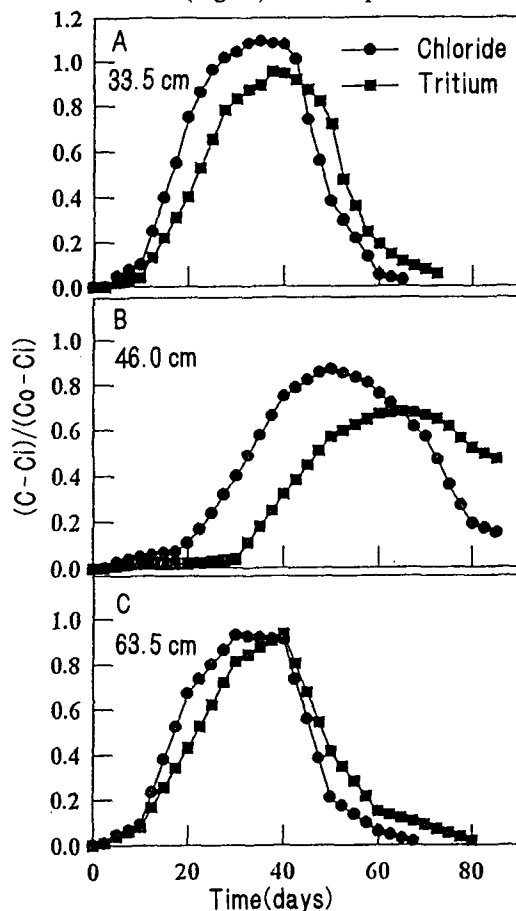


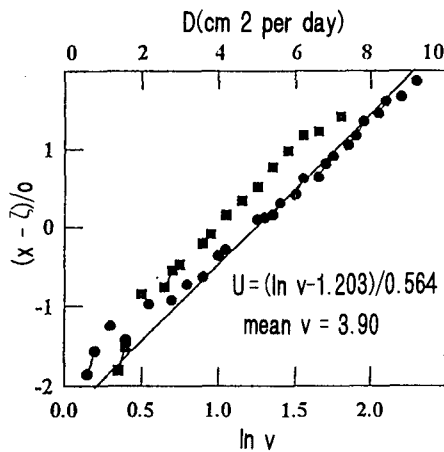
Figure 2. Relative chloride and tritium concentrations measured at a depth of (a) 33.5cm, (b) 46.0cm, and (c) 63.5 cm.

discussed later, could be caused both by adsorption or isotope exchange of tritium.

The relative concentrations of chloride and tritium were plotted for each probe and the corresponding values of  $v$  and  $D$  for each solute were determined by curve fitting with the solution of Eq. [1] and [2] provided by Lindstorm et al. The frequency distributions of the observed values for  $v$  and  $D$  were then determined using the procedure suggested by Biggar and Nielsen(1976). Values of the mean and estimates of the variance for  $v$  and  $D$  were then determined.

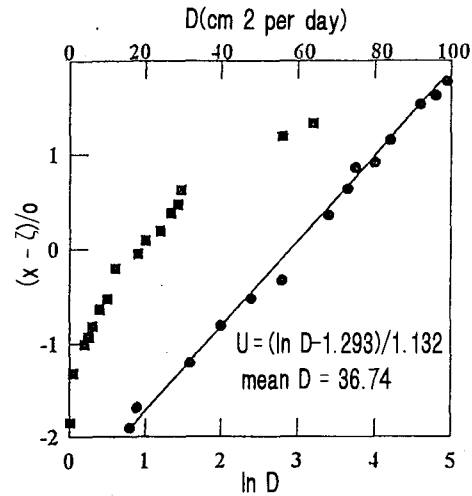
It can be seen from the fractile diagram in Fig. 3. when the probability units  $(x-\xi)/\sigma$ , with  $x$ ,  $\xi$ , and  $\sigma$  representing  $v$  and the mean and standard deviation of  $v$  from the 24 chloride samples, are plotted vs.  $v$ (Square box), the resulting relationship appears nonlinear. Therefore, the observed values of  $v$  are not normally distributed. By plotting the probability units vs.  $\ln v$  as shown in Fig. 3. (solid circles), it can be seen that the probability units appear linearly related to  $\ln v$ , and hence, we conclude that the observed values of  $v$  are better described as a log-normal distribution. For this log-normal distribution, the mean of  $v$  stemming from the chloride samples is  $\exp(\xi + 0.5\sigma^2)$  and has a mean value of 3.90 cm per day. Based on the estimated value of  $s$  equal to 0.564, the probability is 0.95 that the true mean value of  $v$  lies between 3.12 and 5.23 cm per day. The volumetrically measured water infiltration flux at the soil surface can be compared with the above mean values by dividing the measured water flux at the soil surface (2 cm per day) by the average soil water content between the soil surface and the

depth of each sampling probe. The average value of the pore-water velocity for all depths thus estimated from the volumetric infiltration rate was 4.66cm per day, which is within the above-mentioned confidence interval of  $v$  based on the chloride samples.



**Figure 3.** Fractile diagram of pore - water velocity for chloride. Probability unit  $(x - \xi)/o$  are plotted vs.  $v$ (square box) and  $\ln v$ (solid circles) for  $x = v$  and  $x = \ln v$ , respectively.

Figure 4 presents a fractile diagram of the 24 observed values of the apparent diffusion coefficient for chloride. The mean value of  $D$  was calculated to be 36.74  $\text{cm}^2$  per day assuming log-normal distribution, with an expected range of mean value between 22.2 and 85.0  $\text{cm}^2$  per day at the 0.95 probability level. Usually chloride movement is affected somewhat by anion exclusion whereas tritium movement is affected by adsorption or isotopic exchange. A through, in situ analysis of these processes was not possible owing to the spatial variability of the soil(manifested by the range of possible mean values of  $v$  given above). However, batch-type shaking experiments were conducted in the laboratory utilizing soil



**Figure 4.** Fractile diagram of apparent diffusion coefficient  $D$  for chloride. Probability unit  $(x - \xi)/o$  are plotted vs.  $D$ (square box) and  $\ln D$ (solid circles) for respective  $x = d$  and  $x = \ln D$ .

samples removed from each site and depth within the plot.

Twenty four 25-g soil samples were shaken for 24 hours in 25 and 125 ml of solution containing 4.0 or 26.0 meq Cl per liter and 0.2 and 2.0  $\mu\text{Ci}$  tritium per liter. After shaking, the soil was filtered and the amounts of chloride and tritium remaining in solution were determined. Chloride measurements indicated that there was a small amount of exclusion at low concentrations (4.0 meq per liter) while exclusion was essentially zero at higher concentrations (26 meq per liter). Hence, assuming chloride exclusion to be negligible, we can utilize the solutions of Eq. [1] and [2] to yield appropriate values of  $v$ . However, in case of tritium, regardless of concentration or volume of solution added, the amount of tritium remaining in the filtered solution was 0.96 of its original value. Since the tritium concentration

distributions measured in the field as well as in the above laboratory tests indicated that tritium was adsorbed or exchanged on the soil particle surfaces, Eq. [1] modified to include the solute-soil interaction is:

$$\frac{\partial C}{\partial t} + \frac{\partial S}{\partial t} = D(\frac{\partial^2 C}{\partial x^2}) - v(\frac{\partial C}{\partial x}) \quad [5]$$

or

$$\frac{\partial C}{\partial t} = (D(1+R))(\frac{\partial^2 C}{\partial x^2}) - (v(1+R))(\frac{\partial C}{\partial x}) \quad [6]$$

where *s* is the amount of solute associated with the solid phase assumed always to be linearly related to *C* (*S*=*RC*) for both sorption and desorption.

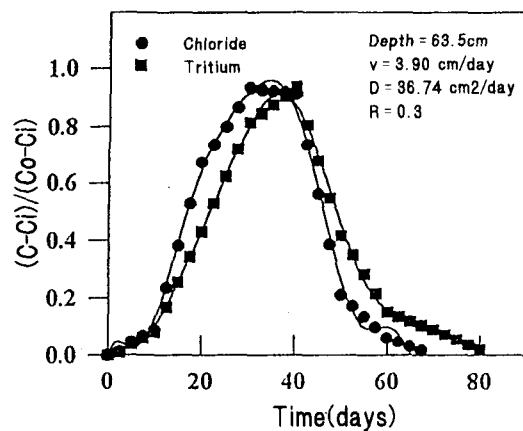
By fitting the solution of Eq. [4] subject to Eq. [2] with the tritium concentration distributions in a manner identical to that for the chloride distributions, and using a value of *R*=0.3, the observed values of *v* and *D* (Eq. [4]) were also found to be log-normally distributed with mean values of 3.78 cm per day and 36.65 cm<sup>2</sup> per day, respectively. At 0.95 probability their respective ranges were 2.99 to 5.15 cm per day and 22.4 to 80.9 cm<sup>2</sup> per day. Because these mean values of *v* and *D* for tritium and their expected ranges are nearly equal to those obtained for chloride, we conclude that the movement of both solutes has been adequately reconciled with that of water through the above equations.

Figure 5 compares chloride data (closed circle) and tritium(closed square) from two soil solution probes at the 63.5-cm soil depth with calculated concentration distributions. Calculated chloride concentration distributions were based on a mean value for *v* of 3.9 cm per day and a mean value for *D* of 36.7 cm<sup>2</sup> per day. Tritium

concentration distributions were calculated with the same values for *v* and *D*, and a value for *R* = 0.30. These concentration distributions represent the manner in which the solute is expected to move through the entire plot based on 24 observations to account for spatial variability within the plot. Distributions at other depths using the same three values of *v*, *D*, and *R* can be calculated similarly.

**CONCLUSION**

Self-diffusion coefficients measured from the diffusion cell significantly differs from the apparent diffusion coefficients observed from field experiment, indicating exclusion of anion and ion exchange for tritium influenced the effective diffusion coefficient. On the other hand, multiplying the flux of water by the solute concentration in the soil solution is a calculation commonly used to estimate the flux of solute within a soil profile. However, if values of *v* and *D* are log-normally distributed,



**Figure 5.** Measured and calculated chloride(circle) and tritium (square) relative concentrations at 63.5 cm. Calculated values are based on *v* = 3.9 cm/d and *D* = 36.7 cm<sup>2</sup>/d, and for tritium *R* = 0.3.



as was shown in this experiment, substantial errors can be made when estimating the amount of solute leaching past a given soil depth. This study shows that extremes in solute displacement rates can and do occur at equal or different depths within an 8-m square field plot. Because average values of the solute concentration and the soil water flux at any soil depth depend upon the pore-water velocity distributio which is also affected by the spatial variability of the soil. Reliable estimates of their mean value can be ascertained only after a through analysis of the frequency distribution of such measurement.

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