

Measurement of Field Soil Hydraulic and Solute Transport Parameters

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ABSTRACT

Agricultural chemical presence in groundwater has drawn attention toward transport processes occurring in soil. Hydraulic conductivity (K) and water-holding capacity of a soil have great influence on water flow and solute transport. However, much of the chemical transport to groundwater can occur through preferential flow pathways. The simplified, preferential flow, mobile-immobile model partitions the water content (θ) into mobile (θ_m) and immobile (θ_{im}) domains, with solute exchange between the domains characterized by the mass-exchange coefficient (α). In this study a sequential tracer application technique was used and K , θ , θ_m , and α were estimated for a series of pressure heads ($H = 10, -30, -60, \text{ and } -150 \text{ mm}$). This method uses a tension infiltrometer to measure both hydraulic and solute transport parameters in situ. The study took place in a no-till corn (*Zea mays L.*) field mapped as a Harps series soil (fine-loamy, mixed, mesic Typic Calciaquoll). Unsaturated values of θ and K were distinct from the saturated values. Similarly, though less clear cut, distinctions between saturated and unsaturated values of θ_{im} , immobile water fraction (θ_{im}/θ), and α were observed. The medians of θ for the sequence of decreasing H values were 0.40, 0.34, 0.34, and $0.33 \text{ m}^3 \text{ m}^{-3}$. The median K values for the same sequence of H were 108, 1.69, 1.51, and $0.72 \mu\text{m s}^{-1}$. The median θ_{im}/θ values for the H sequence were 0.40, 0.28, 0.25, and 0.39. The median values of α for the H sequence were 0.59, 0.015, 0.0028, and 0.0029 h^{-1} . A strong correlation between α and H suggests a velocity dependence of α .

CONCERN about groundwater contamination by agricultural chemicals has led to an examination of the solute transport processes operating in the root zone of field soils (National Research Council, 1989). These processes are greatly influenced by the hydraulic and preferential flow properties of field soil.

Methods based solely on the assumption of flow through total volumetric water content and use of the advective-dispersive model do not always accurately describe mass transport. Many studies have shown that water and chemicals can move through preferential flow pathways (Ehlers, 1975; Thomas and Phillips, 1979; Priebe and Blackmer, 1989). In such nonequilibrium cases, preferential flow is exemplified by asymmetrical breakthrough curves that display both early breakthrough and a tailing or continuing late arrival of solute. In the field, McKay et al. (1993) asserted that preferential flow regions "dominate groundwater flow and greatly increase the rapid lateral and vertical migration of contaminants."

Methods that partition the flow of chemical and water into active and nonactive transport regions can sometimes better describe solute transport in both packed and undisturbed soil columns in the laboratory (Rao et al., 1980; van Genuchten and Wierenga, 1977; Nkedi-Kizza et al., 1983). For instance, the mobile-immobile model simply divides solute transport into two domains. This model was first conceptualized in petroleum engineering by Coats and Smith (1964) and was later expanded and applied to transport in soil columns by van Genuchten and Wierenga (1976, 1977). The mobile-immobile model separates θ into a mobile domain (θ_m) and a complementary θ_{im} . The θ_m contains solute and water that are moving through the soil, whereas θ_{im} contains solute and water that are essentially stagnant. Solute is transported in the mobile domain as an advective-dispersive process, and a diffusive process exchanges solute between θ_m and θ_{im} . The diffusive mass transfer is considered a first-order process and is simply characterized by α .

The mobile-immobile model is popular because of its simplicity and an improved capability in describing preferential flow (van Genuchten and Wierenga, 1976, 1977). Although it has been widely used to describe solute transport in laboratory situations, there have been many fewer applications to field soil. Indeed there exists a need to measure the mobile-immobile parameters at the field scale (Vanclouster et al., 1992). Recent techniques that employ the tension infiltrometer have made it possible to estimate preferential flow parameters in the field (Clothier et al., 1992; Jaynes et al., 1995). These techniques are useful because the tension infiltrometer enables determination of the hydraulic parameters. The Jaynes et al. (1995) technique uses the tension infiltrometer to apply a series of tracers to the soil surface to estimate θ_{im} and α . Casey et al. (1997) used this method in the field to estimate θ_{im} and α values. At a pressure head of -30 mm , they found θ_{im}/θ to range from 0.40 to 0.95 and α to range from 0.01 to 0.3 h^{-1} in a single field soil type.

Laboratory studies on artificially packed soil columns have shown that α and θ_{im} can depend on various factors such as soil water velocity or θ (Nkedi-Kizza et al., 1983; van Genuchten and Wierenga, 1977; Gaudet et al., 1977; Kookana et al., 1993). Clothier et al. (1995) found θ_{im} constant throughout a pressure head range of -30 to -150 mm under field conditions. Also under field conditions, Angulo-Jaramillo et al. (1996) found θ_{im} as well as θ_{im}/θ to decrease as the mean θ decreased.

The objectives of this study were to use the Jaynes et al. (1995) method to estimate θ_{im} and α through a range of H values from 10 to -150 mm in a no-till field soil and to evaluate the behavior of the solute transport parameters in these various hydraulic regimes. Additionally, hydraulic properties of the soil were deter-

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mined using the tension infiltrometer. The measurements of this study were made in the top few centimeters of soil where surface infiltration critically influences runoff and establishes transport processes and transport in the subsoil and beyond.

MATERIALS AND METHODS

Field research took place in 1995 during the last week of June and the first two weeks of July, near Ames, IA. Hydraulic properties of the soil were determined in the first week of the experiments, and the mobile-immobile solute transport parameters were determined in the following two weeks. The experimental site is mapped as a Harps series soil in a no-till corn field. Harps soils are derived from glacial till. Forty measurement sites were located on a rectangular grid. The grid region consisted of four adjacent corn rows, 0.75 m apart, with 10 measurement sites, 0.75 m apart, within each corn row. The separation between the measurement sites varied slightly as a result of irregular spacing of corn plants and rows.

During the first week of experiments, infiltration rates were measured at all 40 sites for a sequence of H values of 10, -30, -60, and -150 mm for each site. This sequence was used to facilitate faster infiltration rates for the lower H values (Logsdon et al., 1993). An automated ponded infiltrometer (Prieksat et al., 1992) was used to determine the saturated infiltration rate, and an automated tension infiltrometer (Ankeny et al., 1988) was used to determine the unsaturated infiltration rates. The base diameters of both the ponded and the tension infiltrometers were 76 mm. The surface of the soil was leveled to ensure good hydraulic contact between the infiltrometer disk and the soil surface. Infiltration was observed for 25 min at each H in the sequence, and the infiltration volume was automatically recorded every 15 s. If steady state was not established with the 25-min interval, a second 25-min measurement interval was done (Logsdon and Jaynes, 1993). At the completion of the sequence of infiltrations, the infiltrometer was removed and a brass cylinder (diameter = 72.5 mm and height = 25.5 mm) was pressed into the center of the infiltration site until the top rim was even with the soil surface. This was done at all 40 sites to mark the exact infiltration area for future tracer application and to sample the soil at the completion of the pending tracer experiments. The ring aided in quick sampling of the soil, while no cracks or compaction were observed in the soil.

The hydraulic conductivity, K , was determined exactly from Logsdon and Jaynes (1993):

$$\ln(K) = H/\lambda_c + \ln[K(0)] \quad [1]$$

where λ_c is the macroscopic capillary length and $K(0)$ is the fitted saturated conductivity at $H = 0$ mm. The inverse macroscopic capillary length ($1/\lambda_c$) is a constant that reflects the slope of $\ln(K)$ as a function of H (White and Sully, 1987). Logsdon and Jaynes (1993) assumed $1/\lambda_c$ to be constant for $H \leq 0$ mm. Both $1/\lambda_c$ and $K(0)$ were estimated from the Logsdon and Jaynes (1993) nonlinear regression technique using the following expression:

$$q(H)/(\pi R^2) = K(0) \exp(H/\lambda_c) + 4K(0) \lambda_c \exp(H/\lambda_c)/(\pi R) \quad [2]$$

where q is the measured steady-state infiltration rate at H , and R is the base radius of the infiltrometer (38 mm).

To calculate K at $H = 10$ mm from Eq. [1], $K(0)$ and $1/\lambda_c$ were estimated from Eq. [2] using a two-point regression between q values measured at $H = 10$ and -30 mm. To calculate the unsaturated K values from Eq. [1], $K(0)$ and

$1/\lambda_c$ were estimated from Eq. [2] using a three-point regression between q values measured at $H = -30, -60,$ and -150 mm (Logsdon and Jaynes, 1993). Only the negative H values of $K(0)$ and $1/\lambda_c$ were reported. The hydraulic conductivity was calculated using the two regressions because K decreases abruptly within a small range of H near $H = 0$ mm (Mohanty et al., 1997). Also, the infiltration rates at zero or positive pressure heads are typically much faster than at negative pressure heads and reflect the contributions of flow caused by large biopores, cracks, or tillage-caused packing voids not representative of the soil matrix (Clothier and Smetten, 1990).

After the hydraulic measurements were completed at all 40 sites, the Jaynes et al. (1995) sequential tracer application technique was done at these same 40 sites. The sequential tracer technique was replicated 10 times for each of the four H values (10, -30, -60, and -150 mm), totaling 40 tracer application areas. The pressure head at which the Jaynes et al. (1995) method was used was randomized in time and placement among the 40 measurement sites.

A suite of fluorobenzoate tracer solutions was sequentially infiltrated at each location as prescribed by Jaynes et al. (1995) and Casey et al. (1997). The fluorobenzoate tracers have been shown to have nearly identical transport characteristics in soil and they are easily extracted from soil for analysis (Bowman, 1984; Bowman and Gibbens, 1992; Benson and Bowman, 1994; Jaynes, 1994). The tracer mixtures were composed of a variation of KCl, 2,6-difluorobenzoate, pentafluorobenzoate, *o*-trifluoromethylbenzoate and 2,3,6-trifluorobenzoate. The order of tracer application was varied so that any error caused by nonidentical tracer transport, recovery, and analysis would be lessened. Four tracer application orders were randomized in time and placement among the 40 sites.

Before any of the tracer solutions were applied, steady-state infiltration was established with a 4 mmol L⁻¹ solution of KCl. Steady-state infiltration was assumed to be achieved after application of the KCl solution overnight (approximately 8 h). After the 4 mmol L⁻¹ KCl solution reached steady-state infiltration, the first tracer solution was applied at the same H . This solution was composed of 3 mmol L⁻¹ KCl and 1 mmol L⁻¹ of the first benzoate tracer. The first tracer was allowed to infiltrate for some time before the second tracer was applied. Tracer solutions were changed after about 0.01 to 0.02 L of solution had infiltrated. The second tracer was applied in a solution formulated of 2 mmol L⁻¹ KCl, 1 mmol L⁻¹ of the first tracer, and 1 mmol L⁻¹ of the second tracer. Again, the second tracer was allowed to infiltrate before the third tracer was applied. The third tracer was applied in a mixture of 1 mmol L⁻¹ KCl, 1 mmol L⁻¹ of the first tracer, 1 mmol L⁻¹ of the second tracer, and 1 mmol L⁻¹ of the third tracer. After the third tracer infiltrated, the final tracer was added. The final solution was composed of 1 mmol L⁻¹ of the first tracer, 1 mmol L⁻¹ of the second tracer, 1 mmol L⁻¹ of the third tracer, and 1 mmol L⁻¹ of the fourth tracer. The application time of the final tracer solution was long enough that the advancing front of all the tracers was well below the sampling depth. This was the time needed to infiltrate approximately 0.02 L of tracer solution. Total application times for the tracer sequence ranged from 0.17 h at $H = 10$ mm to 2.37 d at $H = -150$ mm. Clothier et al. (1995) determined that an infiltration depth of 25 to 30 mm would be sufficient when sampling at a depth of approximately 20 mm; we infiltrated 30 mm and sampled <10 mm. The total electrolyte concentration of each tracer mixture was kept constant (at 4 mmol L⁻¹) by reducing the amount of KCl in each solution. Mixing the tracers in the aforementioned manner resulted in the longest application for the first tracer, the second longest application for the second tracer, and so on for the following two tracers.

The procedures for determining α and θ_{im} at the positive and negative H values were similar, except that a tension infiltrometer was used for negative H values and a ponded infiltrometer was used for $H = 10$ mm. Also, an aluminum ring (diameter = 76 mm, height = 30 mm) was pressed into the soil about 5 mm to prevent lateral movement and to allow the ponding of 10 mm of solution at $H = 10$ mm. The aluminum ponding ring was large enough that it encircled the brass sampling ring in the soil. Having the brass sampling ring in the soil prior to the tracer application helped in the rapid exhuming of the soil sample. Rapid exhuming was especially important at the higher H values because the tracer and water tended to drain quickly. After the soil was sampled, the soil and the brass ring were weighed and a subsample was scraped from the top. The subsample ranged in thickness from 5 to 10 mm. This subsample was sealed in a 100-mL Erlenmeyer flask and weighed, and the remaining soil sample was sealed in a plastic bag to prevent evaporation. The surface subsample was used to determine the tracer concentrations and the rest of the soil was oven dried for water content and bulk density measurements.

Soil samples were taken to the laboratory for tracer analysis, θ , and bulk density measurements. Extractions were done on the 5- to 10-mm surface subsample using approximately 1:1 soil/distilled water mixtures. The extraction mixtures were shaken for 5 min on a wrist shaker and allowed to settle for 5 min. The settled solutions were then decanted through no. 40 filter paper into scintillation vials. After filtration, concentrated CaSO_4 was added to each extract as a flocculating agent, and then the extract was centrifuged at 4000 rpm for 10 min. After centrifuging, the samples were decanted again through a no. 40 filter.

The extracts and input solutions were analyzed for the fluorobenzoate tracer concentrations on a Dionex Series 4500i ion chromatograph (West Mont, IL) according to the method described by Bowman and Gibbens (1992) and Jaynes et al. (1995). For the fluorobenzoates, a SAX column (Regis Chemical Co., Morton Grove, IL)¹ with 30 mM KH_2PO_4 , adjusted to a pH of 2.65 with H_3PO_4 , and 20% acetonitrile (v/v) as the eluting solution was used. The flow rate was 1 mL min^{-1} , and an ultraviolet detector was used with the detection wavelength set to 205 nm.

Immobile water contents and α values were determined using the following expression (Jaynes et al., 1995):

$$\ln(1 - C/C_0) = -\alpha t/\theta_{im} + \ln(\theta_{im}/\theta) \quad [3]$$

where C is the resident tracer concentrations measured in the extracts, C_0 is the input tracer concentrations, and t is the tracer application time. Least sum-of-squares regressions were done for $\ln(1 - C/C_0)$ vs. t . Immobile water contents were calculated from the fitted intercept $[\ln(1 - C/C_0)]$ and the directly measured θ values. The mass-exchange coefficient was found by the fitted slope $(-\alpha/\theta_{im})$ multiplied by $-\theta_{im}$. Time adjustments were not done here as they were done in the Casey et al. (1997) study because the sampling depth was much smaller.

The values of θ_{im} , α , K , λ_c , and θ were evaluated statistically for normal distributions, significant differences, and correlations. Normal and lognormal distributions of these values were tested using a Kolmogorov statistical test. To determine similarities between groups of values at each H , analyses of variance were done at a 0.05 error level. Also, analyses of variance were done to statistically compare the q values measured during the hydraulic measurements and the q values measured

during tracer experiments. Nonparametric Spearman rank correlation tests were used, because the distribution of these values was not readily specified (Steel and Torrie, 1980).

RESULTS AND DISCUSSION

Hydraulic Properties

A soil water characteristic curve in the range close to saturation showed little change in θ below $H = -30$ mm (Fig. 1). The medians and ranges of the θ values were 0.40 (0.37–0.49), 0.34 (0.32–0.39), 0.34 (0.30–0.38), and 0.33 (0.30–0.37) $\text{m}^3 \text{m}^{-3}$ for the corresponding H values of 10, -30 , -60 , and -150 mm.

Water content values at $H = -30$, -60 , and -150 mm were not significantly different at the 0.05 level, and θ values at $H = 10$ mm were significantly higher. This suggests that there was a separation in the pore-size distribution between larger pores at $H = 10$ mm and smaller pores at $H < 10$ mm. At $H = 10$ mm, there were large water-filled pores resulting in higher θ values. As the H decreased below 0 mm, the larger pores drained, resulting in lower θ values. Also, the inflection inferred between $H = 10$ mm and $H = -30$ mm in Fig. 1 suggests that there was a clear separation between flow in the macropore and mesopore regions (Jarvis and Messing, 1995). The separation of water flow into macropore and mesopore regions also suggests that there might have been a separation of solute transport into slow and fast flow domains.

The medians and ranges of K values for the 40 sites (Fig. 2) were 108 (11.2–396), 1.69 (0.09–6.88), 1.51 (0.08–4.35), and 0.72 (0.02–1.79) $\mu\text{m s}^{-1}$ for the respective H values of 10, -30 , -60 , and -150 mm. Infiltration rates varied from the time of the hydraulic property measurements to the time of the solute transport measurements. The infiltration rates during the time of the hydraulic measurements were significantly different at a 0.05 level from those measured during tracer application. The observed infiltration rates from the tracer application were both higher and lower than the previously measured values. Logsdon (1993) and Logsdon and Jaynes (1996) found that infiltration rates varied temporally with soils of the same association and parent material as the current study.

The hydraulic conductivity measurements for $H = -30$, -60 , and -150 mm were not significantly different at a 0.05 level, and were lower than the K values at $H = 10$ mm. Between $H = 10$ and -30 mm there was a large decrease in the median K by nearly two orders of magnitude. The $\ln(K)$ – H relation (Fig. 2) showed K decreasing log-linearly from $H = -30$ to -150 mm with a change of slope between $H = 10$ to -30 mm. Similar to the water characteristic curve (Fig. 1), the break in linearity of the $\ln(K)$ – H function (Fig. 2) further suggested a separation of flow into macropore and mesopore regions (Scotter and Ross, 1994). The change in slope between $H = 10$ and -30 mm in Fig. 2 was partly caused by the method of determining the K values (Logsdon and Jaynes, 1993), in which two separate regressions were used to get the saturated and unsaturated K values. Nonetheless, there still existed a notable change between the unsaturated and saturated K values

¹ Names are necessary to report factualness on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may be suitable.

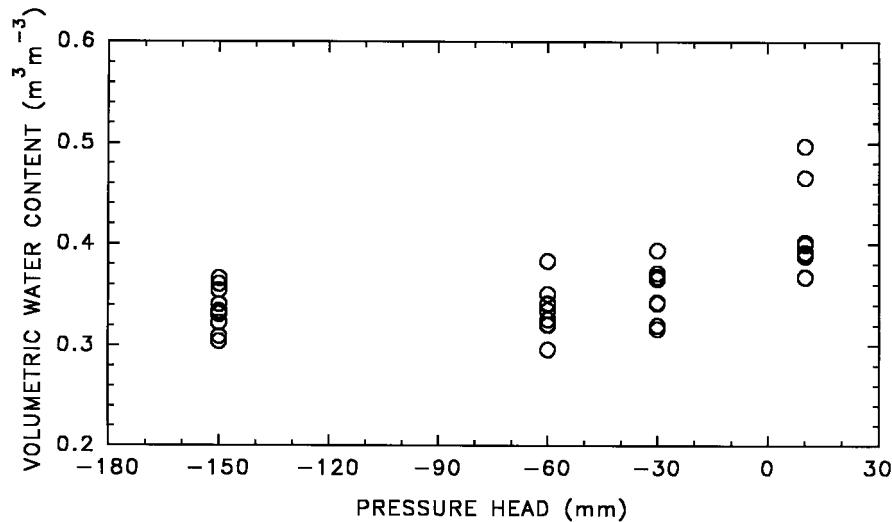


Fig. 1. Wetting soil water characteristic curve, showing the water content as a function of the pressure head.

and measured q values. This was similar to Mohanty et al. (1997), who found K to decrease greatly within a small range of H near 0 mm.

Transport Coefficients

Immobile Water Content

The values of θ_{im}/θ ranged widely at each H value (Fig. 3). For $H = 10, -30, -60,$ and -150 mm, the respective medians and ranges were 0.40 (0.17–0.68), 0.28 (0.11–0.50), 0.25 (0.07–0.38), and 0.39 (0.04–0.60). The θ_{im}/θ values at the three lower H values ($H = -30, -60,$ and -150 mm) were not significantly different from each other at 0.05. This suggests that θ_{im}/θ was constant across the unsaturated H values. Furthermore, the values of θ_{im} at $H = 10$ mm were significantly higher than the other θ_{im} values. Thus it appears that a portion of the saturated pore region, perhaps dead-end pores, did not participate in the mobile flow process. As θ decreased from saturated to unsaturated values, the large macropores drained, including any such dead-end macropores. These dead-end macropores might account for the significantly larger θ_{im} values for the saturated H .

There was a significant correlation between $1/\lambda_c$ and θ_{im}/θ at a 0.05 level. The λ_c was suggested to be correlated with θ_{im}/θ by Clothier et al. (1995) and Angulo-Jaramillo et al. (1996). Angulo-Jaramillo et al. (1996) represented this relationship as an S-shaped function of θ_{im}/θ varying with λ_c . Angulo-Jaramillo et al. (1996) and Clothier et al. (1995) estimated $1/\lambda_c$ using a piecewise linear $\ln(K)$ – H function. In this study, the Logsdon and Jaynes (1993) method was used to estimate $1/\lambda_c$, where the $\ln(K)$ – H function was assumed to be linear for $H \leq 0$ mm. Although the method used here to obtain λ_c was different from the previously mentioned studies, there still appeared to be some relation between λ_c and the θ_{im}/θ as suggested by Clothier et al. (1995) and Angulo-Jaramillo et al. (1996). However, there was no suggested functional shape between the $1/\lambda_c$ and θ_{im}/θ , only a correlation.

Mass-Exchange Coefficient

The median α values and ranges were 0.59 (0.079–4.7), 0.015 (0.0052–0.19), 0.0028 (0.00046–0.012), and 0.0029 (0.00008–0.0072) h^{-1} for the corresponding H values of

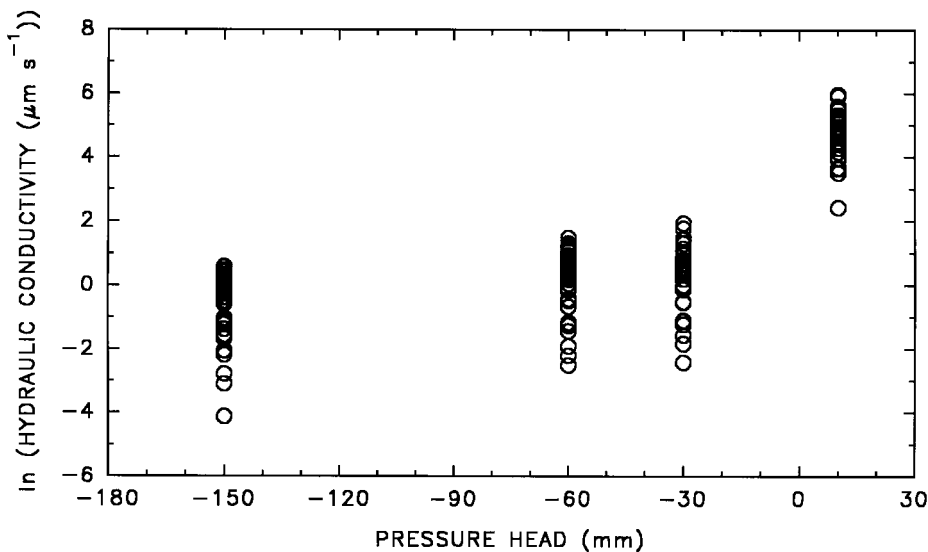


Fig. 2. Relationship of hydraulic conductivity to water pressure head.

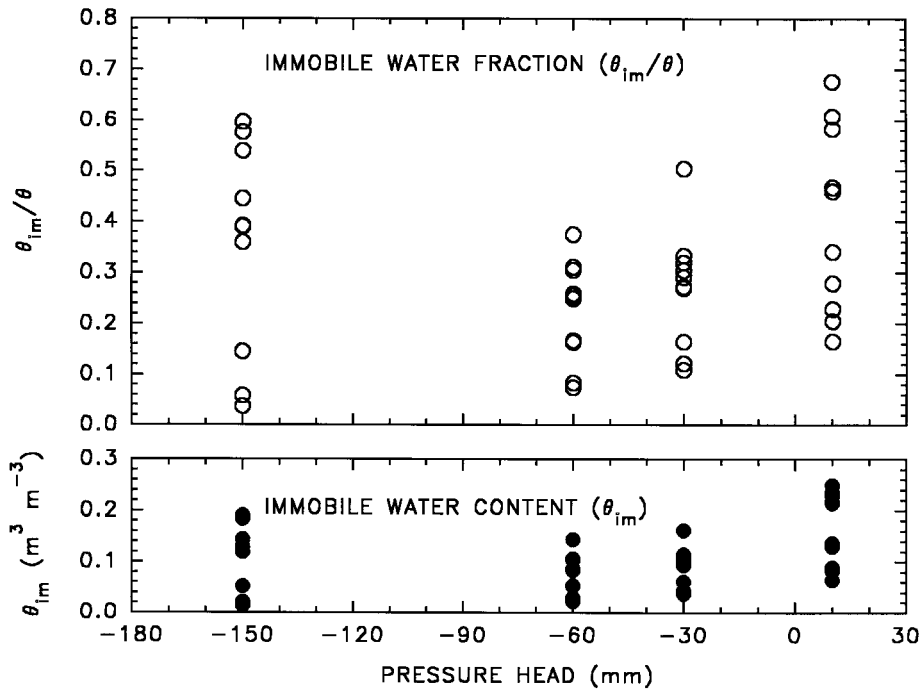


Fig. 3. The immobile water fraction and immobile water content as a function of water pressure head.

10, -30, -60, and -150 mm. A lognormal distribution was assumed by Toride and Leij (1996) to assess the effect of spatial variability of a field-scale solute transport study. In this study, neither the lognormal nor the normal distributions of all 40 α values could be rejected. At each H there were too few values to definitively suggest either distribution of α .

The α values decreased with decreasing H values (Fig. 4). The correlation coefficient between H and α was significant at 0.0001. This correlation implies an association of α with the soil water flow velocity, since lower Darcy fluxes were associated with lower H values. Numerous studies have indicated the same type of correlation in laboratory columns (Kookana et al., 1993; Rao et al., 1980; De Smedt et al., 1986; Li et al., 1994; Bajracharya and Barry, 1997) and field soils (Casey et al., 1997).

Soil water velocity, θ , and α were all independently and significantly correlated to H at 0.0001. This was consistent with previous studies done by Kookana et al. (1993), Rao et al. (1980), De Smedt et al. (1986), and Casey et al. (1997). These correlations may indicate a pressure-head effect on θ , which affects the flow velocity, which in turn has an effect on α . Another possible explanation for the correlation of α with soil water velocity was given by Rao et al. (1980), who suggested that larger equilibrium times caused smaller estimates of α , based on a model in which the soil was made up of porous spheres. Assuming this spherical geometry, the α values in this study should decrease with tracer application time. If the Rao et al. (1980) assumptions are true, then the plots of $\ln(1 - C/C_0)$ vs. t (Eq. [3]) should be concave upward because α would be decreasing with application time. As plotted, the graphs of $\ln(1$

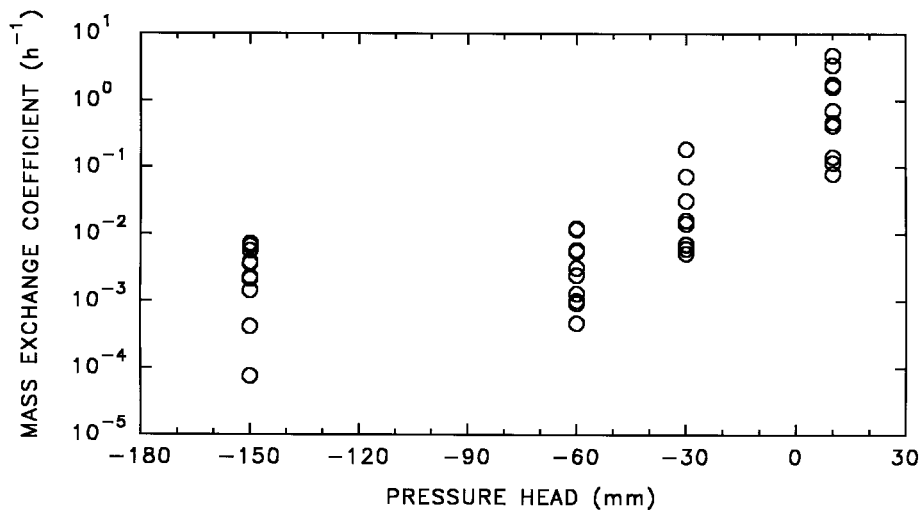


Fig. 4. The mass exchange coefficient as a function of water pressure head.

– C/C_0) vs. t in this study or the Casey et al. (1997) study do not show a concave upward pattern, but rather they are linear.

A division between the unsaturated and saturated α values was observed in Fig. 4. The values of α for $H \leq -30$ mm were sometimes several orders of magnitude lower than α values at $H = 10$ mm. The large difference between the saturated and unsaturated α values might have been caused by the differences in the velocity between the regions.

Immobile water fraction and α values in this study were compared with results from a previous field experiment. Casey et al. (1997) used the Jaynes et al. (1995) technique to determine θ_{im}/θ and α for a Nicollet fine loam at $H = -30$ mm. They reported a range of θ_{im}/θ values from 0.95 to 0.65, and a range of α values from 0.012 to 0.342 h^{-1} . The α values reported here were not significantly different from those found by Casey et al. (1997), but θ_{im}/θ values were significantly lower at 0.05. The two field studies were different in several important ways. The tillage was different: no-till (this study) vs. ridge-till (Casey et al., 1997). Additionally, the corn growth stage was later in the Casey et al. (1997) study. Both of the soils developed from glacial till and they belong in the same soil association; however, the two soils differ in their classification and landscape position.

CONCLUSION

This study was the first combined measurements of $\theta(H)$, $K(H)$, $\alpha(H)$, and $\theta_{im}(H)$ of a field site. This will lead to more in-depth characterization and modeling of coupled water and solute movement in field soil. The method used was unique because it was possible to estimate the hydraulic parameters in addition to the solute transport coefficients of a field soil. For the hydraulic properties, $K(H)$ and $\theta(H)$, there were apparent separations between the saturated and unsaturated values, which indicates a separation of flow between macropore and mesopore regions. Furthermore, a separation between saturated and unsaturated regions was also indicated, although less strongly, in the solute transport coefficients, θ_{im} , θ_{im}/θ , and α .

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In Situ Estimation of the Gaseous Nitrous Oxide Diffusion Coefficient in a Sandy Loam Soil

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ABSTRACT

The estimation of gas exchanges with the soil is important when assessing gas emission to the atmospheric environment or gas consumption by the soil. This estimation often requires the measurement of the diffusion coefficient of the investigated gas. The aim of this study was to develop an experimental method creating limited soil disturbance and based on simple calculation procedures to determine the diffusion coefficient, D_s , for N_2O in soils. This objective was achieved using a N_2O mass flow meter that supplied a continuous and constant flow of gas from below the soil surface until a steady-state N_2O concentration gradient with depth was obtained. The coefficients of diffusion were calculated daily for 6 d, under steady-state concentration gradient, using Fick's first law. The mean value of the diffusion coefficient for N_2O was $1.26 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (CV = 25%) at $0.16 \text{ m}^3 \text{ m}^{-3}$ of air-filled porosity. This value was validated by a transient-state laboratory method using soil cores and compared with empirical estimations of D_s from air-filled porosity determinations. The two experimental methods produced similar values for D_s , and both provided more accurate estimates than the empirical models. The proposed method can be applied to other gases provided an empirical model relating D_s to D_0 (gas diffusivity in free air) is first established. A theoretical study identified the threshold air-filled porosity values below which the flux density must be adjusted to maintain the validity of the D_s calculations.

NITROUS OXIDE is one of the most important trace gases for modeling the greenhouse effect that warms the earth's surface. Moreover, N_2O contributes to the depletion of the ozone layer that allows UV-A and UV-B rays to affect ecosystem productivity. It is generally believed that 70% of N_2O emissions originate from soils (Bouwman, 1990). Although agricultural practices may contribute to a large part of the increase in atmospheric N_2O (Shepherd et al., 1991), most of the sources have not yet been identified.

Nitrous oxide emission from the soil can vary by several orders of magnitude from one location to another,

both spatially and temporally (Mosier, 1989). These differences in measured gas fluxes and in the microbial activity that produces the gases make emission predictions highly uncertain. Soil cover chambers (Lessard et al., 1996) and micrometeorological techniques used to measure N_2O fluxes from agricultural soils to the atmosphere have not established a direct relation between the N_2O concentration in the soil profile and the release of the gaseous form to the atmosphere. Calculations based on model estimates suggest that there is a large lag phase between N_2O production and N_2O release at the soil surface due to gaseous diffusion (Jury et al., 1982).

A permanently placed sampling probe that allows sampling and the measurement of gas concentration changes within the soil profile at a single location (Burton and Beauchamp, 1994) provides useful information about N_2O production and diffusion within the profile during the growing season.

A similar sampling device adapted for the winter season and snow-covered soil allows the calculation of N_2O fluxes using Fick's law of diffusion and average concentration gradients under snow cover (van Bochove et al., 1996). However, the exactness of gas flux calculations based on the concentration gradients driving diffusion throughout a soil profile remains limited by the accuracy with which the diffusion coefficient can be measured or estimated (Jury et al., 1991; Burton and Beauchamp, 1994). Diffusion coefficients are often determined by laboratory core methods that have the disadvantage of disturbing the soil system and creating effects that are difficult to interpret (Tiedje et al., 1989).

Other methods, based on transient-state diffusion (Lai et al., 1976; Ball et al., 1994) or on the steady-state diffusion of a confined gaseous tracer in the headspace of a chamber located at the soil surface (Rolston et al., 1991), have been developed to study gas diffusivity at the field scale. Unlike the transient-state methods, the steady-state method has the advantage of requiring simpler mathematical expressions for the calculation of the diffusion coefficient (McCarty and Johnson, 1995). The objective of our study was to develop an experimental method for the determination of the N_2O diffusivity

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