

Immobile Water Content and Mass Exchange Coefficient of a Field Soil

F. X. M. Casey,* S. D. Logsdon, R. Horton, and D. B. Jaynes

ABSTRACT

Determining the preferential flow characteristics of a soil is important because agrichemicals can contaminate groundwater via preferential flow pathways. A model that predicts solute transport due to preferential flow is the mobile-immobile solute transport model, which partitions the total water content (θ , $\text{m}^3 \text{m}^{-3}$) into a mobile fraction (θ_m) and an immobile fraction (θ_{im}). Recently, an in situ method was proposed for determining the mobile-immobile model parameters of θ_m and mass exchange coefficient (α) between the fractions by using a tension infiltrometer to apply a series of four fluorobenzoate tracers. The objective of this study was to test the in situ technique at 47 sites along a transect in a ridge-till corn (*Zea mays* L.) field of Nicollet soil (fine-loamy, mixed, mesic Aquic Hapludoll). The immobile fraction (θ_{im}/θ) ranged from 0.394 to 0.952 with a median of 0.622. The mass exchange coefficient ranged from 0.000237 to 0.00481 min^{-1} with a median of 0.00123 min^{-1} . These values are similar in magnitude and range to values reported by other investigators, and they follow the same relationships. The values of θ_{im}/θ and α along the transect indicated no obvious spatial trends or spatial correlations. Significant linear correlations did exist between α and soil water flux, α and θ_{im} , and θ and θ_{im} .

PREDICTING THE CHEMICAL TRANSPORT PROPERTIES of soil has risen in priority because the problem of

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groundwater contamination by agrichemicals has increased (National Research Council, 1989). Many studies have shown that water and solutes are transported through the soil profile along preferential flow pathways (e.g., Thomas and Phillips, 1979; Priebe and Blackmer, 1989; Kanwar et al., 1985). These preferential flow pathways provide a route for solute to move rapidly below the biologically active root zone. As a result, chemical persistence and eventual water contamination can occur because biological activities that help the breakdown of agrichemicals are much reduced below the root zone (U.S. Environmental Protection Agency, 1992). Thus, incorporating the preferential flow characteristics of a soil when modeling solute transport is important.

Coats and Smith (1964) described a method to characterize preferential flow by representing the wetted soil pore space, θ , as consisting of two domains, the mobile water domain, θ_m , and the immobile water domain, $\theta_{im} = \theta - \theta_m$. The mobile domain is the water-filled pore space through which water and chemicals are flowing and θ_{im} is the water-filled pore space that contains stagnant chemicals and water.

In the mobile-immobile preferential flow model, a conservative nonsorbing solute is transported by a convective-dispersive process in the mobile domain and enters and leaves the immobile domain by a first-order process:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \quad [1]$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad [2]$$

where C_{im} (mmol L^{-1}) is the solute concentration in the immobile domain, C_m (mmol L^{-1}) is the solute concentration in the mobile domain, D_m ($\text{cm}^2 \text{min}^{-1}$) is the dispersion coefficient in the mobile domain, t is time, q (m min^{-1}) is Darcy flux density, and x (cm) is depth. Equation [2] describes a rate-limited mass transfer between the two domains, and α (min^{-1}) is the mass exchange coefficient. The mean resident solution concentration, C (mmol L^{-1}), is expressed as:

$$\theta C = \theta_m C_m + \theta_{im} C_{im} \quad [3]$$

The mobile-immobile model parameters are normally found by fitting calculated flux concentrations with observed flux concentrations from solute breakthrough experiments (Parker and van Genuchten, 1984; van Genuchten and Wagenet, 1989; Gamedainger et al., 1990). This method often results in close agreement between observed and calculated data, but extensive breakthrough data are needed. Also, this method may not produce parameter values representative of actual field conditions because of soil disturbance in the laboratory.

Clothier et al. (1992) provided a method for determining θ_{im} in situ. The Clothier et al. (1992) method uses a tension infiltrometer (Perroux and White, 1988) to wet the soil until steady-state infiltration is reached. A conservative anionic tracer (Br^-) is then applied and allowed to infiltrate the soil, which is sampled and analyzed for tracer concentrations. This method provides a solution for measuring θ_{im} without doing extensive breakthrough analysis and with minimal soil disturbance, but it offers no information about α .

Similarly, Jaynes et al. (1995) described a field technique that estimates θ_{im} along with α . This technique is an extension of the Clothier et al. (1992) method; however, a sequence of tracers is applied through the tension infiltrometer instead of just one (Ankeny et al., 1988). It was suggested that fluorobenzoate tracers be used because they have nearly identical transport characteristics, are easily measured, and have negligible background concentrations in soils (Bowman, 1984; Bowman and Gibbens, 1992; Benson and Bowman, 1994; Jaynes, 1994). The Jaynes et al. (1995) approach assumes that (i) the initial tracer concentration in the soil is zero, (ii) the tracer concentration in the mobile domain is constant and equal to the input concentration (C_o), (iii) the resident soil solution concentration is equal to C , and (iv) dispersion in the mobile domain is negligible at the time of sampling. Using these assumptions, Jaynes et al. (1995) developed the following relation by integrating Eq. [2] to determine α and θ_{im} :

$$\ln(1 - C/C_o) = -\alpha t/\theta_{im} + \ln(\theta_{im}/\theta) \quad [4]$$

This relation describes the increase of tracer concentration in the immobile domain with time. Plotting $\ln(1 - C/C_o)$ vs. tracer application time (t) results in a straight line with a negative slope. The intercept of the least-square regression gives $\ln(\theta_{im}/\theta)$, and the slope multiplied by $-\theta_{im}$ gives α (Jaynes et al., 1995).

The Jaynes et al. (1995) method provides a means for determining values of α and θ_{im} in situ by using resident tracer concentration measurements without doing a laboratory breakthrough study. It also offers an

advantage over the Clothier et al. (1992) method because it determines α . To date, the Jaynes et al. (1995) method has not been field tested; hence, the first objective of this research was to field test this new method. Further objectives were to: examine the spatial distribution of the field soil properties, compare the field-determined θ_{im} and α with previously published values, examine any correlations between the field soil properties, and compare the Jaynes et al. (1995) method with the Clothier et al. (1992) method.

MATERIALS AND METHODS

Field research was done in a corn field at the Agronomy and Agricultural Engineering Research Center, near Ames, IA. Research occurred in the last week of August and first 2 wk in September of 1994; the research field was ridge-tilled and cultivated, and the soil was mapped as a Nicollet loam. As always, there may be inclusions in the soil map unit. The Nicollet soil is derived from calcareous glacial till and is composed of approximately 0.41 sand, 0.19 coarse silt, 0.18 fine silt, and 0.21 clay. The texture analysis for the soil was done using the pipette procedures found in Soil Survey Staff (1984). The rainfall for the week prior to the experimental period was 86.11 mm and during the research period it was 77.47 mm.

Forty-seven measurements of θ_{im} and α were conducted along a 58-m-long transect within a corn row during the 3-wk period. Measurements were approximately 1 m apart between the corn plants, although spacing of the corn plants caused small variability in the measurement distances. Each measurement site was cleared of any residue and leveled with minimal disturbance to the soil. This was done so that the infiltrometers could make good contact with the bare soil surface. Some measurement sites were over roots and root channels. A 4 mmol L^{-1} solution of KCl was used to wet the soil and establish a constant molar concentration using a 7.6-cm base diameter tension infiltrometer (Ankeny et al., 1988) set at a pressure head of -3 cm. After the KCl solution reached steady-state infiltration, the sequence of four tracers was applied using separate tension infiltrometers for each tracer solution. Detailed laboratory experiments have shown that infiltration rates quickly returns to steady state when a tension infiltrometer is temporarily removed from a soil (Clothier et al., 1992). Tracers were applied in solutions composed of KCl and a variation of 2-6-difluorobenzoate (DFBA), pentafluorobenzoate (PFBA), *o*-trifluoromethylbenzoate (TFMBA), and 2,3,6-trifluorobenzoate (TFBA). The order in which the tracers were applied was varied so that any error caused by non-identical tracer transport, recovery, and analysis would be lessened. Six tracer application orders or series were made and were randomized in time and placement on the measurement transect.

After the 4 mmol L^{-1} KCl solution reached steady-state infiltration, the first tracer was applied. 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 a sufficient volume before the second tracer was applied. A sufficient volume of tracer was about 0.05 to 0.07 L or the amount of tracer needed to infiltrate beyond the sampling depth of 3.76 cm. The second tracer was applied in a solution formulated of 2 mmol L^{-1} KCl, 1 mmol L^{-1} of Tracer 1, and 1 mmol L^{-1} of Tracer 2. Again, the second solution was allowed to infiltrate a sufficient volume, after which a third tracer solution was applied. The third tracer solution was 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 a suitable amount, the final tracer was added. The final solution was composed of

1 mmol L⁻¹ of Tracer 1, 1 mmol L⁻¹ of Tracer 2, 1 mmol L⁻¹ Tracer 3, and 1 mmol L⁻¹ Tracer 4. 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 of the first tracer, the second longest application for the second tracer, and so on for the following two tracers.

After the final tracer application, the tension infiltrometer was removed and a soil sample was taken. The sampling device was a hollow stainless steel cylinder that had a diameter of 7.28 cm and a height of 3.76 cm. The height of the cylinder was chosen to allow for sampling behind the dispersion fronts of the tracers. The sampling cylinder was pressed into the center of each infiltration area, and a soil knife was used to cut around the outer diameter to free the sample from the surrounding soil. A spatula was used to lift the soil sample, which was placed and sealed in a plastic bag to prevent evaporation.

The soil samples were taken to the laboratory for extractions and to determine the water content (θ) and bulk density, ρ_b (g cm⁻³). The soil was extracted by using approximately a 1:1 soil/0.0005 M CaSO₄ solution. The extraction mixture was

shaken for 5 min on a wrist shaker and allowed to settle for 5 min. The solution was then decanted through no. 40 filter paper and stored at 2°C until analysis. The rest of the decantation was oven dried at 105°C and the total dry weight of the soil was measured to calculate the water content and bulk density.

Analysis for the fluorobenzoate tracers was done on a Dionex Series 4500i ion chromatograph (West Mont, IL) as described by Bowman and Gibbens (1992). For the fluorobenzoates, a SAX column (Regis Chemical Co., Morton Grove, IL)¹ was used with 30 mM KH₂PO₄, adjusted to a pH of 2.65 with H₃PO₄ and 20 mL L⁻¹ acetonitrile as the eluting solution. The flow rate was 1 mL min⁻¹ and the detection wavelength was set to 205 nm.

The resulting tracer concentrations from the extraction analysis were divided by the initial tracer concentrations to provide relative concentrations, C/C_0 . The input tracer concentration from the infiltrometer was used for C_0 . The $\ln(1 -$

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

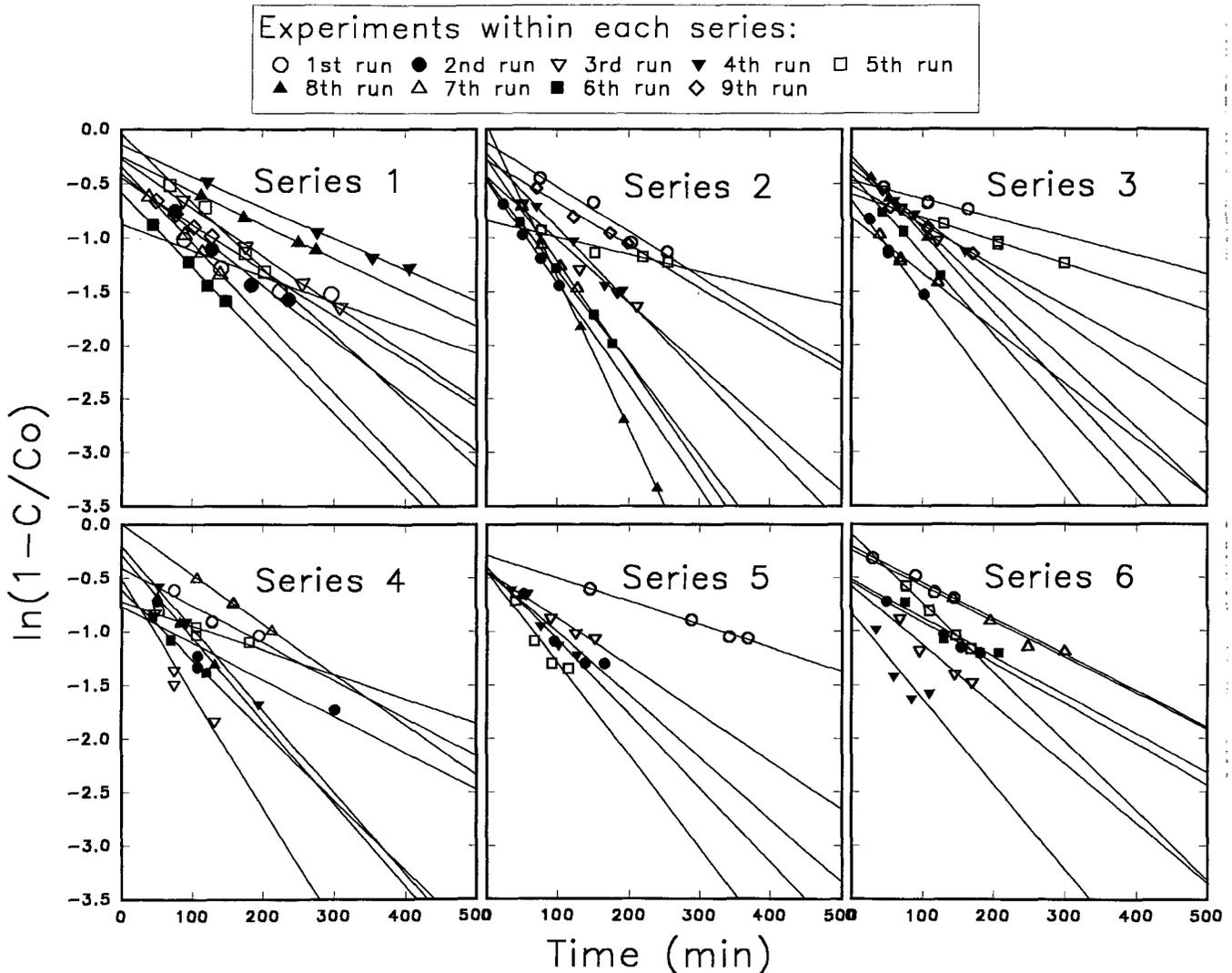


Fig. 1. The increase of tracer concentration in the immobile domain, $\ln(1 - C/C_0)$, vs. tracer application time, t , for all of the measurements. These are arranged according to the six different tracer application orders, which are referred to as series. Individual experiments were conducted within each series and the corresponding symbols represent a single experiment. The application series were randomized temporally and spatially along the measurement transect.

C/C_0) was plotted against time of application and a least sum-of-squares regression line was fitted to the data. Immobile water content and α were determined from the graphs of $\ln(1 - C/C_0)$ vs. t and Eq. [4]. Because the soil samples were not infinitesimally thin, the time of tracer application was slightly adjusted. The adjustments were made so that the effective application time would start when the tracer reached the center of the soil sample. The time adjustments caused about a 5% decrease in θ_{im} and α . Also, semivariograms were created by using the geostatistical software GEOPACK (Yates and Yates, 1990) to determine any spatial correlations. When calculating the semivariograms, an equal spacing (1 m) of measurements was assumed although there was some irregularity in measurement spacing.

The measured values of q , ρ_b , θ , θ_{im} , and α were evaluated for possible correlations between parameters. To evaluate these relations, the nonparametric Spearman rank correlation test was used because the underlying distribution of these values was not easily specified (Steel and Torrie, 1980).

RESULTS

Data Presentation

Graphs of $\ln(1 - C/C_0)$ vs. t were arranged according to the tracer application series (Fig. 1). The series represent various orders in which the tracers were applied. There were six different tracer application orders or series. The symbols represent the tracer concentrations of a separate experiment with their corresponding linear regression. For example, the four solid squares in the graph of Series 1 in Fig. 1 represent the four consecutively applied tracers of experimental run no. six. The coefficient of determination (r^2) for the regression lines in Fig. 1 ranged from 0.770 to 1.00 with an average of 0.965. The overall linearity of the regressions suggests that Eq. [4] is a reasonable representation of the physical processes occurring in the soil, because the data as plotted are not disarranged.

The soil water infiltration rate (q) for 46 infiltration sites had a median of $0.034 \text{ cm min}^{-1}$ with extremes ranging from 0.012 to 0.96 cm min^{-1} . The bulk density ranged from 1.14 to 1.62 g cm^{-3} and the median was 1.33 g cm^{-3} . Water contents (after infiltration at 30-mm pressure head) ranged from 0.339 to $0.458 \text{ m}^3 \text{ m}^{-3}$ with a median of $0.395 \text{ m}^3 \text{ m}^{-3}$. Values of θ_{im} varied from 0.150 to $0.442 \text{ m}^3 \text{ m}^{-3}$ with a median of $0.251 \text{ m}^3 \text{ m}^{-3}$. The θ_{im}/θ ranged from 0.394 to 0.952 with a median of 0.622 . The extremes of the α were 0.000237 to 0.00481 min^{-1} with a median of 0.00123 min^{-1} . One infiltration site was excluded when calculating the statistics because the calculated θ_{im}/θ value was 1.00 even though infiltration was observed.

Spatial Distribution and Frequency of Field Soil Properties

No spatial correlations of q , θ_{im}/θ , or α along the measurement transect were apparent according to the semivariograms (data not shown). The semivariogram of q on the transect and the frequency of q along the transect (Fig. 2a) did not show consistent spatial relations. The histogram of q showed 91.5% of the values occurring between 0.010 and $0.060 \text{ cm min}^{-1}$ (Fig. 2b).

The values of θ_{im}/θ along the transect were extremely variable with no obvious spatial trend (Fig. 3a). The histogram of θ_{im}/θ showed 95.7% of the values between 0.41 and 1.00 (Fig. 3b). The α values were variable along the transect and showed no clear spatial trend (Fig. 4a). The median of the α values was 0.00133 min^{-1} and the histogram of the α values had 97.8% of the values between 0.0002 and 0.0032 min^{-1} (Fig. 4b). Also, the semivariograms for ρ_b and θ showed the same lack of spatial trend displayed by the other parameters.

Comparisons with Earlier Work

To evaluate the θ_{im}/θ values from this investigation, a comparison was made with values reported from other field studies. Gvirtzman and Margaritz (1986) found θ_{im}/θ values that ranged from 0.4 to 0.55 ; these were lower but comparable to the values found in our study (median = 0.622). Conversely, Rice et al. (1986) reported a θ_{im}/θ value of 0.80 , which was higher than the median value found in this study. These field study values differ from those found here, although the values

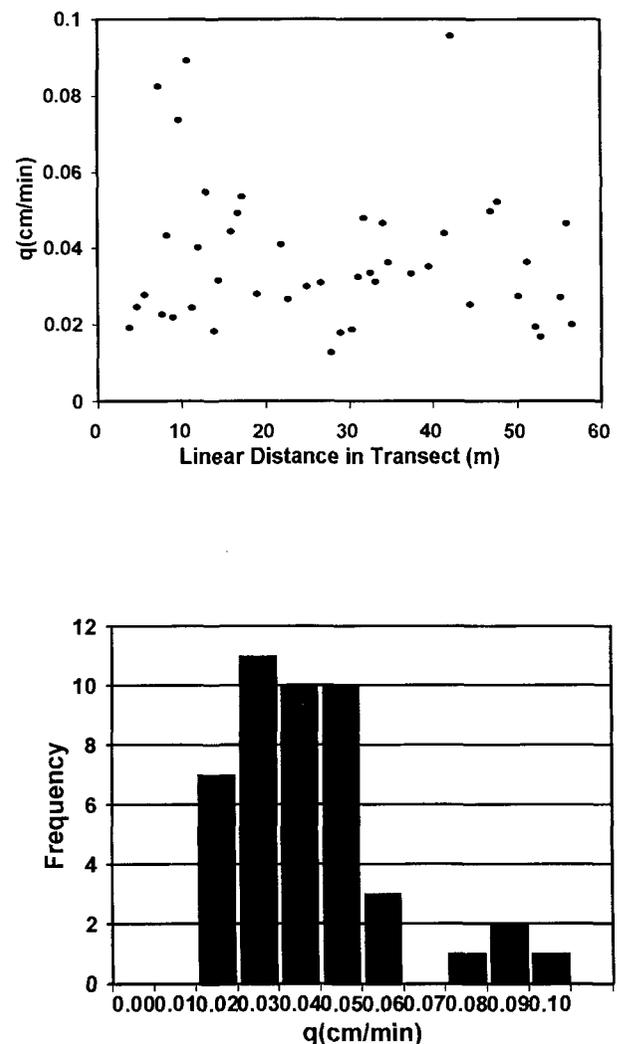


Fig. 2. Soil water infiltration rate (q) along the transect, and histogram of q .

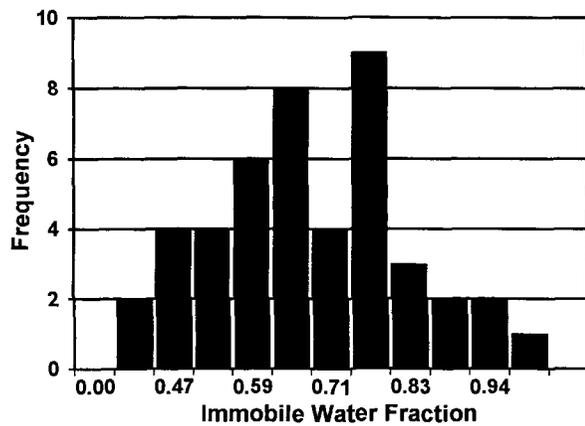
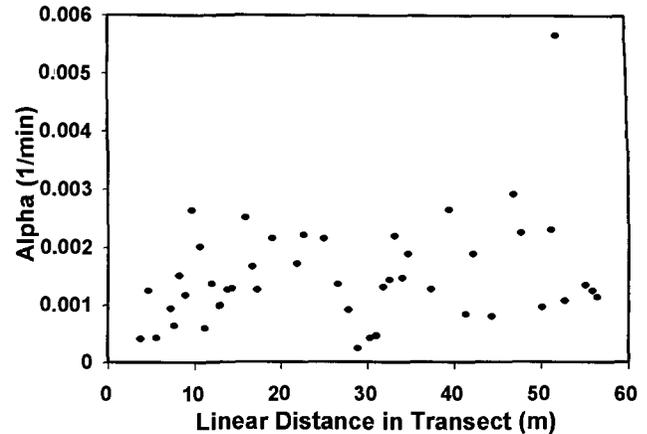
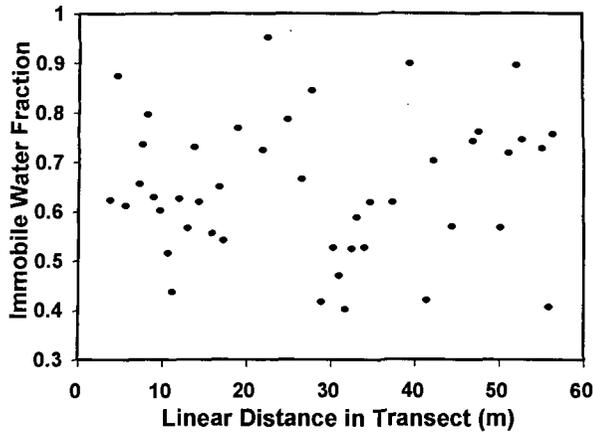


Fig. 3. Immobile water fraction (θ_{im}/θ) along the transect, and histogram of θ_{im}/θ .

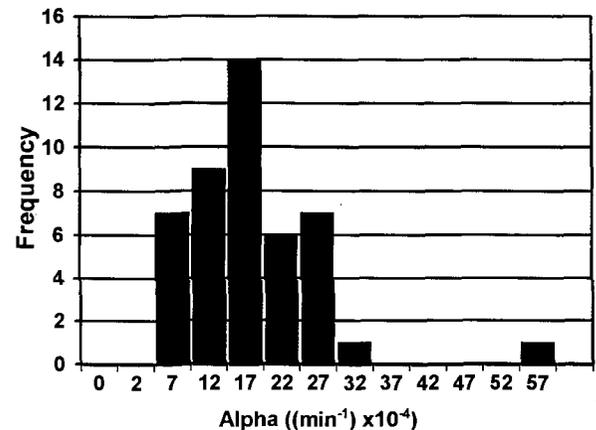


Fig. 4. Mass exchange coefficient (α) along the transect, and histogram of α .

from our study fall within the overall range from the other studies.

In addition to field study comparisons, laboratory study results can be compared. Numerous column breakthrough experiments have reported θ_{im}/θ and α values. Smettem (1984) found θ_{im}/θ ranging from 0.32 to 0.5 and α ranging from 0.000002 to 0.002 min⁻¹ in an undisturbed, weakly structured soil. Nkedi-Kizza et al. (1983, 1984) found θ_{im}/θ ranging from 0.04 to 0.56 and α ranging from 0.00017 to 0.0358 min⁻¹ for columns of sandy loam aggregates. Van Genuchten et al. (1977) reported θ_{im}/θ values of 0.06 to 0.275 and α values that ranged from 0.00003 to 0.00017 min⁻¹ in a clay loam. All of these studies resulted in quite large ranges of θ_{im}/θ and α values. The θ_{im}/θ values found in this study are large compared with previous studies, whereas the α values are quite similar. The differences in θ_{im}/θ may have been caused by differences in the soil textures. The soil texture determines to a large extent soil structure, which greatly influences the characteristics of the transport processes (Jury et al., 1991).

Correlations of Field Soil Properties

There are positive, significant correlations between α and q , α and θ_{im} , and θ and θ_{im} (Table 1). Positive

correlations between α and q have been reported by a number of workers, even though α represents a first-order process and should be independent of q according to Eq. [2] (van Genuchten et al., 1977; Rao et al., 1980; Nkedi-Kizza et al., 1984; De Smedt et al., 1986; Kookana et al., 1993). This correlation was evidenced in the relationship between α and pore water velocity developed by Kookana et al. (1993) (Fig. 5). When the α and pore water velocity values from this study are plotted alongside values from earlier studies, they show the same correlation that Kookana et al. (1993) found. The earlier studies presented in Fig. 5 are from column experiments using different soils and aggregate sizes (Gaudet et al., 1977; van Genuchten et al., 1977; Rao et al., 1980; Nkedi-Kizza et al., 1984; De Smedt et al., 1986; Selim et al., 1987; Seyfried and Rao, 1987; Miller and Weber, 1988; Kookana et al., 1993). Figure 5 also indicates that the α values from this study fall within the range that the earlier workers found.

Skopp et al. (1981) showed α to be proportional to θ_{im} , which is supported by the correlations between α and θ_{im} found here (Table 1). This relationship may be caused by larger regions of contact between the immobile domain and the mobile domain. If the contact be-

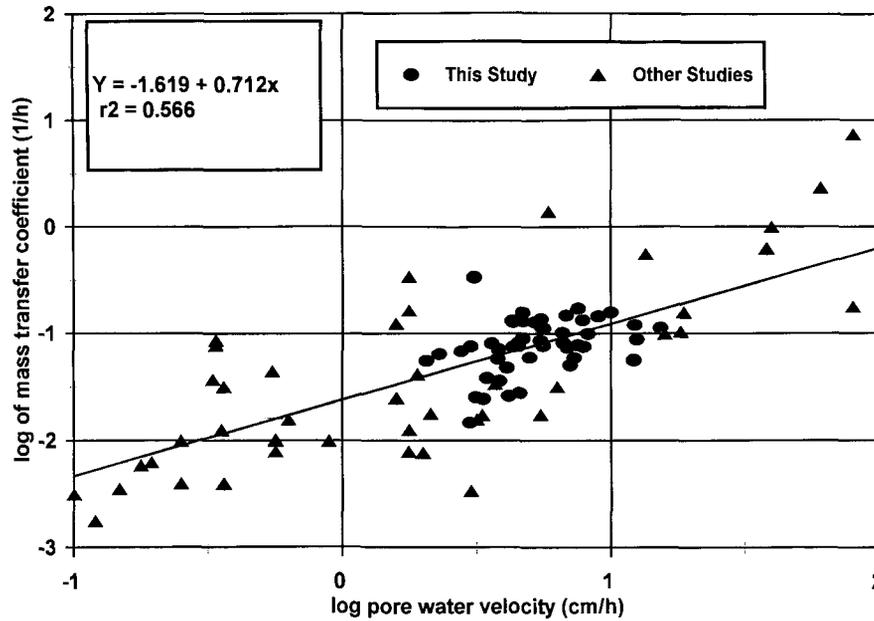


Fig. 5. Graph from Kookana et al. (1993) of the log of the mass exchange coefficient vs. the log of pore water velocity.

tween the domains increases as θ_{im} expands, then α will also increase. The mass exchange coefficient will increase because the larger contact regions will allow for more tracer transfer between the domains.

The correlation between θ and θ_{im} was significant and positive (Table 1). Larger water contents are able to hold more immobile water than smaller water contents, as indicated by this correlation.

The correlations in Table 1 indicate that the Jaynes et al. (1995) method gives results that follow trends found by previous workers. The previous workers found these associations while measuring these parameters predominantly in laboratory experiments. Also, these correlations provide help in expressing the solute transport parameters in terms of measurable physical parameters.

Comparison with Clothier et al. (1992)

Clothier et al. (1992) measured θ_{im}/θ using a tension infiltrometer set at -2 -cm pressure head vs. the -3 -cm pressure head used in this study. The average of θ_{im}/θ that Clothier et al. (1992) reported was 0.49 with a standard deviation of 0.12, which was lower than the mean value here (mean = 0.646 and standard deviation = 0.0624) but just as variable. The lower θ_{im}/θ values may have been caused by differences in soil texture, i.e., a fine sandy loam in the Clothier et al. (1992) study vs. a fine loam used in this study. However, the lower θ_{im}/θ values were most likely caused by the different assumptions of the two methods. No diffusive exchange is assumed between the domains ($\alpha = 0$) in the Clothier et al. (1992) study, thus all tracer in the soil solution is assumed to be in the mobile domain and $C_{im} = 0$. Therefore, the mobile region will be overestimated and the immobile region will be underestimated unless the α is effectively zero.

The Jaynes et al. (1995) method reduces to the Cloth-

ier et al. (1992) method by setting the slope in Eq. [4] equal to zero (i.e., $-\alpha/\theta_{im} = 0$). The Clothier et al. (1992) method is then described by the following:

$$\ln(1 - C/C_0) = \ln(\theta_{im}/\theta) \quad [5]$$

We approximated θ_{im}/θ using Eq. [5] with the first two tracers of each series from our study. The first two tracers that were applied in each series are the tracers that are on the application site the longest. By using the first tracer with Eq. [5], θ_{im}/θ ranged from 0.501 to 0.0357 and the average was 0.274. By using the second tracer, θ_{im}/θ values ranged from 0.532 to 0.0676 and the mean was 0.324.

The θ_{im}/θ values determined using Eq. [5] were lower than those calculated by the Jaynes et al. (1995) method; however, they depend on the mean resident tracer concentrations, which increase with application time. One may argue that these tracer concentrations increase with time because of dispersion in the mobile domain, not diffusion into the immobile domain. Nonetheless, when using Eq. [5] only long tracer application times were considered, where the influence of dispersion on tracer concentrations becomes less significant (Clothier et al., 1995). If Eq. [5] truly represents what is occurring in the soil, then the regressions in Fig. 1 should be flat. Although the Jaynes et al. (1995) technique accounts for diffusion into the immobile domain, it assumes C_m equals C_0 and does not consider a changing tracer con-

Table 1. Spearman correlation coefficients for soil water infiltration rate (q), bulk density (ρ_b), total water content (θ), immobile fraction (θ_{im}), and the mass exchange coefficient (α).

Parameter	ρ_b	θ	θ_{im}	θ_{im}/θ	α
q	0.034	0.0318	-0.0950	-0.196	0.455**
ρ_b	-	0.197	0.257	0.187	0.166
θ	-	-	0.367**	-0.0215	0.097
θ_{im}	-	-	-	-	0.456**

** Significant at the 0.01 probability level.

centration in the mobile domain with time. Because C_m should increase with time, the Jaynes et al. (1995) method tends to overestimate θ_{im}/θ . The tracer concentration in the mobile domain increases with time due to hydrodynamic dispersion in the mobile domain, and it takes time for the tracer to reach input concentrations within the sampling depth. Perhaps the best estimate of θ_{im}/θ is a value between the Clothier et al. (1992) and the Jaynes et al. (1995) estimates.

CONCLUSION

In this study, the Jaynes et al. (1995) method for determining α and θ_{im}/θ was field tested. Currently this method is the only in situ technique that provides estimation for both α and θ_{im}/θ , and is important in the identification of these parameters at a field scale. We were able to do 46 successful field experiments, and report the corresponding field values for θ_{im} and α . Spatial distributions, correlations, and comparisons of the values with other studies were provided. It was found that the solute transport parameters were largely variable on a field scale, with θ_{im}/θ values ranging from 0.29 to 0.95, and α values ranging from 0.00024 to 0.011 min^{-1} . In hopes of expressing the solute transport parameters in terms of measurable physical properties, correlations were tested. Positive, significant correlations were found between α and q , α and θ_{im} , and θ and θ_{im} . Earlier reported field and laboratory study values of α and θ_{im}/θ were compared with values obtained from the Jaynes et al. (1995) method. This was done to show that the Jaynes et al. (1995) technique provided reasonable estimation for α and θ_{im}/θ . Also the Clothier et al. (1992) method was contrasted with the present technique to show that α plays an important part in the transport process and should not be excluded.

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