(Manuscript as appeared in Soil Science, August 1999, Vol 164, No. 8)

THE VERTICAL DISTRIBUTION OF A DYE TRACER IN A LAYERED SOIL

R. C. Schwartz[1], K. J. McInnes[2], A .S. R. Juo[2], and C. E. Cervantes[3]

Solute transport under field conditions is often inconclusive and difficult to measure because of poor spatial resolution of sampling devices. Dye tracers can complement concentration measurements by characterizing the spatial structure of solute flow through soils. This study assessed the influence of antecedent water content, tillage, and residue cover on the pattern of soil water flow in the field as exhibited by a dye tracer. A random walk method for estimating the vertical distribution of the stained soil fraction was used to evaluate the degree to which the advective dispersive equation corresponded to field plot transport. The dye-tracer study was conducted on twelve 0.9 m diameter plots within a 2-ha field in southern Costa Rica. A 4-cm depth of Brilliant Blue FCF solution at 5 g L^{-1} was applied at a rate of 6.81 cm h^{-1} to plots using a spray nozzle. Plots were later excavated to record the vertical distribution of stained soil. The dye patterns demonstrated that significant bypassing can occur within the surface horizon under rainfall intensities below the steady state infiltration rate. Compared to pre-wetted soil, plots with an initially low antecedent water content exhibited significantly greater spreading of dye within the soil profiles. The random walk simulations indicated that the advective-dispersive equation could not describe dye staining patterns unless the dispersion coefficients estimated from column experiments were increased by one order of magnitude. Tillage did not significantly influence the mean penetration and spreading of dye within the entire soil profile as compared to other undisturbed, pre-wetted subplots, but it increased the interaction of the soil with the dye near the surface as indicated by a significantly greater fraction of stained soil in the Ap horizon. (Soil Science 1999;164:561-573)

Key words: Random walk; bypass flow; contaminant transport, tillage.

DYE tracers have frequently been used to study the patterns of flow in structured soils and provide a qualitative assessment of the size and extent of macropores associated with the rapid transport of water and solutes (Bouma et al., 1977; Starr et al., 1978; Omoti and Wild, 1979b; Ghodrati and Jury, 1990; Flury et al., 1994). Such studies have improved our understanding of pore connectivity involved in solute transport processes. For instance, rapidly conducting regions may not necessarily be associated with discrete bio-channels or structural features (Seyfried and Rao,1987). Andreini and Steenhuis (1990) studied preferential movement of dye tracers in tilled and untilled soils and demonstrated that tillage decreased the vertical spreading of dye stains. This decreased spreading of dye as a result of tillage also corresponded to a smaller dispersion coefficient estimated from the breakthrough curves of column displacement experiments for tilled soils.

Received Jan 22, 1999; accepted March 26, 1999.

[1]Conservation & Production Research Laboratory, USDA-ARS, P.O. Drawer 10, Bushland, Tx 79012-0010. Dr. Schwartz is corresponding author. E-mail: rschwart@ag.gov

[2]Department of Soil & Crop Sciences, Texas A&M University, College Station, TX 77843-2474.

[3]Escuela de Ciencias Agrarias, Universidad Nacional, Apartado 86-3000, Heredia, Costa Rica.

Despite the value of dye tracer studies to identify flow paths in soils, results have often been inconclusive inasmuch as they exhibit the presence or absence of dye rather than concentrations. Only spatial or temporal distribution of tracer concentrations resulting from known boundary and initial conditions can provide information pertaining to the dispersive nature of transport and the suitability of dispersion theories. Inferring dye concentration from image analysis of UV or color photographs at present appears unsuitable because of changes undergone by the dye when adsorbed and the variation in color or UV intensity with water content (Starr et al., 1978; Omoti and Wild, 1979a). Moreover, resolution of dye concentrations from color image analysis may be complicated by the occurrence of horizons consisting of more than one dominant matrix color. Thus, in most situations, analysis of dye staining patterns from cross-sectional areas can yield only Boolean information corresponding to the visual presence or absence of the dye. These limitations do not preclude the use of inverse methods to relate dye concentrations obtained from transport equations to the probabilities associated with stained areas averaged perpendicular to the direction of flow. Such an approach would be useful in evaluating the degree to which an assumed transport equa-tion corresponds to the observed distribution of dye in the field.

Flow patterns were observed in small field plots using Brilliant Blue FCF dye. Steady-state laboratory column displacement experiments were conducted using a bromide tracer to estimate the parameters of the advective-dispersive equation (ADE) over a range of water contents and corresponding pore-water velocities. Lastly, a random walk method for estimating the vertical distribution of stained soil was used to evaluate the degree to which transport in laboratory columns corresponded to field plot transport.

RANDOM WALK SIMULATION OF VERTICAL DYE STAIN DISTRIBUTIONS

A particle tracking method applied commonly applied in statistical physics and solute transport problems (e.g. Scheidegger, 1954) is the random walk approach. It consists of calculating both the deterministic and random displacements of particles over time. This type of motion has generally been modeled by the Fokker-Planck equation (Gardiner, 1985), which describes, in the infinite limit, the spatial distribution of particles by a probability density function. For the purposes of this study, solute transport is assumed to conform to the Fickian dispersion theory corresponding to the steady-state, one-dimensional advective-dispersive equation with instantaneous, linear adsorption. Derivation of the random walk step equation as it applies to the advective-dispersive equation is elaborated by Kinzelbach (1988), Tompson et al., (1988) and Uffink (1988). For spatially constant flow velocity, water content, and dispersion, the one-dimensional step equation for advective-dispersive transport of a single particle over time is (Tompson et al., 1988)

$$X(t_n) = X(t_{n-1}) + v\left(X(t_{n-1})\right)\cdot \Delta t + Z_n \cdot \sqrt{2\cdot D\,(X(t_{n-1}))\cdot \Delta t} \quad (1)$$

where $X(t_n)$ is the position (cm) of a particle at time t (h) corresponding to the nth step, $X(t_{n-1})$ is the position of the particle at the previous time step, $v(X(t_{n-1}))$ is the velocity (cm h^{-1}) of the particle evaluated at the previous time step, $D(X(t_{n-1}))$ is the dispersion coefficient (cm^2 h^{-1}) evaluated at the previous time step, Δt is the time increment (h) of each step, and Z_n is defined as

$$Z_n = U\cdot\sqrt{3} \quad (2)$$

where U is a uniform deviate ($-1 < U < 1$) with a mean of zero.

The mass of a single particle must be defined to apply the random walk method. The flux concentration of particles C_{p0} (number of particles per unit fluid volume, cm^{-3}) is defined as

$$C_{p0} = \frac{N}{T\cdot q\cdot \Delta x\cdot \Delta y} \quad (3)$$

where T is the total time of the simulation (h), q is the volumetric flux at the soil surface (cm^3 cm^{-2} h^{-1}), $\Delta x\cdot\Delta y$ is the unit area over which flux is applied (cm^2), and N is the total number of particles released into the upper boundary over time T. Hence, the mass of an individual particle m_p (g) is therefore

$$m_p = \frac{C_0}{C_{p0}} \quad (4)$$

where C_0 is the concentration (g cm^{-3}) for the same particle flux. A fraction of the mass of each particle can be adsorbed instantaneously according to a linear exchange isotherm such that total particle mass m_p consists of the fluid mass m_{fp} and adsorbed mass described by R, the retardation factor. Hence, total mass is can be described as

$$m_p = m_{fp} + (R - 1)\cdot m_{fp} \quad (5)$$

where the fluid phase mass $m_{fp} = m_p/R$. Linear adsorption is incorporated into the step equation by replacing the velocity by a retarded velocity (v/R) and by replacing the dispersion coefficient by a reduced dispersion coefficient (D/R) in Eq. (1). The resident concentration C_r (g cm^{-3}) in a sampling region Ω_s or cell with dimensions $\Delta x \cdot \Delta y \cdot \Delta z$ and containing N_s particles can be defined as

$$C_r = \frac{m_p \cdot N_s}{R_s \cdot \theta_s \cdot \Delta x \cdot \Delta y \cdot \Delta z} \tag{6}$$

where R_s and θ_s are, respectively, the retardation factor and volumetric water content in the sampling region. Let C_{d0} represent the minimum detectable resident fluid concentration (g cm^{-3}) of dye in the soil; it is a function of the visibility of the dye and the image analysis process. Also define this same minimum detectable concentration as one particle per cell. Thus using Eq. (3), (4), and (6), the minimum detectable concentration within Ω_s for the random walk path is

$$C_{d0} = \frac{1 \cdot m_p}{R_s \cdot \theta_s \cdot \Delta x \cdot \Delta y \cdot \Delta z} = \frac{C_0 \cdot T \cdot q}{N \cdot R_s \cdot \theta_s \cdot \Delta z} \tag{7}$$

Assuming that water contents and distribution coefficients do not vary greatly throughout the profile, one can estimate the required number of particles input during the simulation time T as

$$N = \frac{C_0}{C_{d0}} \cdot \frac{T \cdot q}{\bar{R} \cdot \bar{\theta} \cdot \Delta z} \tag{8}$$

where $\bar{\theta}$ and $\bar{R}$ are the average volumetric water content and retardation factor for the soil profile.

Suppose now that a large number of M particles are all released at the inlet boundary for each time step. To distinguish between "stained" and "unstained" cells, a single particle is released into each of the M non-interacting columns (Fig. 1) and permitted to move through the flow field according to the one-dimensional step equation (1). The area of each of the M columns ($\Delta x \cdot \Delta y$) combined with the depth increment (Δz) defines the volume of a single cell that is required to estimate the probability that this cell is stained. The magnitude of M does notinfluence the calculation of the stained-fraction nor the resident concentration, but only affects the resolution with which the random walk approximates these continuous variables. The mean resident concentration for M columns $\bar{C}_r$ is obtained by combining Eqs. (3), (4), and (6) to yield

$$\bar{C}_r = \frac{C_0 \cdot T \cdot q}{N \cdot R_s \cdot \theta_s \cdot \Delta z} \cdot \frac{1}{M} \cdot \sum_{i=1}^{M} N_s(i) \tag{9}$$

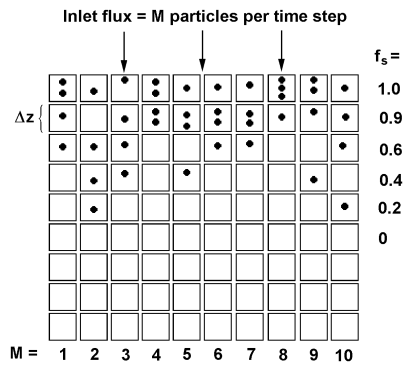

Fig. 1. Schematic showing the manner in which particles are added to columns, and the calculation of stained-fraction with depth for N = 4 and M = 10.

Since one particle per cell in a given column corresponds to the minimum concentration that is detectable with image analysis, the presence or absence of a particle in a cell indicates that this cell is stained or unstained respectively. Let $g(z, i)$ represent a function at depth z for the *ith* column (1 through M) such that

$$g(z,i) = \begin{cases} 0 & N_s(z,i) = 0 \\ 1 & N_s(z,i) > 0 \end{cases} \tag{10}$$

where $N_s(z,i)$ is the number of particles in the cell at depth interval z for the ith column. Note that concentration is zero when there are no particles in a cell, yet the analytical solution will indicate a nonzero concentration because of an infinite propagation of velocity by the effect of dispersion. The stained-fraction of soil with depth $f_s(z)$ can therefore be expressed as

$$f_s(z) = \frac{1}{M} \cdot \sum_{i=1}^{M} g(z,i) \tag{11}$$

Estimates of the mean pore-water velocity, dispersion coefficient, retardation factor, and minimum detectable concentration, can be used to obtain the stained-fraction $f_s(z)$ corresponding to Fickian dispersion from random walk simulations. As such, the movement of each particle is assumed to be uncorrelated over time, which reflects a situation where the correlation lengths of the inhomogeneities are smaller than the step length (Kinzelbach, 1988). Choice of a minimum detectable concentration is the major difficulty with this approach. Dye visibility can be influenced by such factors as water content, shadows,

adsorption, and color of the soil matrix. Thus, C_{d0} could change appreciably with soil depth and, for a given value of N calculated in Eq. (8), the corresponding C_{d0} in each soil horizon will vary as a result of variable adsorption and mean pore-water velocity with depth. Therefore, this procedure can provide only a rough approximation of the stained-fraction of soil over depth expected under Fickian dispersion theory.

Thus far, the development of the random walk step equation has assumed an infinite domain. To correctly describe particle distributions in the presence of boundaries and in media with discontinuous transport coefficients, auxiliary conditions must be specified. For this study, a third-type continuous flux boundary is applied to the upstream inlet. Such a boundary is implemented by instantaneously reflecting particles back into the solution domain when they move out of the domain through the inlet. An outlet boundary of infinite extent is approximated by placing this boundary at a distance far downstream such that upstream concentrations are not influenced. When layered media exhibit discontinuities in effective porosities, dispersivities, and flow velocities, special boundary conditions (Uffink, 1985) or interpolation schemes (Labolle et al., 1996) must be implemented. For this study, we assumed that downstream concentrations do not influence upstream concentrations and thus the appropriate condition at the interface between layers is a third-type continuous flux boundary with macroscopically discontinuous resident concentrations (Leij et al., 1991). The interface condition between two layers was implemented by dividing the time step into two increments if the particle crossed a boundary. The travel distance of the particle was modified by summing the travel distances associated with each layer according to the fraction of time spent in each layer. The fraction of time spent in the layer associated with the position of the particle at the beginning of the time step was computed by solving for Δt in Eq. (1) with $X(t_n)$ set to the distance from the interface.

Figure 2 shows the results of a random walk simulation using the step Eq. (1) with a constant flux inlet, an infinite outlet boundary, and a two-layer medium. The corresponding two-layer analytical solution of the advective dispersive equation (ADE) for resident concentrations (Leij et al., 1991) is also shown in Fig. 2 (as a solid line). Concentrations obtained from the random walk simulation corresponded favorably with the analytical solution of the ADE. For porous media with low dispersivities, the overall shape of the simulated stained-fraction with depth parallels field results of dye coverage obtained for nearly structureless soils (e.g. Flury et al., 1994; Les Barges in Fig. 3).

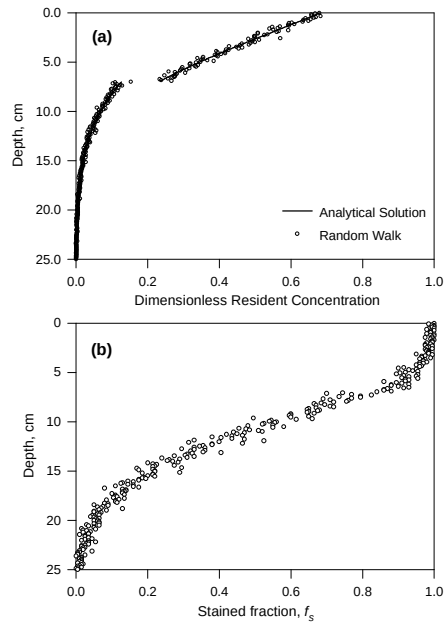

Fig. 2. Simulated concentrations (a) and stained-fraction (b) with soil depth from a random walk simulation with M = 200, N = 400, Δz = .08 cm, D_1 = 65.0 cm^2 h^{-1}, D_2 = 195.0 cm^2 h^{-1}, v_1 = v_2 = 13.62 cm h^{-1}, R_1 = 2.0, R_2 = 3.0, and T = .582 h. The interface between the two layers is located at z = 7.0 cm.

MATERIALS AND METHODS

All field experiments were conducted on a 2-ha site in southern Costa Rica with fine textured Ultisols (clayey kaolinitic semiactive isohyperthermic Oxyaquic Hapludult) derived from sedimentary rocks rich in mafic materials. The site has an average slope of 20% and a mean annual precipitation of 300 cm. The study was conducted during the dry season of 1995 on a site that has been managed under a no-till bean-corn rotation for 10 years. For 20 years the site was a coffee plantation with guaba (*Inga* spp.) shade trees. Upon conversion to annual crops, the field was ploughed. Substantial amounts of residues

(approximately 80% cover) were on the soil surface for the duration of this study.

Dye tracer study

Three field locations within the study site (A, B, and C) were selected and subdivided into four 1.2 x 1.2-m subplots to examine four experimental treatments using a randomized block design. The treatments were: (1) dye application with no pre-wetted soil and residue intact, (2) dye application to a pre-wetted soil with residue intact (3) dye application to a pre-wetted soil after removal of residue, (4) application of dye solution to a pre-wetted soil after residue removal and tilling to a depth of 12 to 15 cm using a hoe.

Subplots were pre-wetted by sprinkling 20 cm of water over the plot and allowing redistribution of water to occur overnight. Immediately prior to each dye application, bulk soil samples at depths of 0.0 to 12.5 and 12.5 to 25-cm were taken near the plot edge to measure gravimetric soil water contents. Mean antecedent volumetric water content at 0 to 12.5-cm depth were 0.27 (± 0.01 SD) $cm^3\ cm^{-3}$ and 0.32 (± 0.04 SD) $cm^3\ cm^{-3}$ at 12.5 to 25- cm depth for dry plots that were not pre-wetted. For the pre-wetted plots, mean antecedent volumetric water contents were 0.38 (± 0.02 SD) $cm^3\ cm^{-3}$ at 0 to 12.5-cm depth and 0.45 (± 0.03 SD) $cm^3\ cm^{-3}$ at 12.5 to 25-cm depth. Brilliant Blue FCF (Flury and Flühler, 1995) was applied at a concentration of 5 g L^{-1} to each of the subplots with a single, stationary spray nozzle. A 4.0-cm depth of dye solution was applied by sprinkling at a constant rate of 6.81 cm h^{-1} to an effective plot diameter of 0.9 m. The coefficient of variation of the spray distribution, obtained by measuring the volume of solution collected in 6-cm diameter cups distributed below the spray nozzle within an 86-cm diameter circular area, was 13%. Approximately two hours after the application of the dye tracer, the lower half of the circular plots were excavated to the depth of maximum dye penetration. Color photos were taken of vertical cross-sections shaded from the sun, using a hand-held camera with a flash, to preserve a record of the dye patterns.

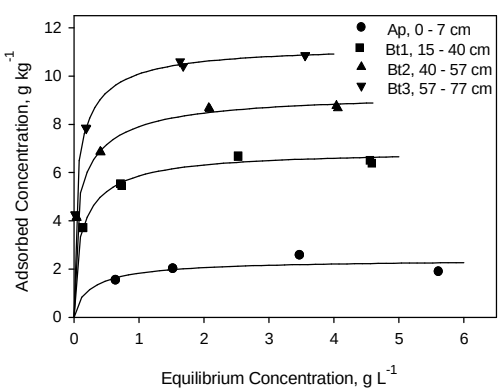

Fig. 3. Batch adsorption isotherms for Brilliant Blue FCF for several horizons. The lines are the non-linear least-squares fit of the general Freundlich isotherm, Eq. (13).

Color slides of stained patterns were digitized at a resolution of 15 pixels per cm of soil depth using a scanner. The images were stored in a red-green-blue (RGB) format for subsequent manipulation by Adobe Photoshop™ [1]. Stained areas were delineated using the color select feature of Adobe Photoshop to build two files that identified pixels over a range of blue and green hues in the digitized image. The two selection files were constructed using all of the images. The file that selected a range of green hues was built by adding stained pixels that were not identified using the initially constructed file to identify blue hues. Once files were constructed, stained pixels were identified in each of the images by using the two color selection files. Selected pixels were converted to black (decimal value = 0), unstained pixels were converted to white (decimal value = 255), and other pixels (e.g. corresponding to labels and the soil surface) that were initially selected and saved on a separate channel were converted to gray (decimal value = 126) color levels to produce a grayscale image. Images were saved as binary character files and used to calculate the fraction of stained soil within 45 cm from plot center and over depth increments of one cm. The complement of the cumulative normal probability distribution

$$F(x) = 1 - \frac{1}{\sigma \cdot \sqrt{2 \cdot \pi}} \cdot \int_{-\infty}^{x} \exp\left(\frac{-(x-\mu)^2}{2 \cdot \sigma^2} \right) dx \quad (12)$$

was fitted to the fraction of stained soil with depth to obtain estimates of the mean dye penetration (μ) and the vertical spreading (σ) of stained soil. Use of the cumulative probability distribution $F(x)$ to derive the statistical properties of the stained soil distribution is reasonable because Eq. (12) also describes normalized concentration with depth at large times for a constant flux concentration inlet condition.

[1]The mention of trade or manufacturer names is made for information only and does not imply an endorsement, recommendation, or exclusion by USDA-Agricultural Research Service.

Batch adsorption of Brilliant Blue FCF

Batch methods were used to obtain Brilliant Blue FCF (792.85 g mol^{-1}) adsorption isotherms for air dry, 2-mm sieved soil samples obtained from plot B. Dye adsorption measurements were made using a background concentration of 0.015 *M* NaCl. Twenty-five mL of 0.015 *M* NaClwith dye concentrations of 6.0, 4.0, 2.0, and 1.0 g L^{-1} were added to 6.0 g air dry soil. These suspensions were gently agitated using a vortex mixer, allowed to equilibrate for 20 hours at 20°C, and then centrifuged to collect the supernatant. The supernatant was diluted with 0.015 *M* NaCl and dye concentrations in these solutions were measured using a colorimeter at a wavelength of 630 nm. Sorbed concentrations were calculated by subtracting the mass of dye in the equilibrium solution from that initially added. The general Freundlich equation expressed as (Kinniburgh, 1986)

$$S = s_T \cdot \left(\frac{\kappa C}{1 + \kappa C} \right)^{\beta} \tag{13}$$

was fitted to batch adsorption isotherms. Here S is the g of solute adsorbed per kg of soil, s_T is the total mass of surface sites (g kg^{-1}), κ is the overall affinity coefficient (L g^{-1}), C is the molar concentration of the solute in the equilibrating solution (g L^{-1}), and β is a dimensionless heterogeneity factor.

Miscible displacement experiments

Large, undisturbed soil cores (10.1 cm i.d.) used for miscible displacement experiments were excavated from areas immediately adjacent to the soil pits in plot B. Undisturbed soil cores were collected at 0 to 15, 20 to 40, 42 to 57, and 57 to 77-cm depths corresponding to the Ap/AB, Bt1, Bt2 and Bt3 horizons, respectively. Cylindrical soil columns (10.1 cm i.d.) were isolated by incrementally forcing a beveled cutting edge coupled to a polyvinyl chloride pipe over a previously carved pedestal of soil. Excess soil material at the bottom and top of the cylinders was trimmed flush and caps were secured to the ends to permit transport to the laboratory in Costa Rica.

A total of 33 miscible displacement experiments were conducted using nine soil columns (three columns for the Ap/AB horizon and two columns for each Bt horizon) using the methods of Schwartz et al. (1999). A unit hydraulic gradient was imposed at pressure heads ranging from -11.0 to 1.0 cm H_2O using 5.0 m*M* $CaBr_2$ as the influent solution and 5.0 m*M* $CaCl_2$ as the solution being displaced. Bromide concentrations in the effluent were measured using an ion-selective electrode. The parameters of the advective dispersive equation (ADE) were identified by fitting the analytical solution of Lapidus and Amundson (1952) to effluent concentrations. For the displacement experiments conducted at the slowest flow rates, the least-squares fit of the ADE solution to measured effluent concentrations was obtained by allowing both D and R vary. At greater pore-water velocities, the ADE was fitted to effluent concentrations by allowing only D to vary and calculating the retardation factor using the distribution coefficient obtained from the fit of the ADE for the same soil column at slow pore-water velocities. Values of the retardation factor exceeded unity due to the presence of goethite (7 to 11%) and an equilibrium pH in the effluent of approximately 4.6 which resulted in a small amount of positive charge in these soils (Schwartz, 1998).

Random walk simulations

Random walk simulations of dye movement were carried out assuming a steady state flux of 6.81 cm h^{-1} in all horizons for a period of 0.582 h and using the results of the miscible displacement experiments described above (Schwartz,1998). Volumetric water contents for each horizon were estimated from the linear interpolation of water content with respect to the flux in soil columns. This permitted the calculation of the mean pore-water velocity for each horizon (Table 1). The dispersion coefficient was estimated from the velocity-dispersion relationships of the ADE for Br^- displacement experiments (Schwartz, 1998). The retardation factor was estimated as

$$R = 1 + \frac{\rho_b \cdot s_T}{\theta} \cdot \left(\frac{\kappa C_0}{1 + \kappa C_0} \right)^{\beta} \tag{14}$$

where C_0 is the concentration of the dye applied to the soil surface. Using Eq. (14) to estimate the retardation factor, actual adsorption would exceed predicted adsorption at dye concentrations less than C_0 = 5.0 g L^{-1} used in this study. The minimum detectable concentration of dye associated with the methodology to identify stained pixels was estimated by mixing 1g of soil with 5 mL of dye solution at concentrations ranging from 0.1 to 2 g L^{-1}, decanting the supernatant, and permitting these stained soil samples to air dry for one-half hour on absorbent paper. The threshold at which dye became detectable was based on the color of pixels located at the exterior edge of regions designated as stained on color bitmap images. The closest match of the prepared stained soil samples to these pixel colors was used to estimate the threshold concentration in each horizon. Adsorbed concentrations in the stained soil samples were back-calculated using the fitted coefficients of the general Freundlich equation (Eq. 13) obtained for each horizon.

TABLE 1

Parameters used in the random walk simulation of dye movement assuming a steady state flux of 6.81 cm h^{-1} in all horizons for a period of 0.582 h.

Horizon	Depth	θ	v	D	R	C_{d0} (g L^{-1}) for indicated condition †			
	cm	m^3 m^{-3}	cm h^{-1}	cm^2 h^{-1}		**1**	**2**	**3**	**4**
Ap	0-7	0.537	12.7	65.2	1.77	0.486	0.43	0.104	0.0104
AB	7-15	0.537	12.7	65.2	3.47	0.0150	0.22	0.053	0.0053
Bt1	15-40	0.551	12.4	91.2	3.28	0.0118	0.23	0.055	0.0055
Bt2	40-57	0.578	11.8	679	4.19	0.0008	0.17	0.041	0.0041
Bt3	57-80	0.556	12.3	747	5.76	0.0004	0.13	0.031	0.0031

‡ C_{d0} is the estimated minimum detectable concentration for condition: **1**, adsorbed concentration of 1.5 g kg^{-1}; **2**, N = 600, Δz = 0.08 cm; **3**, N = 2500, Δz = 0.08 cm; **4**, N = 2000, Δz = 1.0 cm.

RESULTS

Batch adsorption

Batch adsorption isotherms for Brilliant Blue FCF dye were nonlinear and possessed a clearly defined maximum in all cases (Fig. 3). The isotherms were best approximated by the *general* Freundlich equation (13). The isotherms were not well described by the *reduced* Freundlich equation [i.e. Eq. (13) with $\kappa = 1/(1-C)$] due to the presence of clearly defined adsorption maximums. In addition, the Langmuir equation overestimated adsorbed concentrations at low solution concentrations (data not shown).

Since the adsorption isotherms were very steep at low concentrations (Fig. 3), it is apparent that the minimum detectable concentrations were actually a function of the color intensity of the dye when adsorbed to the soil. Once adsorbed to the soil, the hue of the blue dye took on a dull green color that, at low concentrations, was difficult to distinguish from organic stains. Based on the comparison of the color of stained soil samples with the color of pixels located at the outer edge of areas identified as stained, the threshold at which dye became detectable in each of the horizons corresponded to adsorbed concentrations between approximately 1 and 2 g kg^{-1}. Assuming an adsorbed threshold of 1.5 g kg^{-1}, the minimum detectable concentration estimated using the coefficients of the General Freundlich Equation for each horizon ranged from 4×10^{-4} g L^{-1} in the Bt3 horizon to 0.5 g L^{-1} in the surface horizon (Table 1). Appropriate values of Δz and N were chosen for the random walk simulation based on Eq. (8) and these results.

Flow patterns

Dye patterns exhibited by untilled subplots were characterized by incomplete staining of the surface horizon and an accumulation of dye at and just below the interfacial area between the Ap and AB horizons (Figs. 4 and 5). In both the Ap and AB horizons, the stained regions were not associated with discrete bio-channels or structural features. Tilled subplots exhibited rather uniform dye staining patterns in the Ap horizon without much of the bypassing characteristic of untilled plots (Fig. 4). At greater depths, however, stained regions were associated with ped interfaces, roots and root channels irrespective of the treatment.

Incomplete staining of the surface horizon was enhanced when dye was applied to initially dry soil profiles (Fig.5). For these subplots, much of the Ap horizon remained unwetted as well as unstained. This enhanced “bypass” of both water and dye in initially dry soil profiles is likely attributed to the water repellency exhibited by peds in the surface horizon. Once wetted, however, these peds did not exhibit any visual evidence of water repellency (i.e. water drops infiltrated into peds within a time period of less than five s). Flow paths through the surface horizon exhibited in many of the images for untilled plots cannot be attributed to surface ponding since the application rates were one order of magnitude less than the steady state infiltration rate at this site (Schwartz, 1998). Although small saturated areas appeared on the soil surface during the application of the dye, these areas were not associated with flow patterns exhibited immediately below the surface. This suggests that, for these soils, bypass flow is generated below rather than at the surface.

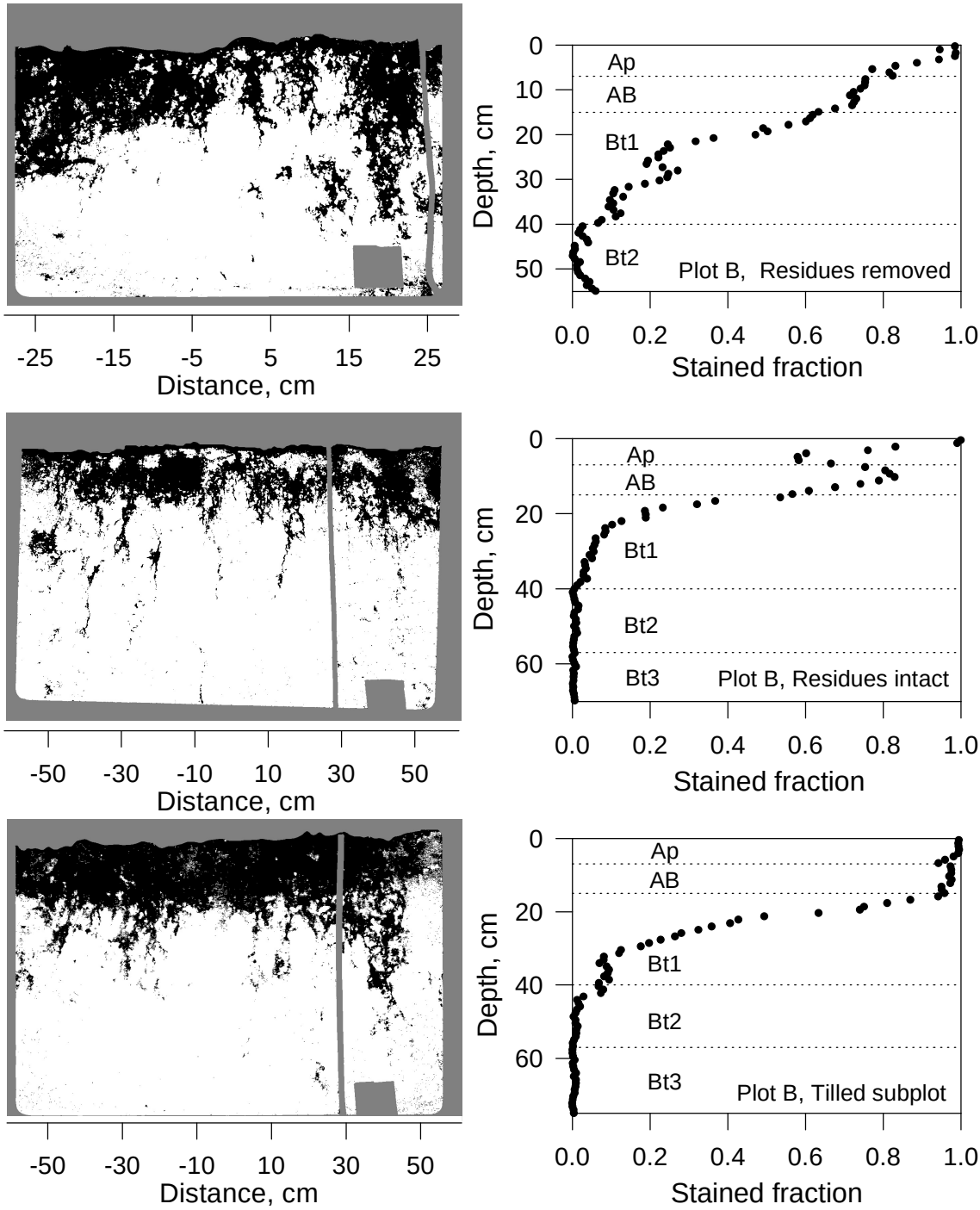

Fig. 4. Vertical cross-sections of stained (black pixels) sub-plots (left) and the corresponding fraction of stained soil area (right) as a function of depth for plot B after a sprinkling application of 4.0 cm dye solution. The depth scale on the stained-fraction plots applies also to the adjacent left image. Gray areas in the image are labels or exterior regions that were not counted in the calculation of the fraction of pixels stained. Some images are tilted to correct for slope.

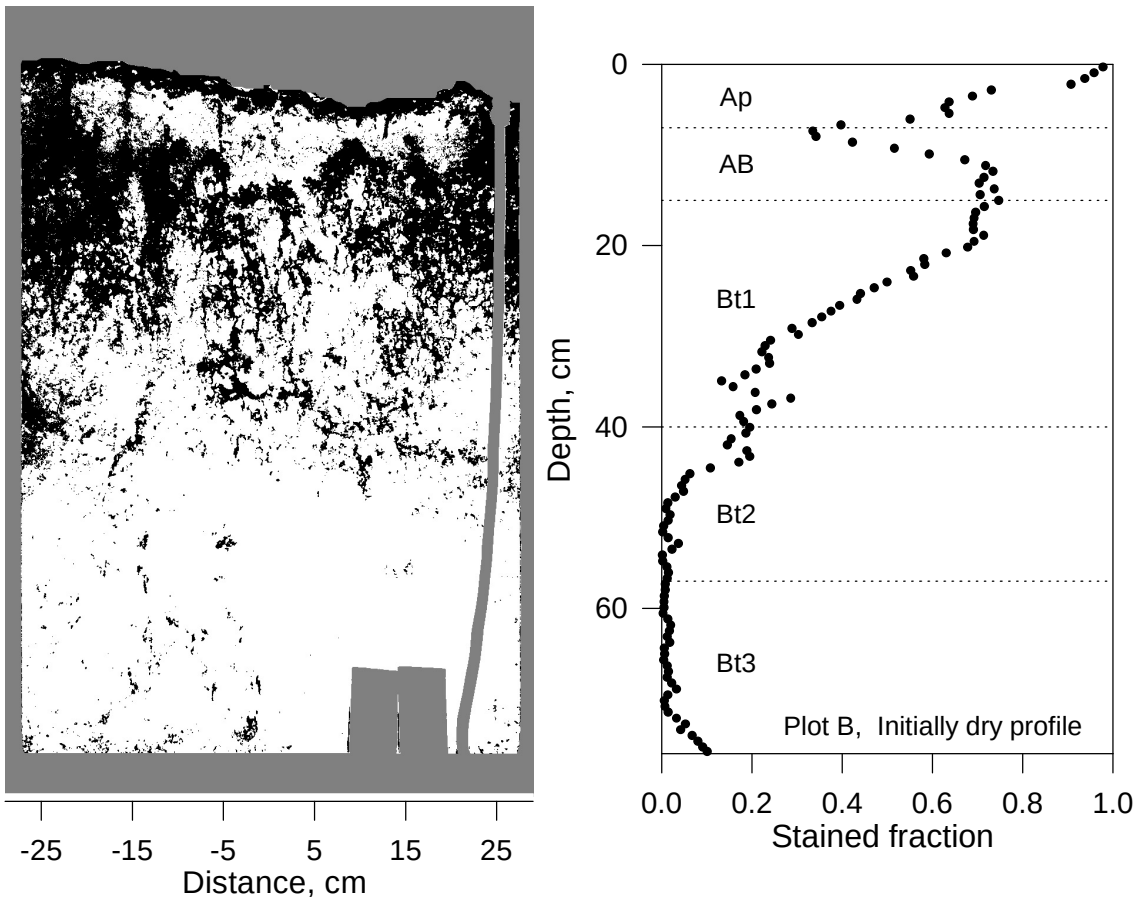

Fig. 5. Vertical cross-section of the stained (black pixels) sub-plot (left) and the corresponding fraction of stained soil area (right) as a function of depth after a sprinkling application of 4.0 cm dye solution to the initially dry soil profile of plot B. The depth scale on the stained-fraction plots applies also to the adjacent left image. Gray areas in the image are labels or exterior regions that were not counted in the calculation of the fraction of pixels stained.

Vertical Dye Distribution

The fraction of area stained by the dye as a function of soil depth is shown in Figs. 4 and 5. Analysis of variance indicated that there was a significant (p = 0.012) treatment effect for the vertical spread (σ) of the distribution of stained soil. Although tilled subplots exhibited the lowest vertical spreading of stained soil in all plots, multiple comparison of means using Duncan's Multiple Range Test indicates that no significant difference existed among the treatments that were pre-wetted (Table 2). However, dye applications under the dry antecedent moisture conditions resulted in a significantly greater spreading of dye (Table 2). A significant (p = 0.0098) treatment effect for the analysis of variance of the fraction of stained soil in the Ap horizon suggests that tillage increased the interaction of dye with this horizon (Table 2).

The random walk simulation of the vertical distribution of stained soil fraction for plot B using three different assumed minimum detectable concentrations is shown in Fig. 6a. These simulations assumed steady state flow and underestimated dye adsorption over the entire concentration range for each soil horizon. Hence, random walk simulations should overestimate the depth of dye penetration because i) for the initially wet soil profiles in the field, approximately one-quarter of the water applied would fill empty pores before steady state flux could be achieved, and ii) the underestimation of adsorption using linearized isotherms would also increase predicted transport rates. Comparison of the random walk simulations (Fig. 6a) with the plot B vertical distributions of dye (Fig. 4) suggests that the dye moved considerably further in the field than that predicted using dispersion coefficients obtained from column displacement experiments. For the parameters used

TABLE 2

Mean dye penetration, vertical spreading, and stained-fraction in the Ap horizon as influenced by treatments applied to subplots.

	Mean dye penetration, μ cm	Vertical spreading, σ cm	Stained-fraction in Ap horizon
Not pre-wetted, residue	19.2 †	29.1 a‡	0.72 a
Pre-wetted, residue intact	15.2	15.6 b	0.78 ab
Pre-wetted, residue	19.4	13.5 b	0.88 bc
Pre-wetted, tilled	20.5	9.2 b	0.97 c

† Treatment effect not significant with respect to mean dye penetration.
‡ Within columns, values followed by the same letter are not significantly different ($P < 0.05$).

in this random walk simulation, decreasing the minimum detectable concentration had little effect in increasing the depth at which the stained-fraction approached zero. Apparently, the simulated concentrations declined steeply at around 20 to 25 cm and the predicted fraction of stained soil became insignificant at these depths. In contrast, a 10-fold increase in the dispersion coefficient for each horizon (Fig. 6b) produced vertical distributions of stained soil fractions similar to those in Fig. 4 as well as in the other pre-wetted subplots. Clearly, the solute spreading in the field

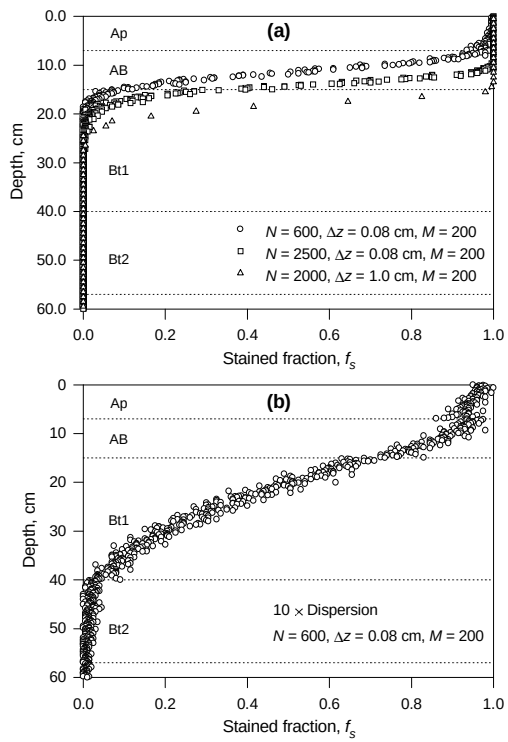

Fig. 6. Simulated fraction of soil stained with respect to soil depth for (a) the dispersion coefficients listed in Table 1 and (b) for dispersion coefficients 10 times greater. The corresponding minimum detectable concentration for each simulation and horizon is listed in Table 1.

was greater than that predicted by dispersion coefficients obtained from column displacement experiments. The influence of soil horizonation on the stained-fraction with depth was observed on many subplots. This effect is clearly manifested by the discontinuity of the slope of the stained-fraction × depth relationship at the transition zone between the Ap and AB horizons exhibited by untilled plots (Figs 4 and 5). Less pronounced transition zones between deeper horizons are distinguishable for some vertical dye distribution patterns. This phenomenon is likely a consequence of a lack of pore continuity between horizons and abrupt changes in media properties which give rise to changes in mean pore-water velocity and solute spreading. Abrupt changes in stained-fraction at the Ap-AB interface also may be linked to the tillage of the field when it was converted to annual crops. Random walk simulations also produced a discontinuity (in the macroscopic sense) between the Ap and AB horizons (Fig. 6b). In this case, the discontinuity of the stained-fraction was caused by an increase in the retardation factor, which is manifested as slower pore-water velocities and smaller dispersion coefficients in the simulation.

DISCUSSION AND CONCLUSIONS

The dye patterns exhibited in this soil demonstrate that significant bypassing can occur under rainfall intensities below the steady state infiltration rate. As indicated by the dye staining patterns, preferred pathways in the Bt horizons were associated with ped interfaces and biochannels. This suggests that in the subsoil, limits on water transport through the matrix regions caused water to be channeled through these larger, continuous pores. In contrast, the fingering pattern observed in the surface horizons (0 - 15 cm) did not appear to arise from horizontal variations in soil properties that could limit transport. From field observations and thin sections, the Ap and AB horizons lacked large peds (> 1 cm) that would laterally limit diffusive or advective exchanges to generate the observed flow patterns. In addition, column displacement experiments indicate that dispersion generated by the slow exchange of solute between intra-aggregate and inter-aggregate regions was negligible in the Ap and AB horizons at flux rates less than 10 cm h^{-1} (Schwartz, 1998).

The greater dispersion in the field compared with column studies as indicated by the random walk simulations is frequently observed and usually attributed to the laboratory measurement scale being too small to encompass the full heterogeneity of field plots. (Jury and Flühler, 1992). Both column studies and thin sections suggest that horizontal variability in soil properties influencing transport under steady state flow conditions for the Ap/AB horizons was at a smaller scale than the column size. For the displacement experiments of Schwartz (1998), the range in dispersivity exhibited by the Ap/AB soil columns at similar water fluxes was relatively narrow (4.2 ± 1.0 cm). This outcome is supported by field observations and thin-sections that indicate a lack of large structural features in the Ap and AB horizons. Staining patterns in the field, however, show that there are large horizontal variations over distances greater than 10 cm, the diameter of laboratory columns. Thus, horizontal variability in staining patterns in the Ap and AB horizons does not seem to arise from the horizontal variability in soil properties.

Instabilities generated near the soil surface (which were absent in the steady-state column experiments) may be responsible for much of the discrepancy between field and column generated dispersion. Erratic flow patterns such as fingering, distribution flow, and preferential flow have been previously identified as potentially important processes that influence lateral solute mixing in the field (Ritsema and Dekker, 1995; Flühler et al., 1996). Fingered flow patterns were obviously generated by the presence of water repellent soil peds in the surface horizon of initially dry plots. Ritsema et al. (1998) have proposed that such fingers represent permanent flow pathways where repeated wetting and drying over time has led to leaching hydrophobic substances from ped and pore surfaces. Although water repellency is usually associated with coarse textured soils that possess small specific surface areas (Ma'shum et al., 1989), development of water repellence has been detected in fine textured soils (Giovannini et al., 1983; Dekker and Ritsema, 1996) and also in weathered oxidic soils (Chan, 1992). It is unlikely that water repellency was a major factor in the development of fingered flow in the pre-wetted plots because water drops infiltrated instantly into wetted peds obtained from the Ap horizon. In general, dry soils will characteristically lose their hydrophobic properties upon complete wetting (Wallis and Horne, 1992). Instability in pre-wetted plots may have been produced by the presence of large voids that reduce the water-bubbling pressure of the porous media and therefore increase the probability for the onset of instability at the wetting front (Wang et al., 1998).

Results of this study indicate that disturbance of the soil surface by hoeing reduced the spreading

of dye and increased the interaction of the dye with the surface horizon. Similar effects of tillage reducing dispersion and bypass flow have also been reported by Andreini and Steenhuis (1990) and Wu et al.(1995). Such an effect is anticipated because tillage destroys the large-scale spatial features that promote the generation of large variances in pore-water velocity. Moreover, under conventional tillage practices, conditions are not conducive to the occurrence of water repellence (Chan, 1992) and this in turn promotes more uniform wetting of the profile. Tillage would therefore increase the interaction of surface applied solutes with the surface horizon. Under no-till management, however, residence times of solute already within the undisturbed surface horizons would be expected to be longer than in tilled soils. This may be important when native sources of N make significant contributions to crop requirements.

ACKNOWLEDGMENTS

This work was supported in part by the Soil Management Collaborative Research Support Program (USAID Grant No. DAN-1311-G-SS-6018-00).

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