Frequency distribution of water and solute transport properties derived from pan sampler data

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Abstract. Modeling of water and solute movement requires knowledge of the nature of the spatial distribution of transport parameters. Only a few of the field experiments reported in the literature contained enough measurements to discriminate statistically between lognormal and normal distributions. To obtain statistically significant data sets, six field experiments at four different sites were performed. Different degrees of macropore and matrix flow occurred at each site. In each experiment a solute pulse was added followed by artificial or natural rainfall. Sixteen thousand spatial distributed fluxes and solute concentrations were collected with wick and gravity samplers. Spatial distributions of solute velocity, dispersion coefficient, water flux, and solute concentration were determined over different timescales ranging from 1 hour to the duration of the experiment. A chi-square test was used to discriminate between the type of frequency distributions. The spatially distributed water and solute transport parameters when averaged over the experimental period were found to fit the lognormal distribution when macropore flow dominates. Otherwise, when only matrix flow occurs a normal distribution fitted the data better. Under no-till cultivation, hourly concentration and water flux are lognormally distributed, while tillage makes the tracer concentration to be normally distributed. Spatial frequency distributions of daily solute concentration change in time: Concentrations were normally distributed when the bulk of the solute broke through with the highest concentrations and lognormally distributed in the beginning and end of the experiment. Daily water flux was found to be lognormally distributed throughout the experiment, but the distribution varied between water applications: Shortly after water application, when wick and gravity pan samplers collected water predominantly from macropores and normally distributed at later times when mostly matrix pores were sampled with wick pan samplers.

1. Introduction

The quality of groundwater and surface waters is increasingly being compromised through recharge water that still contains significant concentrations of surface-applied chemicals such as fertilizers and pesticides [*Clothier et al.*, 1996]. Spatial distribution of the invading solute is an important factor in the amount of solutes that reach the groundwater [*Jury et al.*, 1982]. Realistic modeling in field soils require, therefore, the spatial and temporal variation of the parameters describing water and solute transport [*Biggar and Nielsen*, 1976; *Jury*, 1982, 1985; *Simmons*, 1982; *Sposito et al.*, 1986].

Numerous studies have focused on the spatial variability of water and solute transport. The most notable studies were by *Biggar and Nielsen* [1976]. A review of other early works is given by *Jury* [1985]. Moisture content was found to be normally distributed [*Rogowski*, 1972; *Nielsen et al.*, 1973; *Bababola*, 1978; *Russo and Bresler*, 1981], while infiltration rate,

solute velocity, saturated hydraulic conductivity, and dispersion coefficient were usually lognormally distributed [*Rogowski*, 1972; *Nielsen et al.*, 1973; *Biggar and Nielsen*, 1976; *Warrick et al.*, 1977; *Van De Pol et al.*, 1977; *Bababola*, 1978; *Russo and Bresler*, 1981; *Sisson and Wierenga*, 1981; *Wilson and Luxmoore*, 1988].

There are several shortcomings in the above mentioned studies, making their results tentative at best. The sample sizes were usually too small. About 20–30 observations are required to distinguish between normal and lognormal distributions [*Rao et al.*, 1979]. Only *Nielsen et al.* [1973], *Biggar and Nielsen* [1976], *Warrick et al.* [1977], *Nassehzadeh-Tabrizi and Skaggs* [1983], and *Hagerman* [1990] had data sets that were large enough. Another drawback was that visual inspection was used for establishing normality or lognormality. More rigorous methods are the chi-square test [*Russo and Bresler*, 1981] and the Kolmogorov-Smirnov test [*Rao et al.*, 1979]. In this regard it is of interest that in the sufficiently large data sets of *Nassehzadeh-Tabrizi and Skaggs* [1983] and *Hagerman* [1990] the hypothesis of either normality or lognormality using the Kolmogorov-Smirnov test could not always be accepted.

We carried out six experiments at four different locations in which we observed the spatial distribution of water and solutes flow with grid pan samplers with the goal to summarize the spatial distribution of these parameters. The grid pan samplers, consisting of 25 individually sampled cells of 6.1 by 6.1 cm, are superior over porous cup samplers in sampling water and solute fluxes in the unsaturated soil [*Boll*, 1995]. The

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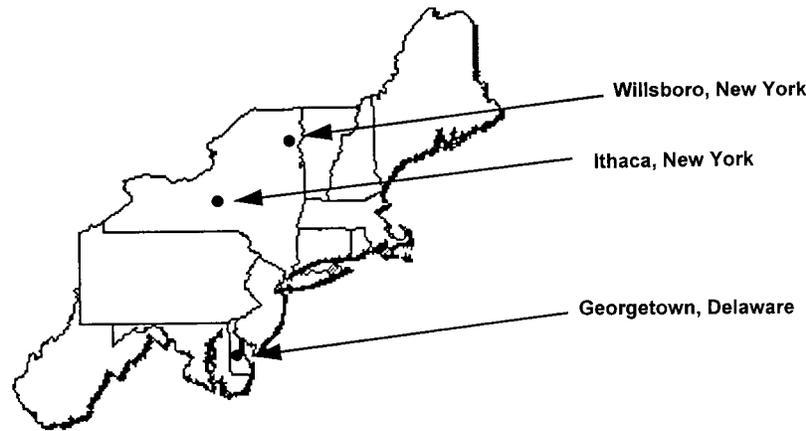
Figure 1. Location of experimental sites.

spatial distribution of fluxes, velocities and dispersion coefficients are examined. The effect of macropores and averaging over different timescales is discussed as well.

2. Materials and Methods

Six experiments were carried out at four sites (Figure 1). In each experiment a pulse of nonadsorbed tracer (chloride or bromide) was applied and was followed by irrigation or natural rainfall. Samples were collected regularly with wick and gravity pan samplers, installed at a depth of 0.6–0.7 m in 0.9-m-long tunnels excavated in the side of a trench (Figure 2). Each sampler consisted of 25 cells, each 6 by 6 cm, which were sampled separately. Cells of wick samplers have wicks that are 45 cm long. The solutions were collected in bottles that were changed periodically. The trench was left open to facilitate the sampling. In all, 25 breakthrough curves were obtained for each pan sampler. Additional details for the individual experiments are outlined in Table 1 and are given after the four sites are described.

The four experimental sites were the University of Delaware Research Center in Georgetown ("Delaware"); Cornell University's Thompson Vegetable Farm near Freeville, New York ("Freeville"); Cornell University's Experimental Research Farm in Willsboro, New York ("Willsboro"); and Cornell University's orchard in Ithaca, New York ("Orchard"). Described below are land uses and the soils for each of the four experimental sites.

2.1. Freeville

The soil at the Freeville site is a well-drained Genesee silt loam (fine-loamy, mixed, nonacid, mesic Typic Udifluvent), characterized by 0.6 m of dark brown loamy soil containing 30,000–50,000 worm and root channels per square meter in diameters ranging from 0.5 to 3 mm, overlying a dark brown silt loam to very fine sandy loam. A substratum of layers of gravel and sand exists at approximately 1.8 m. The saturated hydraulic conductivity is between 35 and 120 cm d^{-1} [*Neeley*, 1965].

2.2. Delaware

The upper 0.6–0.8 m of the Evesboro sandy loam (mesic, coated Typic Quartzipsamment) is a rather structureless, single grain, yellowish-brown loamy sand with remnants of roots from an old tree stand. Layers of fine sand (or occasionally grayish

loam) and coarse material, typical of Pleistocene fluvial deposits, occur below 0.8 m depth. For the upper 0.3 m the average hydraulic conductivity is 4 m d^{-1}, and for the 30–60 cm depth it is 2.5 m d^{-1} [*Ireland and Matthews*, 1974].

2.3. Orchard

The Hudson silty clay loam consists of a pale brown fine-grained soil with a subangular blocky structure and hexagonal shaped peds of 0.2–0.3 m in diameter. Surface connected cracks were present, some as wide as 10–20 mm. For the upper 25 cm the hydraulic conductivity ranges from 40 to 120 cm d^{-1}, and for depths from 0.25–1.10 m the conductivity is between 1 and 40 cm d^{-1} [*Neeley*, 1965]. During the summer we measured much higher conductivities because of the flow of water through the macropores [*Merwin et al.*, 1994].

2.4. Willsboro

The upper 0.4 m of the Rhinebeck Variant clay (illitic, mesic Aeric Ochraqualfs) is grayish brown with a moderate medium granular structure penetrated by many roots. Lower in the profile, the structure became angular blocky with rocks present and fewer roots. In the 0–0.3 m soil layer, the average conductivity is 60 cm [*Bro*, 1984]. It decreases to less then 1 cm d^{-1} for the layer between 30 and 60 cm. At deeper depths the conductivity increases again to approximately 60 cm d^{-1} [*Olson et al.*, 1982]. Water movement in the layer from 30 to 60 cm is through macropores only [*Steenhuis et al.*, 1990].

2.5. Experimental Procedures

Two experiments were performed at the Freeville site, E1 and E2; two at Delaware, E3 and E4; one in the orchard, E5; and one at Willsboro, E6. Of these experiments, one was car-
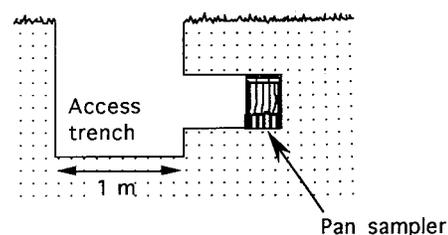

Figure 2. Sampling setup.

Table 1. Summary of Field Experiments

	Freeville 1	Freeville 2	Orchard	Delaware 1	Delaware 2	Willsboro
Soil type	silt loam	silt loam	silty clay loam	sandy loam	sandy loam	sandy clay loam
Type of tracer	bromide	bromide	bromide	chloride	bromide	chloride nitrate
Type of pulse application	solution	solution	solution	solution	solution	flakes
Pulse concentration	7.8×10^{-3} kg L^{-1}	14.5×10^{-3} kg L^{-1}	7.8×10^{-3} kg L^{-1}	2.2×10^{-3} kg L^{-1}	1×10^{-2} kg L^{-1}	4000 kg Cl ha^{-1}, 23 kg N ha^{-1}
Pulse length, cm	4	4	3.5	4	2	NA
Type of water application	sprinkler	sprinkler	sprinkler	sprinkler	natural rainfall	sprinkler
Duration of rainfall	2–3 h d^{-1}	13.5 hours	2–3 h d^{-1}	6 hours: 10 min on, 35 min off	variable	2 events: 7, 4.75 hours
Rainfall rate, cm h^{-1}	1.5	1.5	1.5	1.5	variable	0.9
Length of study, days	21	1	21, 12	21	131	2
Total applied water, cm	84	20	49, 35	63	40	15
Depth to sampler, cm	60	60	60	60–70	60–70	60
Sampler type (number)	wick (2), gravity (2)	wick (2), gravity (2)	wick (2), gravity (2)	wick (2)	wick (2)	wick (4)

ried out with natural rainfall, four had daily intermittent rainfall, and one had continuous rainfall.

2.5.1. Experiment 1 (E1). Two wick and two gravity pan samplers were installed in a grass covered plot in Freeville. Twenty millimeters of artificial rainfall were applied twice a day (10 A.M. and 4 P.M.) starting on July 25, 1990. The rainfall rate was 10–15 mm h^{-1}. On August 2, after a constant pan sampler outflow pattern had been achieved, a 7.8 g L^{-1} bromide solution was applied for 1 day, followed by 22 days of artificial rainfall as before. Water samples were collected daily to determine outflow volume and bromide concentration. Drainage outflow was also measured between three irrigation events as follows: starting 15 days after bromide application, samples were taken 4 and 16 hours after the 4 P.M. irrigation and, on the following day, 0 and 3 hours after the 10 A.M. irrigation and 0 and 2 hours after the 4 P.M. irrigation.

2.5.2. Experiment 2 (E2). This experiment was also carried out in Freeville and used the same four samplers as in E1. The grass covered plot was irrigated three times with 20 mm of water on June 24, 1991. The next day, a pulse of 20 mm of water containing 14.5 g L^{-1} bromide was applied. The bromide pulse was followed immediately by a continuous water application of 11.5 hours at a rate of 15–20 mm h^{-1}. Water samples were collected from all four samplers 1.5, 4, 5.5, 7.5, 9.5, 11.5, and 13.5 hours after the start of pulse application and analyzed for outflow volume and bromide concentration.

2.5.3. Experiment 3 (E3). At the Delaware site four wick pan samplers were installed: one in a plot which was under ridge tillage (RT), two under reduced tillage (chisel plow and disk) and an application of poultry manure (PM1 and PM2), and one under reduced tillage with a winter cover crop of rye and white clover (WC). The plots were irrigated twice with 40 mm of water and on July 16, 1992, a 40 mm of a solution with 2.2 g L^{-1} chloride solution was applied to each plot, followed by 21 days of artificial rain. The rain was applied from 6 A.M. until noon in cycles of 10 min on and 35 min off. The total amount of rain on the plots was 40 mm d^{-1}. Water samples were collected daily to determine outflow volume and chloride concentration.

2.5.4. Experiment 4 (E4). The location and the samplers were identical to those in E3. E4 was carried out from October 1992 to March 1993. A 10 g L^{-1} bromide solution in 20 mm of artificial rainfall was followed by approximately 400 mm of natural rainfall during 131 days. Samples were collected weekly to biweekly, depending on the occurrence of rain events, to determine outflow volume and bromide concentration.

2.5.5. Experiment 5 (E5). In the orchard, two plots were used, offset by 20 m: a mowed-grass-covered plot and a moss-covered plot. Each plot had one wick and one gravity pan sampler installed. On July 18, 1991, water was applied to the grass plot at a rate of 10–15 mm h^{-1} for 3–4 hours. A pulse of 6 g L bromide was added to the first irrigation. Irrigation was continued daily until August 12 except for 6 days. The moss plot was irrigated daily (except three times) from July 29 until August 12. The first irrigation contained 6.8 g L^{-1} bromide. Water samples were collected daily to determine outflow volume and bromide concentration.

2.5.6. Experiment 6 (E6). For the Willsboro site two wick pan samplers were installed in a no-till plot (NT) and two in a conventionally tilled plot (CT). Twenty-three kg N ha^{-1} on May 5, 1993, and 4000 kg Cl ha^{-1} on August 17, 1993, were surface-applied followed by two 9 mm h^{-1} irrigation events on August 18 and 19, 1993, lasting 7 hours on the first day and 4.75 hours the second day. Samples were collected seven times: 0, 2, 15, and 18 hours after the end of the first irrigation and 0, 2, and 18 hours after the end of the second irrigation. For each sample, outflow volume and NO_3 and Cl concentrations were determined.

2.6. Data Analysis

The first step in the data analysis was to reduce the approximately 6000 data points of concentration and flow to properties related to the transport of water and solutes for each cell. Then we averaged the transport parameters over different time periods and determined the spatial frequency distributions for the data. Finally, we performed statistical analysis and checked if the spatial distribution was lognormal or normal.

2.7. Transport Properties

The transport related parameters were averaged over three timescales: hour, day, and the experimental period defined as the time from the pulse application till the water application was stopped. At this time, the solute concentration was small. For each cell, the parameters averaged over the experimental period consisted of solute velocity (v_s), dispersion coefficient (D), and the average flux, (q_{avg}); v_s and D were found by fitting cumulative outflow and bromide or chloride concentration to the convective-dispersive equation with flux type boundary conditions using CXTFIT [*Parker and van Genuchten*, 1984]. An estimate of v_s and D for the orchard and Willsboro experiments could not be obtained because the convec-
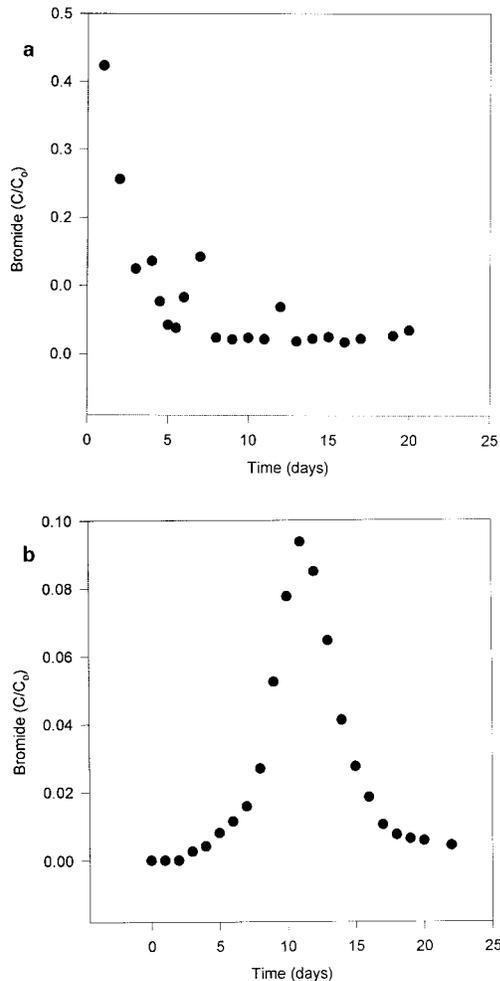
Figure 3. Example breakthrough curves for a cell: (a) orchard site (cell 22 in gravity sampler in E5) and (b) Freeville site (cell 11 in wick sampler in E1).

tive-dispersive equation could not describe solute flow through macropores at these sites. Figure 3a is a typical breakthrough curve at the orchard and Willsboro sites. These types of curves can be represented by a model in which the solute is distributed in a surface layer to the macropores [*Steenhuis et al.*, 1994]. Figure 3b is an example of a breakthrough curve for the Freeville and Delaware sites. Fitting the data with CXTFIT for the Freeville and Delaware sites requires the assumption that a variable water application rate can be replaced by the cumulative drainage. *Wierenga* [1977] showed that this assumption was valid. CXTFIT cannot estimate pore volumes directly. Therefore the following procedure was used: A pore volume was estimated and used as input for the CXTFIT, which returned a retardation factor. To obtain the actual pore volume (P_v), the estimated pore volume was multiplied by the calculated retardation factor. The travel time (T) to the sampler was found as

$$T = \frac{P_v}{q_{\mathrm{avg}} A} \tag{1}$$

where q_{avg} is the average water flux over the duration of the experiment and A is the area of the cell. Finally, the average solute velocity was calculated as

$$v_s = \frac{d}{T} \tag{2}$$

where d is the depth of the sampler. The average flux per cell, q_{avg}, was calculated by dividing the cumulative drainage volume from each cell by the duration of the experiment.

Daily averaged parameters include the flux (q_d) and the concentration (C_d) and were computed for three experiments: E1, E3, and E5. The other experiments were of too short a duration to obtain sufficient data points. For E3, q_d and C_d of only days 3 through 12 were analyzed because concentrations were very low from days 13 through 21; q_d and C_d of both plots in E5 were analyzed separately because the experiment on the grass plot started 10 days before the experiment on the moss plot. The flux (q_h) and concentration (C_h), which were averaged over periods of several hours, were determined for experiments E1 and E6. In these experiments, detailed sampling occurred between irrigation events.

2.8. Frequency Distributions

Data from the 25 cell wick samplers were noninteracting, providing samples representative of the native soil flux through each region. The cells were physically separated and any lateral flow through the soil was unlikely because the ability to take up water in the wick is large compared to the soil water fluxes. For example, the saturated hydraulic conductivity of the wick is 800 cm/h [*Knutson and Selker*, 1994]; for a sandy loam it is 4.4 cm h^{-1}, for a sandy clay loam it is 1.3 cm h^{-1}, for a silt loam it is 0.45 cm h^{-1}, and for a silty clay loam it is 0.07 cm h^{-1} [*Carsel and Parrish*, 1988]. Although the mathematical analysis of the flow pattern above the wick is very complicated, it is obvious from the analysis of *Rimmer et al.* [1995] that for homogeneous soils when the ratio of flux to the conductivity of the wick is large, the disturbance in flow is small. The gravity pan samplers form capillary fringe above the sampler and, as we will see later, the assumption of noninteracting is not valid anymore. Only for the silty clay loam the flux-conductivity ratio could be close to 1. In this case the soil is not homogeneous and the water movement takes place through the more permeable soils between the dense peds. The dense peds prevent any sideways flow. For this reason, gravity pan and wick samplers give the same result for these silty clay soils.

Normal and lognormal distributions were considered because they are used most frequently for describing the spatial variability of soil and water transport properties [*Rao et al.*, 1979]. Goodness-of-fit tests were applied to the grid pan sampler data to characterize the spatial variability of v_s, D, q_{avg}, q_d, q_h, C_d, and C_h. A χ^2 analysis was used to test two null hypotheses, Ho: (1) The observations were drawn from a population with a normal distribution, $N(\mu, \sigma)$, and (2) the observations were drawn from a lognormal distribution, ln $N(\mu, \sigma)$. The χ^2 analysis is a comparison between the actual number of observations and the expected number of observations according to the hypothesized distribution, as measured in a selected set of intervals [*Snedecor and Cochran*, 1967]. A smaller χ^2 value means that the data more closely approach the selected distribution. The number of degrees of freedom is the number of class intervals reduced by 3. Note that a fit of the actual data to the normal distribution does not exclude the fit of the natural logarithm of the actual data to the normal distribution, and vice versa.

The maximum possible sample size (n) was 100 (four samplers with 25 cells each). When pan sampler types or tillage

Table 2. Selection of Data Sets for χ^2 Analyses

Experiment	Total Data Set	Subset 1	Subset 2	Subset 3
Delaware 1	4 wick	2 wick in PM1, PM2	1 wick in RT*	1 wick in WC
Delaware 2	4 wick	2 wick in PM1, PM2	1 wick in RT*	1 wick in WC
Freeville 1	2 wick, 2 gravity	2 wick	2 gravity	⋯
Freeville 2	2 wick, 2 gravity	2 wick	2 gravity	⋯
Orchard	2 wick, 2 gravity	1 wick, 1 gravity in grass plot	1 wick, 1 gravity in moss plot	⋯
Willsboro	4 wick	2 wick in NT plot	2 wick in CT plot	⋯

Subsets were based on tillage treatment or sampler type. Wick, wick pan sampler; gravity, gravity pan sampler; PM, poultry manure; RT, ridge tillage; WC, winter cover; NT, no-till; CT, conventional tillage.
*Insufficient data for analyses, sample size <25.

treatments were different, the data were analyzed with both the maximum possible sample size and the appropriate subset(s) (Table 2). More specifically, in E1 and E2, in Freeville, data from all four samplers and, separately, data from wick and gravity pan samplers were analyzed. In E3 and E4, in Delaware, data from all four plots (poultry manure (PM1 and PM2), ridge tillage (RT), and winter cover crops (WC)) and from one subset (PM1 and PM2) were tested. Data from the RT and WC plots could not be analyzed as a subset because of low sample size ($n < 20$–30). In E5, in the orchard, data from all four samplers were analyzed and subsets were based on management practice, one wick pan and one gravity pan sampler for each plot. In E6, at Willsboro, subsets were created by tillage treatment: two wick pan samplers in the NT plot and two in the CT plot (Table 2).

Throughout the sections 3 and 4 the following convention is used: If the χ^2 analyses showed that the maximum possible sample size had the same type of distribution as the subset(s), the overall results are presented. Otherwise, if the distributions were different, the subsets are displayed.

3. Results

The χ^2 of the spatial frequency distribution are given for the parameter sets that are averaged over either the experimental period, day, or (several) hours. First, the "experimental averaged" spatial frequency distributions are presented.

3.1. χ^2 Tests Applied to Parameters Averaged Over the Experimental Period

Solute velocity (v_s), dispersion coefficient (D), and average water flux (q_{avg}) are properties describing the average water and solute transport in each cell over the whole experimental period. Note that the solute velocity was derived from the concentration data and not by dividing the average flux by an

average water content. The χ^2 values for the v_s, D, q_{avg}, and sample size are shown in Table 3. In general, the data fit the lognormal distribution in more cases than the normal distribution. Specifically, in experiments E1 and E2, at Freeville on the silt loam soil, v_s, D, and q_{avg} fit the lognormal distribution (lowest χ^2) under intermittent rainfall (E1) and the normal distribution under continuous rainfall (E2), although not in all cases significant at the 5% level. A trend similar but less distinct can be seen for experiments E3 and E4 for the sandy loam soil in Delaware. Experiment E3, which had the low χ^2 values for the lognormal distribution, took place during the summer with high amounts of (intermittent artificial) rainfall. In contrast, experiment E4, for which the parameters were more normally distributed than for E3, occurred during the winter, when there was less (and more uniform) recharge under natural rainfall conditions. Table 3 also shows that for experiments where the irrigation water was applied daily (experiments E1, E3, and E5), q_{avg} was lognormally distributed; however, note that the difference between normality and lognormality was less for lighter-textured soils than for the more clayey soils.

3.2. χ^2 Tests Applied to Parameters Measured Daily

In experiments E1, E3, and E5 sample bottles were collected daily. Changes in the frequency distribution of the daily water flux, q_d, and daily bromide concentration, C_d, are illustrated for experiments with wick pan sampler 1 of experiment E1 in Figure 4. The q_d and C_d in the 25 cells of wick pan samplers are shown for days 4, 10, and 19. On day 4, C_d varied strongly within the sampler. Note that in Figure 1 the cell in the middle of the sampler with high concentration is likely caused by a pore directly connected to the surface. On day 10, when the peak concentrations in the sampler occurred, the spatial variation of C_d had decreased considerably. The middle cell with the high concentration on day 4 has on day 10 a concentration

Table 3. Results of χ^2 Test of Goodness-of-Fit of the Normal Distribution, Applied to v_s, ln v_s, D, ln D, q_{avg}, and ln q_{avg}

Experiment	v_s	ln v_s	D	ln D	q_{avg}	ln q_{avg}
Delaware 1, wick ($n = 50$)*	13.1† (7)	9.5† (7)	48.7 (7)	10.1† (7)	14.2 (7)	9.1† (7)
Delaware 2, wick ($n = 43$)	25.0† (7)	18.0† (7)	16.5 (7)	12.4† (7)	9.5† (7)	13.9† (7)
Freeville 1, wick ($n = 50$)	16.1 (7)	8.6† (7)	64.1 (7)	25.3 (7)	22.0 (7)	11.5† (7)
Freeville 1, gravity ($n = 47$)	109 (6)	14.3 (6)	320 (6)	11.9† (6)	34.8 (7)	3.5† (7)
Freeville 2, wick and gravity ($n = 72$)	18.4 (5)	37.8 (5)	11.9† (6)	44.5 (6)	9.7† (7)	20.3 (7)
Orchard, wick and gravity ($n = 100$)	⋯	⋯	⋯	⋯	77.3 (7)	4.2† (7)
Willsboro, wick ($n = 100$)	⋯	⋯	⋯	⋯	45.9 (9)	13.0† (9)

Observed frequencies in each class interval were made the same; degrees of freedom are given in parentheses.
*n, sample size.
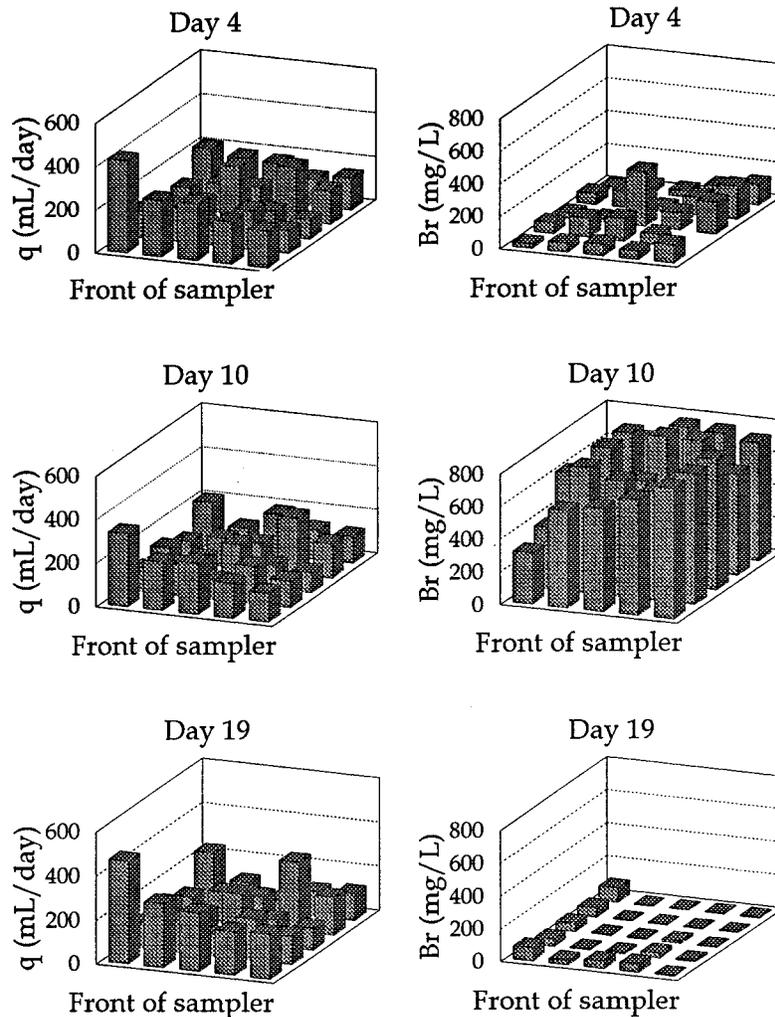†Null hypothesis is accepted at the 0.05 level [*Snedecor and Cochran*, 1967].

Figure 4. Daily water flux (q_d) and bromide concentration (C_d) for 25 cells in wick pan sampler 1 for days 4, 10, and 19 in experiment 1 (E1).

that is relatively lower than the remaining cells: Solute-free rainwater was now carried through the same surface connected macropore. Towards the end of the experiment (day 19), bromide concentrations were low and the spatial variation was less. The spatial distribution of daily water flux, q_d, did vary much less than the solute spatial distribution of the concentrations. For example, the front most left cell always had the highest flux.

Figures 5–8 show the χ^2 values for q_d and C_d as a function of time for E1, E3 (subset PM1 and PM2), and E5. The χ^2 values below the horizontal line are significant at the 5% level. The trends observed in Figure 4 are confirmed by the analysis in Figure 5. While the daily flux, q_d, fitted the lognormal distribution best throughout the experimental period for all three experiments, the spatial distribution of the daily solute concentrations, C_d, changed in time and between experiments. For experiments E1 and E3, which used the wick samplers on the light textured soil, the solute distribution clearly fitted the normal distribution when the peak concentrations occurred, which was around day 11 in the E1 (Figure 6) and day 4 in the PM plots in E3 (Figure 7) [*Boll*, 1995]. Before and after the peak concentration, the C_d's of E1 and E3 fitted the lognormal distribution better than the normal distribution for the wick samplers. The gravity pan samplers (Figure 6) showed a different distribution than the wick pan samplers. The wick pan samplers collected all of the water and more than 80% of the bromide mass. The gravity pan samplers had recoveries of less than 50% for water and bromide, indicating horizontal movement (and bypass flow) in the capillary fringe above the samplers. As will be more clear later, gravity pan samplers cannot be used in sandy soils for collecting samples. For experiment E5 with the macropores in the subsoil (Figure 8), q_d always fit the lognormal distribution, while for C_d the χ^2 test indicated a fit to both the normal and lognormal distribution. The latter may be due to low sample sizes for C_d, because some of the cells in contact with the low conductivity peds did not collect enough sample for chemical analysis.

3.3. χ^2 Tests Applied to Parameters Measured Hourly

For the three experiments E1, E2, and E6 samples were collected at intervals of less than a day for at least part of the experiment. The distributions for E6 and E1 are the most interesting and the results are shown below.

For experiment E6 in Willsboro with conventional tilled (CT) and the no-till (NT) plots, Table 4 lists the χ^2 goodness-of-fit of the normal and lognormal distribution of hourly water
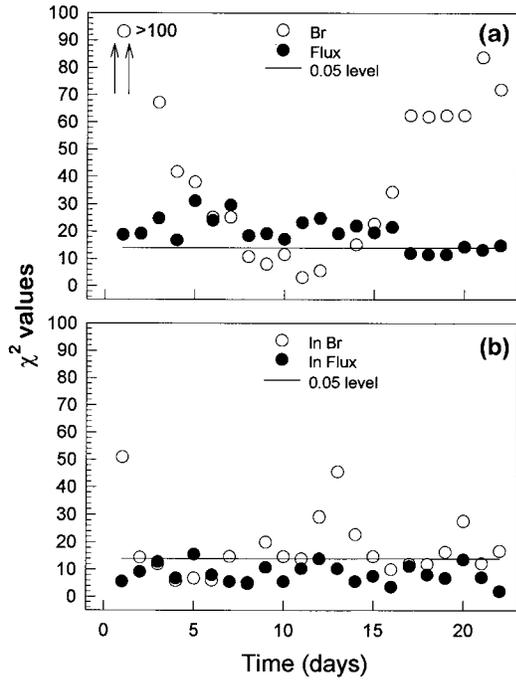
Figure 5. Results of χ^2 tests for goodness-of-fit of the (a) normal and (b) lognormal distributions to daily water flux (q_d) and daily bromide concentration (C_d) versus time for wick samplers in experiment 1 (E1).
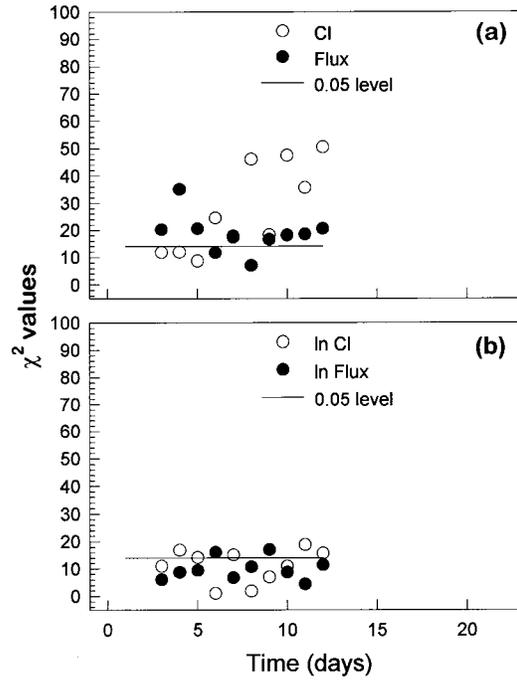

Figure 7. Results of χ^2 tests for goodness-of-fit of the (a) normal and (b) lognormal distributions to daily water flux (q_d) and to daily chloride concentration (C_d) versus time for wick samplers in experiment 3 (E3).

flux, q_h, and hourly concentration, C_h, of chloride and nitrate. Chloride was applied the day before the water application, NO_3 was applied 3 months earlier. Previous experiments at the same site [*Shalit and Steenhuis*, 1996; *Steenhuis et al.*, 1990]

showed extensive preferential flow, especially in the layer from 30 to 60 cm. In a soil with macropore flow, q_h fits the lognormal distribution better than the normal distribution. As expected, lognormality of q_h in the NT plot was much more
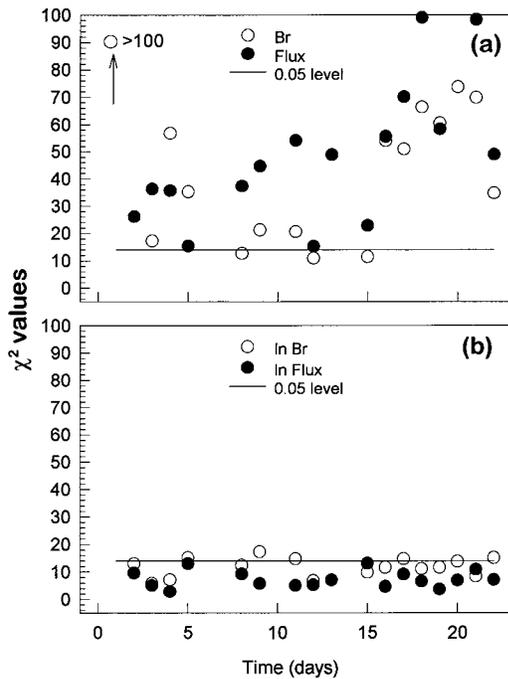

Figure 6. Results of χ^2 tests for goodness-of-fit of the (a) normal and (b) lognormal distributions to daily water flux (q_d) and daily bromide concentration (C_d) versus time for gravity samplers in experiment 1 (E1).
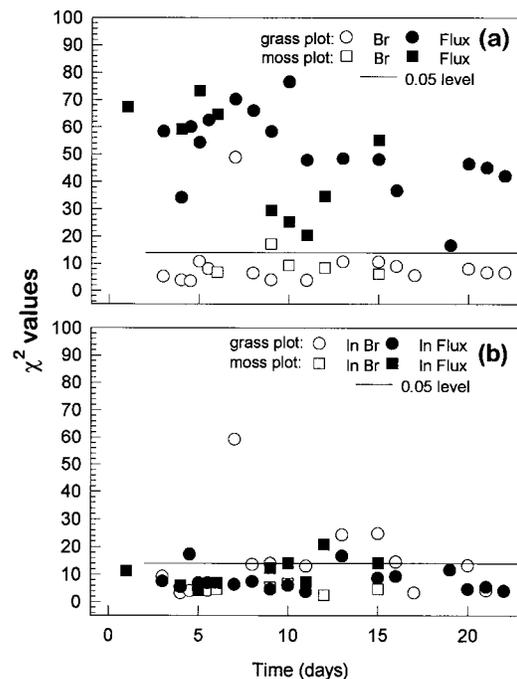

Figure 8. Results of χ^2 tests for goodness-of-fit of the (a) normal and (b) lognormal distributions applied to daily water flux (q_d) and daily bromide concentration (C_d) plotted versus time for wick and gravity samplers in experiment 5 (E5).

Table 4. Results of χ^2 Test of Goodness-of-Fit of the Normal Distribution for q_h, ln q_h, and C_h, and ln C_h (Cl and NO$_3$) in Willsboro, Experiment E6

Sampling Time After Irrigation	No Tillage									Conventional Tillage								
	n	q_h	ln q_h	n	Cl	ln Cl	n	NO$_3$	ln NO$_3$	n	q_h	ln q_h	n	Cl	ln Cl	n	NO$_3$	ln NO$_3$
0 hours after 1st	50	42.2	2.92*	49	30.8	8.0*	49	6.3*	2.8*	38	12.8	22.8	38	6.2*	23	38	6.0*	5.3*
2 hours after 1st	50	29.5	1.52*	49	28.6	3.4*	50	16.9	9.1*	43	11.5	12.2	43	5.7*	9.9	43	4.0*	1.8*
15 hours after 1st	50	21.1	1.52*	47	26.1	4.7*	49	21.1	12.3	47	27.6	12.4	43	2.1*	15.4	47	7.1*	3.5*
18 hours after 1st	49	41.1	10.8	48	27.5	3.9*	39	9.2*	3.1*	39	38.7	14.7	39	3.9*	13.2	29	2.6*	1.2*
0 hours after 2nd	49	28.6	1.71*	47	29.7	13.3	49	11.7	6.8*	50	51.9	5.4*	49	10.8	3.1*	49	4.8*	5.4*
2 hours after 2nd	50	27.7	1.43*	50	8.8*	4.0*	50	26.2	8.5*	48	29.3	7.7*	48	7.7*	11.8	48	3.6*	4.8*
18 hours after 2nd	50	22	1.24*	50	4.3*	3.8*	50	27.8	11.6	50	11.6	8.5*	50	2.6*	8.0*	50	1.2*	2.6*
All data combined†	347	214.6	11.2*	340	152.8	12.4*	327	103.2	24.5	315	113.4	28.3	310	10.1*	59.1	305	23.2	6.8*

Expected frequencies in each class interval were made equal; degrees of freedom = 4; n, sample size.
†Degrees of freedom = 9.
*Null hypothesis is accepted at the 0.05 level [*Snedecor and Cochran*, 1967].

significant (as indicated by the lower χ^2 values) than in the CT plot. Nitrate that was distributed throughout the profile at the time of the experiment 3 months after application also showed a lognormal distribution.

For chloride the concentration C_h fit the lognormal distribution in the no-till (NT) plot and fit the normal distribution in the conventional tilled (CT) plot. Similarly, for NO$_3$, the C_h fit more closely the lognormal distribution in the NT plot. In the CT plot, however, C_h fit the normal and lognormal distribution equally well when data of each sampling interval were analyzed separately. For the latter the χ^2 test was not very strong (Table 4). Previous experiments on these types of soils [*Steenhuis et al.*, 1994] have shown that the plow layer acts as a distribution zone that equalizes the concentrations and funnels water and solutes into the macropores. This type of process can be described by a linear reservoir that is mathematically equivalent to a well-mixed reservoir. The no-till plot does not have such a well developed distribution zone. Intensive mixing in the distribution layer leads to a normal distribution as will be discussed later.

The two gravity and wick samplers for the experiment E1, at Freeville, are used to highlight the differences in gravity and wick pan samplers. Table 5 shows the results of the χ^2 test of goodness-of-fit of the normal and lognormal distribution for hourly water flux (q_h) for wick and gravity pan samplers in E1, starting at 15 days after the tracer application. Tests where Ho

Table 5. Results of χ^2 Test of Goodness-of-Fit of the Normal Distribution, Applied to Hourly Drainage Flux, q_h, and ln q_h of Wick and Gravity Pan Samplers in the Freeville 1 Experiment 15 Days After Start of Application

Time After Irrigation	Wick Pan Sampler			Gravity Pan Sampler		
	n	q_h, mL h^{-1}	ln q_h, mL h^{-1}	n	q_h, mL h^{-1}	ln q_h, mL h^{-1}
4 hours after 1st	50	23.6	8.6*	50	96.0	16.8
16 hours after 1st	50	17.6	53.8	2	···	···
0 hours after 2nd	50	47.6	11.8*	25	35.4	6.6*
3 hours after 2nd	50	18.8	2.2*	25	31.4	5.0*
0 hours after 3rd	50	143	16.6	42	58.9	6.6*
2 hours after 3rd	49	13.2*	6.1*	35	17.8	7.0*

Expected frequencies in each class interval were made equal; degrees of freedom = 4; n, sample size.
*Null hypothesis is accepted at the 0.05 level [*Snedecor and Cochran*, 1967].

was accepted at the 0.05 level are marked. For the gravity pan sampler, q_h clearly fit the lognormal distribution, while q_h of the wick pan samplers fit the lognormal distribution in the samples that represent the irrigation event itself. In the consequent sampling representing the drainage phase the spatial frequency distribution for the flux becomes more normally distributed for the wick samplers but not for the gravity pan samplers. It is likely that macropores are significant contributors during the irrigation event (hence a lognormal distribution). During this drainage phase the matrix flow dominates and one would expect a more normal distribution. The gravity pan samplers do not show this trend because of their inability to collect matrix flow.

4. Discussion

Unlike earlier research in which usually only parameters that averaged the properties over the experimental period were analyzed, this study shows that the spatial distribution patterns are complex and vary in time and between soil types. Despite this, some generalizations can be made: When macropore flow dominates, the spatial frequency distribution for water flux fits the lognormal distribution (q_{avg} for E5 and E6 in Table 3). Under matrix flow conditions and uniform percolation rates, water flux becomes more normally distributed (E2 and E4 in Table 3). Intermittent applications lead to lognormally distributed fluxes.

The daily solute concentration patterns follow more or less the same trends as the average water fluxes with the exception that when the bulk of the solutes breaks through (i.e., when the highest concentrations occur), the spatial distribution becomes normal. The concentration findings are in accordance with findings of *Germann* [1988, 1991] and *German and DiPietro* [1996], who stated that for any type of diffusive transport a minimum mixing length, L, is needed to apply theoretical equations such as the convective-dispersive equation. If L is far smaller than the depth of the sampler, one expects a normal distribution of the flux density of the transport medium. We can expect a small L in a homogeneous soil with a stable wetting front. Field soils are seldom homogeneous [*Flury et al.*, 1994], and L can vary over a wide range. In situations where there are many relatively small macropores, such as in Freeville, one can expect under steady state rainfall a normal spatial distribution for most parameters when all pores are contributing. This was the case for E2. The L becomes large for profiles with soils that have a small conductivity and pores

going directly from the surface to the sampler. The no-till plot at Willsboro and the moss-covered plot in the orchard are examples. At these sites the dense matrix prevent any intermixing and we found that a lognormal distribution fitted the daily concentration data best. The other treatments at the same two sites, grass and conventional tillage, were characterized by a distribution layer at the surface where the solutes and water are funneled in the macropore. Because the solute particles travel along different length streamlines to the macropores in the subsoil, this is equivalent to intensive mixing [*Gelhar and Wilson*, 1974] and a small *L*.

Another aspect that affects *L* is the water application method. For short high water pulses, such as those for Freeville, in experiment E1, and for Delaware, in experiment E3, the depths over which complete mixing take place is longer than for steady state conditions. An explanation why can be derived from the early works of *Lawes et al.* [1882], who reported that profiles drain from the top down through the macropores. Thus drainage gives a few pores the opportunity to drain the water and solutes from the surface to the sampler. This concentration is higher initially shortly after application than the matrix flow. Figure 4 shows this very well for the cell in the middle. Under steady state recharge conditions in Freeville (E2) there is no drainage phase and natural rainfall conditions during the winter in Delaware (E4) the amount of daily rainfall is small and consequently drainage effects are less.

5. Conclusions

Normal and lognormal distributions were compared to frequency distributions of solute velocity, dispersion coefficient, water flux, and solute concentration for different soils under different water application rates after solute application. The results of this study suggest that these water and solute transport properties fit the lognormal distribution when macropore flow dominated the transport process. When transport took place in all pore spaces (i.e., the mixing length was sufficiently small), the data showed that the lognormal distribution was not appropriate for describing the distribution of water and solute transport properties.

Under no-till, water flux and the concentration of chloride applied a day prior to irrigation were lognormally distributed, while the presence of a tillage layer caused chloride concentration to be normally distributed and water flux less significantly lognormal. Under transient conditions, frequency distributions of daily tracer concentration were not constant over time. Shortly after tracer application, when solute transport through macropores occurred, tracer concentration was lognormally distributed. When the bulk of the solutes broke through, tracer concentration became normally distributed. In contrast, water flux remained lognormally distributed at all times. Finally, when pan samplers collected water mainly from macropores, water flux was lognormally distributed. On the other hand, when matrix pores were sampled, the water flux best fit the normal distribution.

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