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Solute transport in a layered field soil: Experiments and modelling using the convection–dispersion approach

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Abstract

Greater understanding of the processes affecting solute transport in field soils is required to meet the ever-increasing demand for improved management of field-applied chemicals. In this study, we sought to elucidate the effect of distinct interfaces between horizons of strongly-contrasting texture on solute transport. Field experiments of solute transport were performed on a soil consisting of three layers of different texture in which porous cup samplers had been installed at four depths in twenty sites. Similar experiments were done in a lysimeter of area 2 m^2 and 1 m deep. Convection–dispersion modelling was first attempted using the lysimeter data. This was successful, provided that the surface 250 mm of soil were not used to calibrate the model coefficients. Layering within the profile appeared to have little effect on solute transport. The transport porosity was found to be just two-thirds of the water-filled porosity. However, convection–dispersion modelling of the field data was not particularly successful, probably due to the spatially-variable nature of solute transport coupled with variation in the water application pattern. Textural differences in the soil seemed to be overwhelmed by both small-scale heterogeneity of water application and local variation of solute movement through the soil, especially near to the soil surface. It appears that the hydraulic processes occurring in the surface soil require more attention by modellers of solute transport than they have been afforded in the past.

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1. Introduction

Those who need to predict or understand the movement of chemicals through field soils implicitly work with layered soils. Yet a review of the literature relevant to the effect of soil layers on solute transport reveals that this topic is usually studied theoretically rather than experimentally. When experiments have been done, the soil studied has usually been repacked soil rather than undisturbed field soil. Here we seek to understand the effect of a natural soil horizon interface on the movement of a conservative tracer.

Models of solute movement pertaining to layered soils include those of Shamir and Harleman (1967), Bruch (1970), Al-Niami and Rushton (1979), Gureghian and Jansen (1985), Barry and Parker (1987), and Leij et al. (1991). Most of these models assume that the order of the soil layers does not affect solute movement, and also that solute movement in each layer is independent. The former assumption was affirmed by the experimental work of both Selim et al. (1977), and Dyson and White (1989). Dyson et al. (1990), and Jury and Roth (1990) developed theory to deal with the circumstance where solute transport in the layers could not be assumed independent. This, they consider, might arise for example where solute movement was rapid at one particular place in the soil because water application was consistently high there also (Jury and Roth, 1990).

Despite this plethora of layered-soil models of solute transport, few have been compared with data from field experiments. Field soils are often naturally layered. However except where the layering is in the form of distinct horizons of substantial thickness, changes in solute transport within these layers can not in itself be studied, but becomes part of the overall heterogeneity. Starr et al. (1978, 1986) described one of the few field experiments on layered soils. However, the experiments were not carried out with the specific intention of determining the correlation of solute transport across an interface.

The convection–dispersion equation has long formed the basis of our understanding of solute transport. This model states that the dispersivity, or the ratio of the dispersion coefficient to the velocity, will remain constant with time and depth. However, experimental evidence shows that contrary to model assumptions, the dispersivity may increase with depth and time. Following the field work of both Jury et al. (1982) and Butters and Jury (1989) it seems that the linear growth in the dispersivity, previously observed in aquifers, may also occur in soils. Growth in the dispersivity arises as a result of local correlation of the solute "parcels" velocities caused by poor lateral dispersion in relation to the measurement time. If this poor lateral connection in the soil exists, then what will be the result when, as is common in soils, a horizon interface is encountered? Will any correlation in velocities be destroyed, or will it persist through the transition across the boundary? The persistence of any correlation will affect the shape of the solute breakthrough curve; therefore, this has practical implications for the movement of contaminants downwards to groundwater.

Here the effect of the interfaces between soil layers on solute transport is the main subject studied. We consider both field experiments and modelling via the convection–dispersion approach.

2. Theory

For one-dimensional, steady water flow through a soil of uniform water content, the convection–dispersion equation (CDE) of solute transport may be represented as:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial c^2} - v\frac{\partial c}{\partial z} \tag{1}$$

where c is solute concentration in the soil solution [M L^{-3}]; t is time [T]; v is the pore-water velocity [L T^{-1}]; z is depth [L]; and D is the dispersion coefficient [L^2 T^{-1}]. Since 1967, when Biggar and Nielsen drew upon Taylor's (1953) CDE equation for flow in a capillary tube to analyse their experiments of miscible displacement, the CDE has held a pre-eminent position in solute transport research. The CDE and its more-sophisticated variants, such as the mobile–immobile CDE of Coats and Smith (1964) and van Genuchten and Wierenga (1976), have been applied, albeit with varying degrees of success, to data from repacked and intact column experiments, as well as field experiments.

In what appeared to be a significant break with the previously largely-mechanistic modelling of solute transport, Jury (1982) and then Jury et al. (1986) proposed that a transfer function model (TFM) be used to describe and predict solute transport in soil. The central concept of the TFM is the probability density function (pdf) of the length of time taken for a "parcel" of solute to travel through some depth of soil (Jury et al., 1986; Jury and Roth, 1990).

Given here in a form suitable to model solute transport under steady water flow through soil, the TFM may be presented as:

$$c(z,t) = \int_0^t c(z,t')f(z,\, t-t')\mathrm{d}t' \tag{2}$$

where f is the transfer function pdf [T^{-1}].

Any function with the properties of a pdf can be treated as a transfer function. This was aptly demonstrated by Sposito et al. (1986) when they reformulated the mobile–immobile CDE model of van Genuchten and Wierenga (1976) into a TFM. More recently, Scotter et al. (1993) have re-analysed Burns' (1975) model within a TFM framework. Thus the TFM has particular utility as a framework for assessing different models of solute transport.

Jury and Roth (1990) showed that the Fickian pdf:

$$f(z,t) = z(4\pi Dt^3)^{-1/2}\exp[-(z-vt)^2/4Dt] \tag{3}$$

was, when applied as a transfer function within a TFM, a solution of the CDE given in Eq. 1 for a Dirac delta function input. As this is essentially the one-dimensional steady-state CDE expressed as a TFM, Eq. 3 is appropriate to model "infinite-time" behaviour (Jury and Flühler, 1992). Jury and Roth (1990) called this particular form of the model a convective–dispersive TFM. Here we use it as a convenient method with which to evaluate the CDE against data from field experimentation.

The CDE is conventionally written with time as the independent variable. Yet the data to be presented here will be most easily analysed with respect to cumulative drainage, I. Roth et al. (1991) presented a form of the CDE dependent on cumulative drainage and applied it to unsteady flow in a field soil. Here, a simpler technique is employed. For every 10 mm of drainage, a day will be assumed to have passed. This is equivalent to saying,

$$t = I/J_{\mathrm{w}} \tag{4}$$

and that the drainage flux density, J_{w} will be prescribed as being 10 mm day^{-1}. Note that neither this operation, nor the manipulation of the CDE performed by Roth et al. (1991) take into account the possibility that the magnitude of drainage flux density will affect solute transport, except in so far as its effect on the cumulative drainage. Thus it is assumed that solute transport is affected only by I.

3. Materials and methods

All the experimental work was done on a dairy farm near Palmerston North, New Zealand, in a field of recent alluvial soil, the Manawatu fine sandy loam. This soil has been described fully by Clothier et al. (1978). The profile consists of three texturally, morphologically and hydrologically distinct layers. The upper layer is composed of sandy loam which overlies a fine sand horizon, which is above a deep coarse sand layer. Within the section of the field used for the study here, the experimental plot, the upper layer of sandy loam had an average depth of 0.4 m, with range 0.3–0.5 m. The second layer of fine sand extended to an average depth of 0.85 m, with range 0.7–1 m.

In 1967, a weighing lysimeter was installed in this plot by carefully repacking soil to the same depth layering and bulk density as found in the surrounding soil. Previously this lysimeter had been used both as a non-weighing drainage lysimeter (Clothier et al. 1977a, b) and as a weighing lysimeter for water balance experiments (Green et al., 1984). Field et al. (1985) also used the lysimeter for an experiment involving the leaching of simulated cattle urine. The lysimeter had a surface area of 2 m^2 and was 1 m deep. The soil profile consisted of 500 mm of sandy loam above 400 mm of fine sand. Beneath these two layers were 100 mm of gravelly coarse sand. Porous ceramic tubes, air entry value −20 kPa, were installed in the base of the gravelly sand layer. A vacuum pump was used to drain the lysimeter and a liquid trap allowed measurement of the drainage volume and collection of a sample of the leachate.

An infra-red photograph taken of the paddock in 1983, at a time of developing crop water stress, was used to identify an area close to the lysimeter which was thought to have a reasonably uniform depth to the coarse sand layer. Within this area, holes for neutron-probe access tubes were augered on a 10 m by 10 m grid at each of 33 sites. The depths to each of the interfaces were noted. Then 20 sites were chosen on the basis of similarity of the depths of the interfaces. Fig. 1 shows the relative position of these 20 sites, as well as the layout of the instruments within each site.

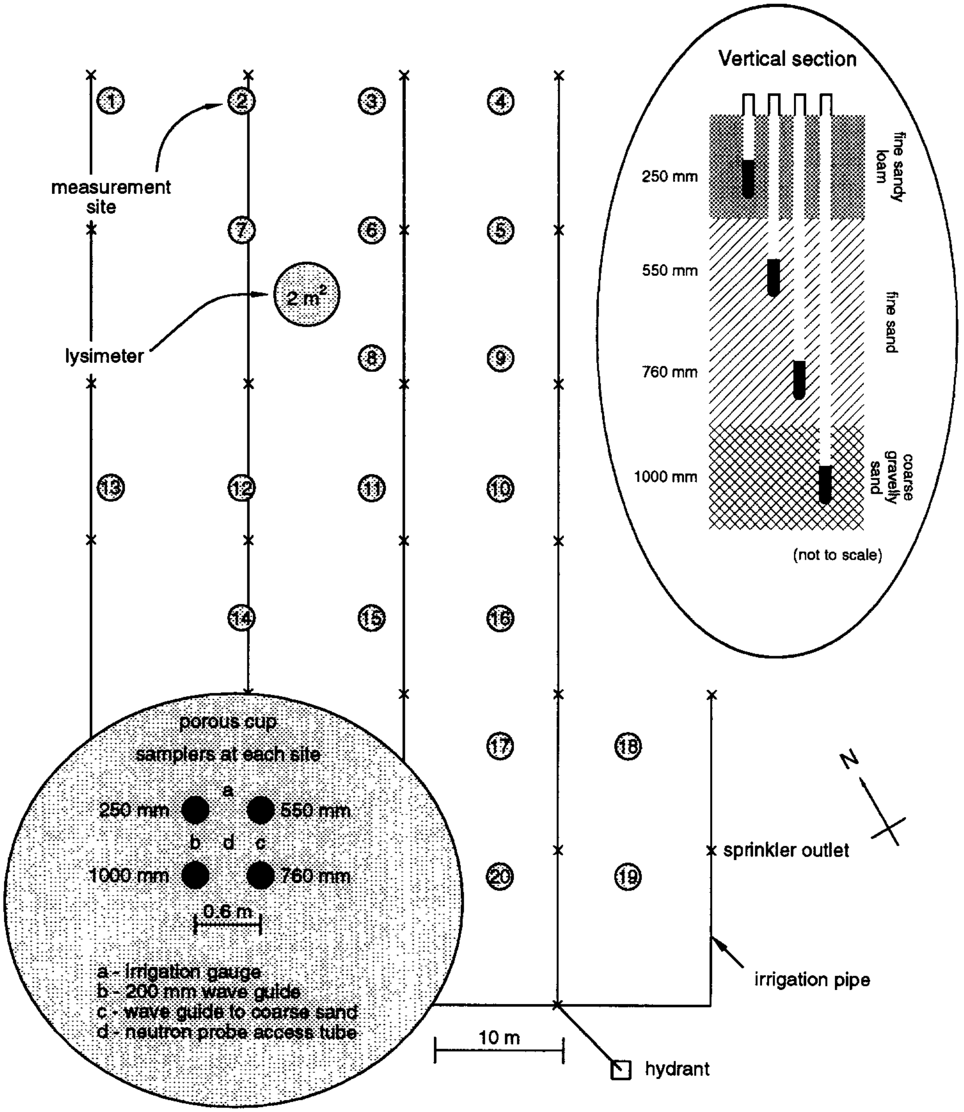

Fig. 1. Layout of the field plot showing positions of the 20 sampling sites and the lysimeter. Note that in the lysimeter the 1000-mm sampler was replaced by the drainage from the lysimeter.

Much of the data presented here arise from samples of the soil solution obtained via porous cup samplers. These samplers comprised a ceramic cup attached to a polyvinylchloride (PVC) pipe which had an attachment to allow the imposition and maintenance of a vacuum. The porous cups were obtained from SoilMoisture Equipment Corporation (Santa Barbara, California, U.S.A.) and had an air entry value of ~ 100 kPa. At each site four suction cup samplers were installed. Their relative positions are shown in Fig. 1. Not all the samplers were installed to the same depth in the coarse sand because at many sites the presence of large stones prevented insertion to the intended depth of 1050 mm. The mean depth was 1000 mm but the range was from 860 to 1050 mm.

To collect a sample a vacuum of ~ -80 kPa was applied to each sampler with a SoilMoisture Equipment Corporation hand-test vacuum pump. The sampler was then sealed and the sample of soil solution allowed to collect under falling vacuum for $\sim$ 1 h. If insufficient sample had been collected after this hour, the vacuum was re-applied for a further hour. Thirty ml of the collected solution were stored in a vial and the remainder discarded. Samples were stored at 3°C.

A time domain reflectometer (TDR, SoilMoisture Equipment Corporation IRAMS Trase System I) was used to determine the amount of water stored within the soil profile. Stainless-steel wave guides were installed at each site in the positions shown in Fig. 1.

A sprinkler irrigation system was used to supply additional water to the plot. Water input at each site was measured using 62-mm-diameter plastic catch cans. The application rate for the irrigation system averaged over the plot area was 5 mm h^{-1}. Samples of the irrigation water were kept for chemical analysis.

In order to construct a water balance an estimate of the evapotranspiration was required. Priestley and Taylor's (1972) estimate of evapotranspiration has previously been demonstrated to work for well-watered pasture in the Palmerston North weather (Scotter et al., 1979; Green et al., 1984). The input data required to calculate this estimate, sunshine hours and air temperature, were taken from a standard meteorological site situated $\sim$1 km distant from the experimental site. Rainfall was measured close to the plot.

Two experiments are described here. The first was in the winter and spring of 1988, and involved the field and the lysimeter. In 1990 a second experiment concentrated on the lysimeter alone.

3.1. The field experiment

The first experiment used the 20 sites described above. By supplementing rainfall with irrigation, a steady drainage of $\sim$ 10 mm day^{-1} was established. Soil solution samples were then collected to measure the initial chloride concentration in the soil solution. Then, in April 1988, a fertiliser spreader was used to apply KCl. The aim was to apply $\sim$ 95 g m^{-2} Cl^- in two, perpendicular passes of the plot. The application rate and uniformity were measured by placing 11 catch cans beneath the path of the spreader. However before the KCl was spread, at each of the 20 measurement sites an area of 0.75 by 0.75 m was covered with plastic sheeting to mask the porous cup samplers. This allowed the area immediately above the samplers, and also the lysimeter, to have fertiliser applied more accurately by hand. The final application rate across the field was 92 g m^{-2} Cl^- with a standard error of 8 g m^{-2} Cl^-. The lysimeter was also spread with KCl at a rate of 95 g m^{-2} Cl^-.

Immediately following the final application of fertiliser, irrigation was restarted.

Soil solution samples were collected following the first irrigation (day 1). Soil solution samples were then collected daily for the next 8 days. Following day 9, samples were collected approximately every two or three days for 12 days.

On day 16, after the paddock had been grazed by cows for the first time since the start of the experiment, it became evident that the soil structure at the surface had deteriorated and that, during irrigation, incipient ponding of the soil surface was occurring. The most probable initial cause of this was sealing of the soil surface during the grazing. Furthermore, over the first few days after the KCl application, the concentration of salt in the top soil was quite high. Reduced earthworm casting activity and some dead earthworms were observed on the soil surface. However, the effects of this were not evident until after the plot was grazed. Mid-way through the experiment there was renewed surface casting activity, but still at a lower rate than observed in the neighbouring unfertilised soil.

After this decrease in the hydraulic conductivity of the surface soil became evident, the frequency of irrigation was first decreased, and then ceased altogether. When ponding was first noticed, cumulative drainage was ~ 180 mm, and measurements of solute concentration showed the peak in the pulse of solute to be below 250 mm. Thus, solute flow was unlikely to have been unduly affected by the surface conductivity changes. Hence after day 22, rainfall was the only water input to the plot, and as a result the drainage flux became intermittent and dropped to an average of ~ 3 mm day^{-1}. The movement of solutes slowed considerably and samples were taken less frequently. At first, the lysimeter was drained every day. Once irrigation was stopped it was drained only after significant rainfall.

3.2. The lysimeter experiment

The basic experimental design of the second lysimeter experiment was similar to the first. Soil solution samplers were installed in the lysimeter at depths of 250, 550 and 760 mm (equivalent to the field installation) to provide data complementary to the drainage which was measured at 1000 mm. The lysimeter was pre-irrigated and samples were obtained from the porous cup samplers and also from the drainage water in order to establish antecedent solute concentrations. In July 1989, 30 g m^{-2} Br^{-}, in the form of solid reagent grade KBr, was applied to the surface of the lysimeter. The KBr was washed into the soil with 2 mm of irrigation.

At first irrigation was applied using a hand-operated pressure sprayer. Approximately 20 min were required to apply the 2 mm of water held in the sprayer's reservoir to the lysimeter. During the application no ponding was observed. At day 38, after 162 mm of drainage from the lysimeter, a watering can was used to apply water because the pressure sprayer was inconveniently slow. It took ~4 min to apply the 5 L in the watering can and the soil was allowed to rest for 6 min before the next 5 L were applied. Occasionally some ponding was observed, but this water always disappeared well before the next 5-L application. The solute peak was at a depth of ~550 mm when the application method was changed. It is therefore unlikely that

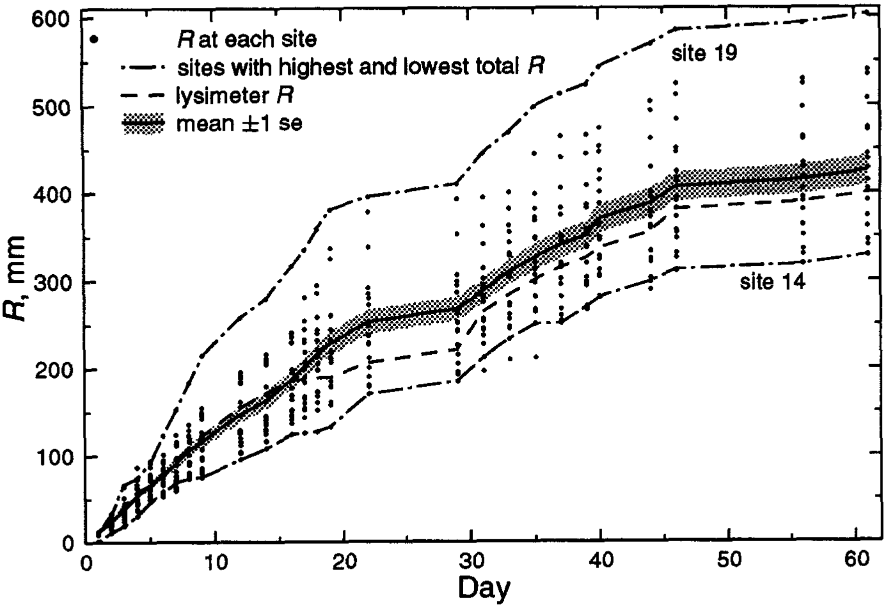

Fig. 2. Cumulative irrigation input (R) to each sampling site and the lysimeter. Day 0 was April 27, 1988.

changing the water application method had any effect on the solute movement measured at depth.

When necessary the herbage was cut to ~20-mm height and removed from the lysimeter. The herbage was retained for bromide analysis.

3.3. Chemical analytical methods

The majority of the soil solution samples were analysed for chloride using the Tecator® FIA Star Analyser (Florence and Farrar, 1971). Bromide concentration was determined using an Orion® Research Bromide Specific Ion Electrode (model 94-35A). All bromide determinations were carried out with a background concentration of 0.15 M $NaNO_3$ as an ionic strength adjuster.

Chloride was extracted from soil samples with 0.05 M K_2SO_4 and a known soil/solution ratio of approximately 1:3. Moisture content was determined on a subsample of the soil at the same time as the extraction to allow solute concentration in the soil solution to be calculated. Chloride concentration in the extractant was analysed on the flow injection analyser as for the soil solution samples with 0.05 M K_2SO_4 as the carrier.

Bromide was extracted from the herbage by a method similar to that of White and Ayoub (1983) and the concentration determined using the specific ion electrode.

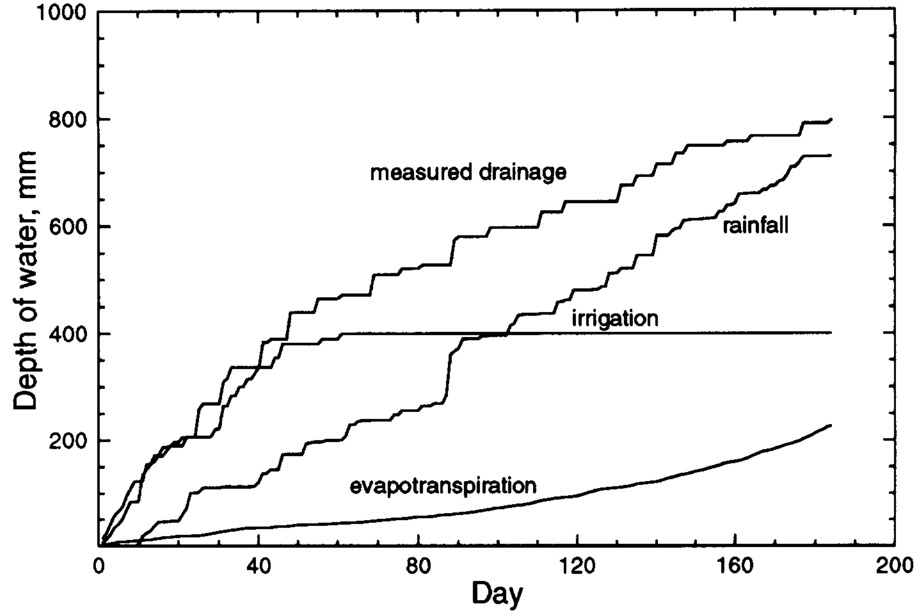

Fig. 3. Water balance for the lysimeter in 1988 experiment showing evapotranspiration, irrigation, rainfall and drainage.

4. Results and discussion

4.1. The field experiment

The cumulative irrigation input, *R*, at each site is shown in Fig. 2. For any particular irrigation event, the sample distribution of the irrigation was better described by a lognormal than normal distribution. The mean and standard error (se), shown on Fig. 2, were calculated assuming a lognormal distribution by the method of Sichel (1952). When each site was ranked with regard to its cumulative irrigation input, the rankings remained reasonably constant with time. For example, the sites receiving the highest total (site *19*) and the lowest total (site *14*) amount of irrigation water are identified in Fig. 2. Such temporal invariance reflects the stationary pattern of irrigation. So in this instance using the field average irrigation input for each site could lead to significant error in the shape of the breakthrough curve (BTC).

The temporal pattern of rainfall over the experimental period is shown in Fig. 3. When considered on a medium-term basis, over say 10 days, the amount of rain falling was reasonably constant. Exceptions to this were the periods between days 21 and 23 when there were 54 mm of rain, and on day 88 when there were 76 mm of rain. The trend in evapotranspiration over the period can be seen in Fig. 3. From approximately the beginning of the experiment to day 100, the daily amount of evapotranspiration was ~ 0.7 mm day^{-1}. After this time, the rate of evapotranspiration increased as spring approached. Cumulative measured drainage from the lysimeter, seen in Fig. 3, remained relatively constant at 10 mm day^{-1} for approximately the first 20 days. After irrigation was discontinued, the drainage rate declined to $\sim$ 3 mm day^{-1}.

Solute transport may not only be variable depth-wise at any one site, but is also likely to be spatially variable at the same depth across the paddock. Fig. 4 shows the suction cup data from all four depths of measurement. Because the irrigation input at each site was measured independently cumulative drainage I, calculated by water balance, was different for each site. Chloride concentrations from the shallower depths exhibit the positive skew typical of a pulse input of solute. This skew, which gives the impression of a lognormal distribution is not necessarily indicative of an underlying lognormal distribution of solute transport times. It could just be a consequence of the boundary condition, as noted by Gardner (1967). Jury and Roth (1990) pointed out that it is necessary to examine solute transport at a number of depths, or times, in order to discriminate between alternative distributions of solute transport times. Here in Fig. 4 at greater depths the spread of solute has become less skewed, so indicating the danger of determining an underlying distribution based on samples from a single depth.

The concentration in the drainage from the lysimeter was comparable to that from the 1000-mm-deep suction cups. Even though there were differences with respect to the horizontal extent of the sampled volume, the geometry of the streamlines during sample accumulation, and the tension at which the sample was collected, the BTC from the lysimeter falls within the general scatter of the porous cup data.

4.2. *The lysimeter experiment*

The data from the single porous cups installed in the lysimeter at 250, 550 and 760 mm, along with the outflow from the lysimeter at 1000 mm, are shown in Fig. 5. The orderly sequence of the data is pleasing. This was especially so considering the small sample area for the top three BTC's compared with the 2-m^2 collection area for the lysimeter outflow. These data thus represent a very useful data set with which to examine solute transport. This will be done prior to considering the more-complex data derived from the field experiment in 1988.

Where solute transport has been measured at more than one depth, or time, the traditional method of modelling has been first to calibrate the appropriate equation by considering both the input boundary condition at the soil surface and the measured trend in solute concentration at a particular depth. Attempts can then be made to predict solute concentrations at other depths or times. This method will first be applied to the data collected during the 1990 experiment on the lysimeter.

4.3. CDE *modelling of the lysimeter experiment*

The simplest modelling approach is taken first. Solute transport was modelled as if the soil were vertically homogeneous and that the convective–dispersive TFM of Eqs. 2 and 3 applies. Thus the equivalent to the CDE of Eq. 1, will be applied to the data. The data were first transformed using Eq. 4 to obtain time as the independent variable

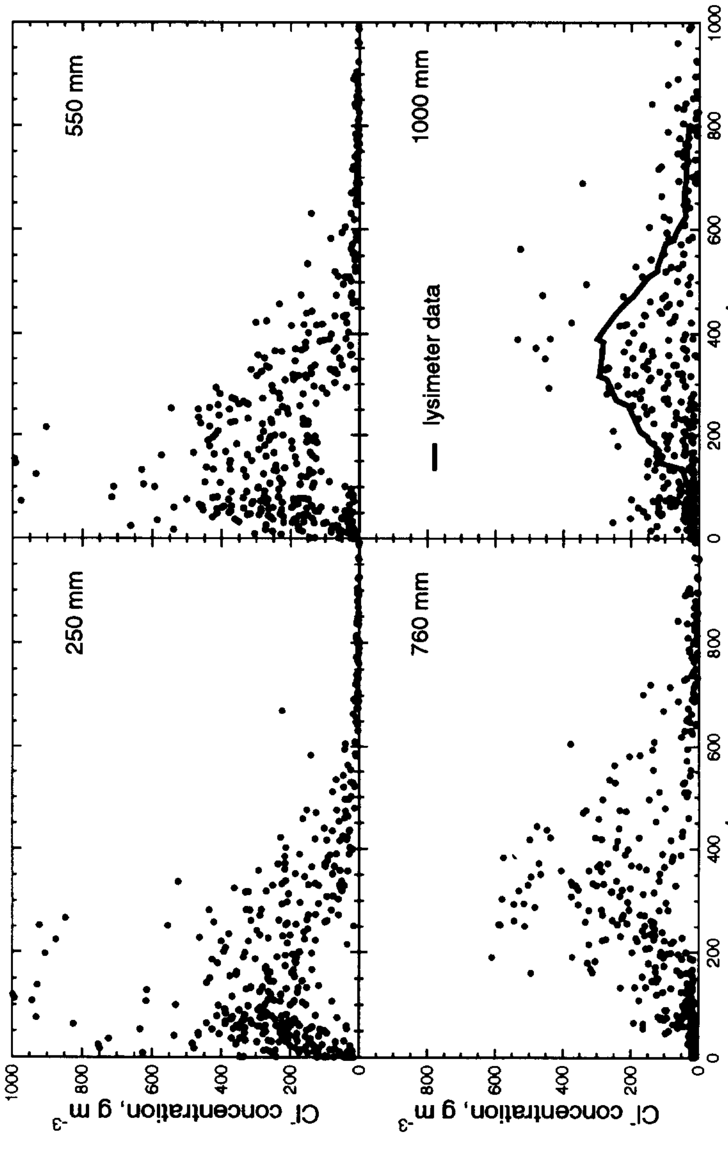

Fig. 4. Chloride concentrations from the porous cup samplers for all sites and depths in 1988. *I* is the cumulative drainage.

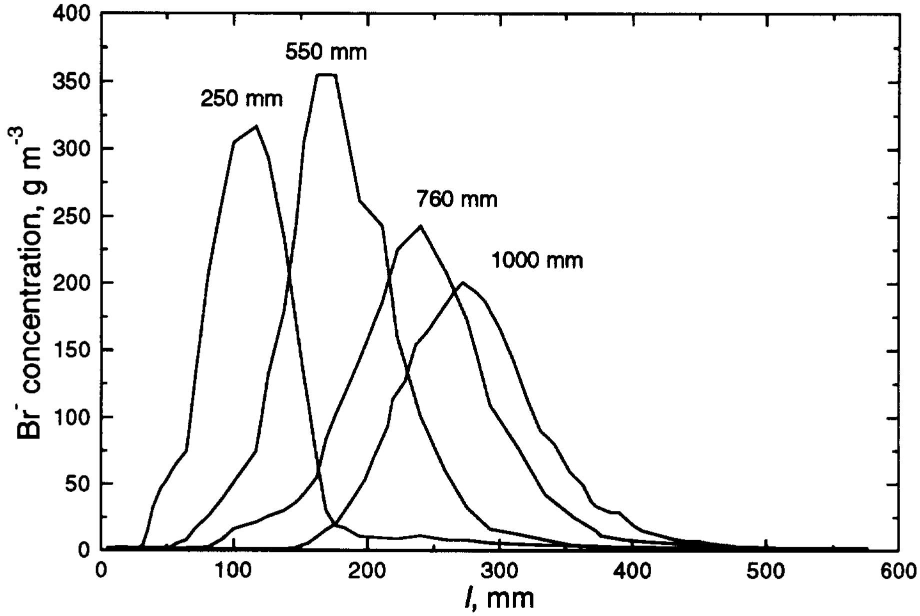

Fig. 5. Porous cup and outflow bromide concentrations measured in the lysimeter during the 1990 experiment. *I* is the cumulative drainage.

and then concentration was normalised so that an equal mass of solute was found beneath each BTC. These coefficients, fitted using a Dirac delta function input, are given in Table 1 and the fit of the calibrated CDE to the data shown in Fig. 6. A nonlinear fitting routine, NAG-E*04*FDF, was used to determine the coefficients as the CDE for each BTC.

Jury et al. (1986) defined that part of the water-filled porosity that solute travelled through as being the transport porosity, θ_{st} [L^3 L^{-3}], and it has become common to estimate this porosity as the ratio of the drainage flux density to the pore-water velocity. For the CDE fitted to the BTC measured at 250 mm v was 21 mm day^{-1}, and the data were transformed using Eq. 4 to obtain a drainage flux density of 10 mm day^{-1}. Thus a θ_{st} of 0.48 appeared to result. In this layer of soil, the volumetric water

Table 1

Coefficients of the CDE fitted to the lysimeter data (we assume a Dirac delta function input at the surface as the input data and J_w was 10 mm day^{-1}) — the apparent transport volume, θ_{st}, and dispersivity, λ, are also given

z (mm)	D (mm^2 day^{-1})	v (mm day^{-1})	θ_{st}	λ (mm)
250	220	21	0.48	10
550	370	28	0.36	13
760	460	28	0.36	16
1000	470	31	0.32	15

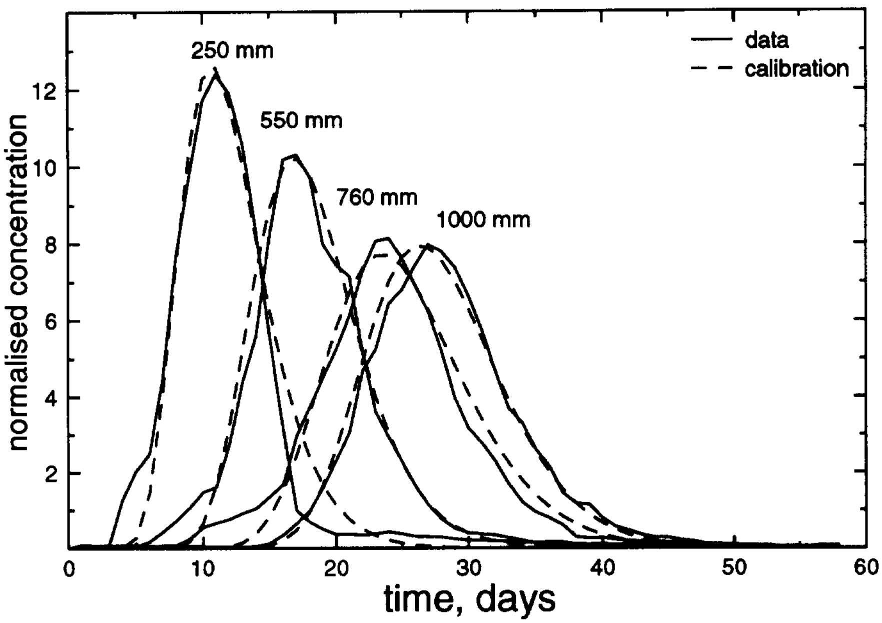

Fig. 6. Normalised BTC's from the lysimeter in 1990 with calibrated Fickian transfer functions. *I* is the cumulative drainage.

content was measured by TDR on several occasions, both before and after irrigation, and on average was observed to be 0.36. The saturated water content of this soil in the field nearby was 0.43 (Clothier and Smettem, 1990). Thus the porosity through which the solute would appear to have moved is greater than the saturated water content of the soil. Obviously this is not possible. This apparently anomalous result has been previously observed (e.g., Starr et al., 1978; Butters et al., 1989; Tillman et al., 1991) and is attributable to preferential flow.

Preferential flow is usually thought to lead to an earlier arrival of solute than might otherwise be predicted. This is correct if the solute is contained within the soil pores through which the water is preferentially moving. However if, upon application of solute to the soil surface, the solute had moved into parts of the pore volume that were being bypassed by the infiltrating water, preferential flow would lead to the solute arriving at depth somewhat later than predicted. Movement of solute into soil micropores can be induced in response to fluctuating water content during intermittent water flow (Tillman et al., 1991) or perhaps when a solute is applied to a slightly dry soil surface. Such movement of the solute into the micropores would render the solute more resistant to leaching.

Further down Table 1 are presented the D- and v-values found when the convective–dispersive TFM was calibrated to the data collected at greater depths. Between the surface and these greater depths the calibrated D and v are both seen to increase. This increase in v could be interpreted as a decrease in θ_{st} to 0.36 at both 550- and 760-mm depths, and a further decrease to 0.32 at 1000-mm depth. This occurred despite the profile of θ remained reasonably constant with depth at 0.36. Thus, in this analysis, there appears to be no obvious linkage between θ and θ_{st}.

The calibrated D parameters show a depthwise increase. Dispersion increased more quickly than the velocity, so the net effect upon the dispersivity (D/v) is a rise from 10 to 15 mm over the depth of measurement. This is within the lower range of dispersivities reported by Gelhar et al. (1985), and Beven et al. (1993). Good predictions of solute transport to depths greater than 250 mm will not arise from a CDE calibrated at 250 mm.

From the dispersivity values obtained via the calibrated D and v parameters, it would appear that either the soil is not transporting solute in accord with the form of the CDE given in Eq. 1 or the assumptions made are incorrect. We now seek to investigate whether the layering of the soil affected solute transport, and also the alternative possibility that the flow was representative of stochastic–convective transport where dispersivity increases linearly with depth and time. However, depthwise increase in v indicates that the centre of mass of the solute is not progressing down the soil profile at a steady pace. This then excludes the possibility that a simple stochastic–convective model, ignoring layering, could successfully predict the solute transport regime. Nor is it likely that solute transport mechanisms remained constant within a layer, but only varied in the different layers. This is especially clear in the soil between the surface and 250 mm. This depth interval appears to have quite different transport properties than the soil between the surface and 550 mm. The sandy loam horizon lies between the surface and 500 mm deep. So the measurements at 550 mm are influenced only by 50 mm of fine sand soil, yet the parameters found to fit the 550-mm data are very different from those obtained by fitting the 250-mm data. It would appear that solute transport was rather slow between the surface and 250 mm. However, below 250 mm water seemed to be much more effective at moving solute downward.

To interpret these results we need to consider both the physical structure of the surface soil and the manner of the water application and the solute input regime. First, we note that the structure of the soil was most highly developed in the top 250 mm. It was this zone through which the majority of pasture plant roots traversed. Soil fauna were also more active in the surface soil. Secondly, the intermittent water input would have been at its most variable in the upper part of the soil profile. At greater depths the extremes in the variability of the surface water application would be smoothed by transit through the soil (Philip, 1983). Also, this surface zone soil, consequent upon the occurrence of incipient ponding and subsequent flow down macropores, might be considered to be the most prone to preferential flow.

Additionally, it is not clear if the pulse input of solid fertiliser to the soil surface resulted in a pulse input of solute directly into the mobile soil water. If some of the solute dissolved into the immobile water within soil aggregates or was convected into the micropores by capillarity, then subsequent slow diffusion back into the mobile water would cause the late and dispersed BTC seen at the 250-mm depth seen in Fig. 5.

For all these reasons solute transport can be quite different in the surface soil than deeper in the profile. Therefore it may be inappropriate to include this part of the soil

Table 2
Calibrated CDE parameters of the Fickian pdf, apparent transport porosity, θ_{st}, and dispersivity, λ (these result from using the data measured at 250 mm in the lysimeter as the input function)

z (mm)	D ($mm^2 \ day^{-1}$)	v ($mm \ day^{-1}$)	θ_{st}	λ (mm)
550	720	37	0.27	19
760	850	38	0.26	22
1000	630	36	0.28	18

profile in a calibration which is then intended to predict solute transport to greater depths. Alternatively, the transfer function CDE could be calibrated using the solute concentration data measured at 250 mm as the input, rather than the impulse function that was assumed to apply at the soil surface. The data collected at 550 mm, and deeper, can then provide the output solute concentrations necessary to calibrate D and v.

For an analytical solution of the transfer function equation to be found, the input function must be one of a restricted group of functions. It was unlikely that the solute concentrations measured at 250 mm would conform closely to one of these functions. Hence such misrepresentation of the input data would add considerable error to the calibration. To obviate the need for a specified input function, the transfer function equation was fitted to the data in its integral form:

$$c(250+z,\ t) = \int_0^t c(250, t')f(250+z,\ t-t')\mathrm{d}t' \tag{5}$$

which is equivalent to the travel time pdf for independent soil layers presented by Jury and Roth (1990). This then allowed the data collected at 250 mm to be inserted directly into the equation.

In contrast to the parameters derived assuming a Dirac delta function at the surface (Table 1), here both D and v are reasonably constant with increasing depth (Table 2). This is an indication that the soil may indeed be transporting solute in a convective–dispersive manner, at least below the 250-mm depth.

It remains unclear as to what was happening in the top 250 mm of soil, except we note that it was substantially different from what was happening in the lower soil. It is unlikely that the impulse application of solute in the soil surface indeed resulted in an impulse of solute to the mobile soil water. This upper region of the soil profile is the most "disturbed" and biologically-active zone. Thus such failure is not surprising.

Below 250 mm deep, the average solute velocity was found to be 37 mm day^{-1} (Table 2). Using the prescribed J_w of 10 mm day^{-1}, this yields an effective solute transport porosity, θ_{st} of 0.27. Measurements of water storage in the lysimeter to the depths of 200 and 500 mm, showed the water content between these two depths to be 0.39. Thus, the immobile water content, θ_{im} [$L^3 \ L^{-3}$], might now be calculated from the CDE as being 0.12.

An alternative method (Dyson et al., 1990) for determining θ_{st} is to compute the mean I of the BTC at each of 250 and 550 mm. We can then divide the difference

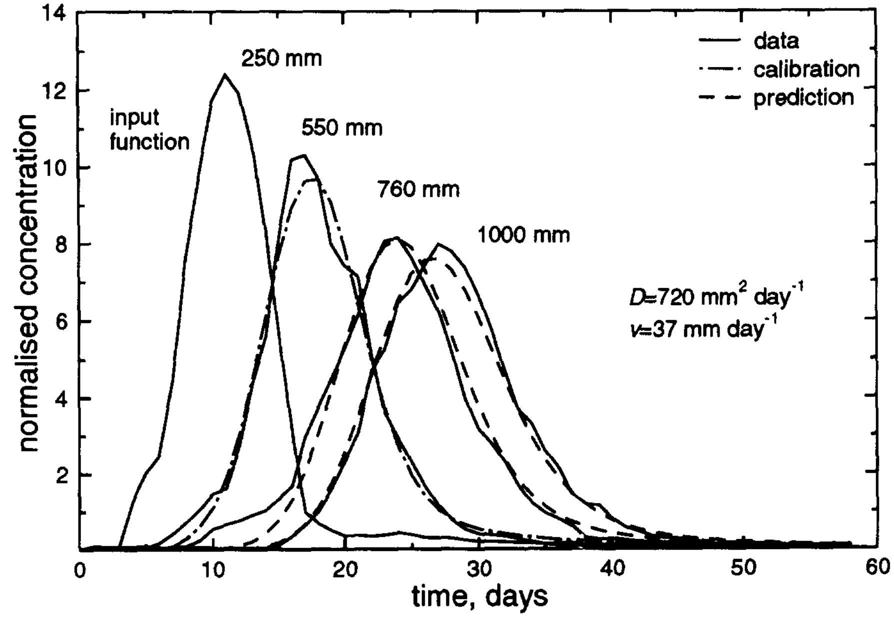

Fig. 7. 1990 lysimeter data and a CDE calibrated with the 250-mm data as the input and the 550-mm data as the output. Predictions of solute transport to 760 and 1000 mm are based on the calibration between 250 and 550 mm and using the 250-mm data as the input function. I is cumulative drainage.

between these two measures by the increment in depth, i.e. 300 mm. This produced an estimate of θ_{st} of 0.17 and therefore of θ_{im} of 0.22. Why should these two estimates of θ_{im} be so different? For the simple reason that measurements continued longer after the peak passed the 250-mm depth than at any other depth, the 250-mm data has a long tail which is not seen a greater depth. It is likely that this tail has affected the calculation of the mean for 250 mm. Ignoring the tail of the 250-mm data from the calculation of the mean resulted in an estimate of 0.22 for θ_{st} and θ_{im} of 0.17. This highlights possible errors involved in these calculations.

In the surface of the Manawatu fine sandy loam Tillman et al. (1991) estimated the immobile water content to be 0.18, and Clothier et al. (1992), using a direct measurement technique found, θ_{im} to be 0.20. Thus the estimates calculated from the mean I-values are in agreement with the others. The slow transport seen here in the top 250 mm would appear to be a result of the solute first moving into the immobile water and then subsequently "bleeding" slowly from the immobile to the mobile water in the soil. There were two mechanisms by which solute could move to the immobile water upon application of the solid fertiliser. First, the fertiliser granules may dissolve directly into the water of the aggregates. This would be particularly true for the small crystals of laboratory-grade KBr used here. Additionally the light applications of water initially could have encouraged solute to move into the aggregates via a combination of both mass flow and diffusion. Once within the aggregates this solute would then only become amenable to leaching once it moved back into the mobile water.

Table 3
CDE parameters fitted to the 1988 field data with either a Dirac delta function at the soil surface or the data measured at 250 mm as the input function

Output depth (mm)	Input							
	Dirac delta function at $z = 0$ mm model parameters				data measured at 250 mm			
	D (mm^2 day^{-1})		v (mm day^{-1})		D (mm^2 day^{-1})		v (mm day^{-1})	
	mean	se	mean	se	mean	se	mean	se
250	1090	170	8	0.5				
550	2130	310	18	1	2170	1540	83	14
760	900	100	18	1	1050	340	26	3
1000	1380	220	18	1	2050	840	26	3

se = standard error.

Predictions of solute transport to the greater depths of 760 and 1000 mm, but still using the 250-mm data as the input, may be made using the parameters determined from the fit obtained between the 250- and 550-mm data. These predictions are shown in Fig. 7. Not surprisingly, an excellent rendition of the data is obtained. All indications are that with the exception of the surface soil and under the boundary conditions imposed, solute was transported in accordance with the form of the CDE given in Eq. 1. Of note is that the simple, but distinct, layering of the soil at 500 and 900 mm did not appear to have any measurable effect on solute transport.

4.4. CDE *modelling of the field data*

The successful CDE analysis applied to data of solute transport from the 1990 lysimeter experiment using the 250-mm data as the input will now be applied to the data collected during the field experiment.

Table 3 contains data analogous to that in Tables 1 and 2, but here presented for the field data. The second and third columns give average fitted D and v using a Dirac delta function as the input. The last two columns are for the fitted equation, using the 250-mm data as the input. In both cases the transfer function in Eq. 3 has been fitted individually to the BTC's at the 20 sites. Both the average and the standard error of the average of the parameters are shown.

Analysis of Table 3 reveals a somewhat different pattern in the field data to that seen in the lysimeter experiment. Examining first the values of v resulting from the Dirac delta function input, it is again noted that the data collected at 250 mm are anomalous. The v is found to be uniformly 18 mm day^{-1}. But at 250 mm it is less than half that. It cannot simply be that the 250-mm samplers were not adequately sampling the actively moving solute, as the mass balance of solute was correct. Note that the mass balance was calculated using the irrigation input to the individual sites, rather than the average irrigation input. By examination of the v resulting from the Dirac delta input, it was also clear that these data could not be explained by solute initially moving into some immobile porosity, and then moving slowly back into the moving water. Improved understanding of the solute input and the nature of the samples collected by porous cups, and how they might be affected by soil structure and the water regime, may aid the interpretation of this data. However, from Table 3 it is clear that calibration of the CDE, assuming a Dirac delta input at the soil surface, to the 550-mm data would lead to good predictions of the centre of mass of the 760- and 1000-mm data. This was not so in the lysimeter study.

Calibration of the CDE to the lysimeter data using the 250-mm data as the input function resulted in D and v remaining constant with depth. Similar analysis of the field data show no such trend. If the velocity is indeed constant with depth, then it is difficult to invoke a mechanistic explanation for a decrease in the dispersion coefficient. With the large uncertainty on all the estimates of D, simply considering D to be constant would not be inappropriate.

Given current understanding, it would appear that these field data cannot be adequately modelled using the CDE approach. Rather it is unlikely that these data provide a true reflection of the spreading of solute in the field soil. Probably solute transport is itself so variable that the 20 samples from each depth are inadequate. Spatial variability of the irrigation could also have been important.

5. Conclusions

The convection–dispersion model was applied first to the more well-behaved data collected in the lysimeter, then to more-variable field data. Modelling the lysimeter data was successful, provided that the surface soil was not included in the analysis. Solute transport processes in the surface soil appeared different from those operating at depths below. This may result from either the nature of the solute input, or from the water flow regime of the surface soil. The changes in soil texture and structure with depth, apart from the surface soil, appeared to have no effect on solute transport.

The same modelling strategy was not however successful when applied to the field data. With the exception of the 250-mm data, the pore-water velocity parameters made reasonable sense. The pattern of the fitted D parameter however defied explanation. The most likely reason for this was the highly-variable nature of solute transport and water movement in this soil.

Although the application of a process-based model to the data increased our understanding of the factors affecting solute transport in the lysimeter, it has left many questions regarding the field data unanswered. In an effort to discover more of solute transport in the field, in the following companion paper, a non-mechanistic model will be used. This model subdivides θ_{st} into convective and dispersive components, and also considers θ_{st} to comprise non-interacting flow paths. Such delineation of θ_{st} may reveal more of solute transport processes and add insight to the nature of solute transport variability.

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References

Al-Niami, A.N.S. and Rushton, K.R., 1979. Dispersion in stratified porous media: Analytical solutions. Water Resour. Res., 15: 1044–1048.

Barry, D.A. and Parker, J.C., 1987. Approximations for solute transport through porous media with flow transverse to layering. Transport Porous Media, 2: 65–82.

Beven, J.K., Henderson, D.E. and Reeves, A.D., 1993. Dispersion parameters for undisturbed partially saturated soil. J. Hydrol., 143: 119–43.

Biggar, J.W. and Nielsen, D.R., 1967. Miscible displacement and leaching phenomenon. In: R.M. Hagan, H.R. Haise and T.W. Edminster (Editors), Irrigation of Agricultural Lands. Agronomy 11. Am. Soc. Agron., Madison, WI, pp. 254–274.

Bruch, J.C., 1970. Two-dimensional dispersion in short laboratory cores. Soc. Pet. Eng. J., 17: 91–99.

Burns, I.G., 1975. An equation to predict the leaching of nitrate uniformly incorporated to a known depth or uniformly distributed throughout a soil profile. J. Soil Sci., 31: 175–202.

Butters, G.L. and Jury, W.A., 1989. Field scale transport of bromide in an unsaturated soil, 2. Dispersion modelling. Water Resour. Res., 25: 1583–1589.

Butters, G.L., Jury, W.A. and Ernst, F.E., 1989. Field scale transport of bromide in an unsaturated soil, 1. Experimental methodology and results. Water Resour. Res., 25: 1575–1581.

Clothier, B.E. and Smettem, K.R.J., 1990. Combining laboratory and field measurements to define the hydraulic properties of soil. Soil Sci. Soc. Am. J., 54: 299–304.

Clothier, B.E., Scotter, D.R. and Kerr, J.P., 1977a. Water retention in a soil underlain by a coarse-textured layer. Soil Sci., 123: 392–390.

Clothier, B.E., Scotter, D.R. and Kerr, J.P., 1977b. Drainage flux in a permeable soil underlain by a coarse-textured layer. Soil Sci. Soc. Am. J., 41: 671–676.

Clothier, B.E., Pollock, J.P. and Scotter, D.R., 1978. Mottling in soil profiles containing a coarse-textured horizon. Soil Sci. Soc. Am. J., 42: 761–763.

Clothier, B.E., Kirkham, M.B. and McLean, J.E., 1992. In situ measurements of the effective transport volume for solute moving through soil. Soil Sci. Soc. Am. J., 56: 733–736.

Coats, K.H. and Smith, B.D., 1964. Dead-end pore volume and dispersion in porous media. Soc. Pet. Eng. J., 4: 74–84.

Dyson, J.S. and White, R.E., 1989. A simple predictive approach to solute transport in layered soils. J. Soil Sci., 40: 525–542.

Dyson, J.S., Jury, W.A. and Butters, G.L., 1990. The prediction and interpretation of chemical movement through porous media: The transfer function model approach. Electr. Power Res. Inst., Palo Alto, CA, EPRI Rep. EN-6853.

Field, T.R.O., Theobald, P.W., Ball, P.R. and Clothier, B.E., 1985. Leaching losses of nitrate from cattle urine applied to a lysimeter. Proc. Agron. Soc. N.Z., 15: 137–141.

Florence, T.M. and Farrar, Y.S., 1971. Spectrophotometric determination of chloride at the parts-per-billion level by the mercury II, thiocyanate method. Anal. Chim. Acta, 54: 373–377.

Gardner, W.R., 1967. Movement of nitrogen in soil. In: W.V. Bartholomew and F.E. Clark (Editors), Soil Nitrogen. Agronomy Monographs 10. Am. Soc. Agron., Madison, WI, pp. 550–572.

Gelhar, L.W., Mantoglou, A., Welty, C. and Renfeldt, K.R., 1985. A review of field-scale physical solute transport processes in saturated and unsaturated porous media. Electr. Power Res. Inst., Palo Alto, CA, EPRI Rep. EA-4190.

Green, A.E., Clothier, B.E., Kerr, J.P. and Scotter, D.R., 1984. Evapotranspiration from pasture: A comparison of lysimeter and Bowen ratio measurements with Priestley–Taylor estimates. N.Z. J. Agric. Res., 27: 321–327.

Gureghian, A.B. and Jansen, G., 1985. One-dimensional analytical solutions for the migration of a three-member radionuclide decay chain in a multi-layered geologic medium. Water Resour. Res., 21: 733–742.

Jury, W.A., 1982. Simulation of solute transport using a transfer function model. Water Resour. Res., 18: 363–368.

Jury, W.A. and Flühler, H., 1992. Transport of chemicals through soil: Mechanisms, models, and field applications. Adv. Agron., 47: 141–201.

Jury, W.A. and Roth, K., 1990. Transfer Functions and Solute Movement through Soil: Theory and Applications. Birkhauser, Basel.

Jury, W.A., Stolzy, L.H. and Shouse, P., 1982. A field test of the transfer function model for predicting solute transport. Water Resour. Res., 18: 369–375.

Jury, W.A., Sposito, G. and White, R.E., 1986. A transfer function model of solute transport through soil, 1. Fundamental concepts. Water Resour. Res., 22: 243–247.

Leij, F.J., Dance, J.H. and van Genuchten, M.Th., 1991. Mathematical analysis of one-dimensional solute transport in a layered soil profile. Soil Sci. Soc. Am. J., 55: 944–953.

Philip, J.R., 1983. Infiltration in one, two, and three dimensions. In: Advances in Infiltration. Proc. Natl. Conf., Chicago, IL, Dec. 12–13, 1983. Am. Soc. Agric. Eng., St. Joseph, MI, pp. 1–13.

Priestley, C.H.B. and Taylor, R.J., 1972. Assessment of the surface heat flux and evaporation using large scale parameters. Mon. Weather Rev., 100: 81–92.

Roth, K., Jury, W.A., Flühler, H. and Attinger, W., 1991. Transport of chloride through an unsaturated field soil. Water Resour. Res., 27: 2533–2541.

Scotter, D.R., Clothier, B.E. and Turner, M.A., 1979. The soil water balance of a fragiaqualf and its effect on pasture growth in central New Zealand. Aust. J. Soil Res., 17: 455–465.

Scotter, D.R., White, R.E. and Dyson, J.S., 1993. The Burns' leaching equation. J. Soil. Sci., 44 (in press).

Selim, H.M., Davidson, J.M. and Rao, P.S.C., 1977. Transport of reactive solutes through multi-layered soils. Soil Sci. Soc. Am. J., 41: 3–10.

Shamir, U.Y. and Harleman, D.R.F., 1967. Dispersion in layered porous media. Proc. Am. Soc. Civ. Eng., Hydraul. Div., 93: 236–260.

Sichel, H.S., 1952. New methods in the statistical evaluation of mine sampling data. Trans. London Inst. Min. Metall., 61: 261–288.

Sposito, G., White, R.E., Darrah, P.R. and Jury, W.A., 1986. A transfer function model of solute transport through soil, 3. The convection–dispersion equation. Water Resour. Res., 22: 255–262.

Starr, J.L., de Roo, H.C., Frink, C.R. and Parlange, J-Y., 1978. Leaching characteristics of a layered soil. Soil Sci. Soc. Am. J., 42: 386–391.

Starr, J.L., Parlange, J-Y. and Frink, C.R., 1986. Water and chloride movement through a layered field soil. Soil Sci. Soc. Am. J., 50: 1284–1390.

Taylor, G., 1953. Dispersion of soluble matter in solvent flowing slowly through a tube. Proc. R. Soc. London, Ser. A, 219: 186–203.

Tillman, R.W., Scotter, D.R., Clothier, B.E. and White, R.E., 1991. Solute movement during intermittent water flow in a field soil and some implications for irrigation and fertiliser application. Agric. Water Manage., 20: 119–133.

van Genuchten, M.Th. and Wierenga, P.J., 1976. Mass transfer in sorbing porous media, I. Analytical solutions. Soil Sci. Soc. Am. Proc., 40: 473–480.

White, R.E. and Ayoub, A.T., 1983. Decomposition of plant residues of variable C/P ratio and the effect on soil phosphate availability. Plant Soil, 74: 163–173.