Spatial and temporal distribution of solute leaching in heterogeneous soils: analysis and application to multisampler lysimeter data

Gerrit H. de Rooij a,*, Frank Stagnitti b,1

a Sub-department Water Resources, Department of Environmental Sciences, Wageningen University, Nieuwe Kanaal 11, 6709 PA Wageningen, The Netherlands
b Centre for Applied Dynamical Systems and Environmental Modelling, School of Ecology and Environment, Deakin University, P.O. Box 423, Warrnambool, Victoria 3280, Australia

Received 13 April 2001; received in revised form 11 July 2001; accepted 6 September 2001

Abstract

Accurate assessment of the fate of salts, nutrients, and pollutants in natural, heterogeneous soils requires a proper quantification of both spatial and temporal solute spreading during solute movement. The number of experiments with multisampler devices that measure solute leaching as a function of space and time is increasing. The breakthrough curve (BTC) can characterize the temporal aspect of solute leaching, and recently the spatial solute distribution curve (SSDC) was introduced to describe the spatial solute distribution. We combined and extended both concepts to develop a tool for the comprehensive analysis of the full spatio-temporal behavior of solute leaching. The sampling locations are ranked in order of descending amount of total leaching (defined as the cumulative leaching from an individual compartment at the end of the experiment), thus collapsing both spatial axes of the sampling plane into one. The leaching process can then be described by a curved surface that is a function of the single spatial coordinate and time. This leaching surface is scaled to integrate to unity, and termed $S$ can efficiently represent data from multisampler solute transport experiments or simulation results from multidimensional solute transport models. The mathematical relationships between the scaled leaching surface $S$, the BTC, and the SSDC are established. Any desired characteristic of the leaching process can be derived from $S$. The analysis was applied to a chloride leaching experiment on a lysimeter with 300 drainage compartments of 25 cm$^2$ each. The sandy soil monolith in the lysimeter exhibited fingered flow in the water-repellent top layer. The observed $S$ demonstrated the absence of a sharp separation between fingers and dry areas, owing to diverging flow in the wettable soil below the fingers. Times-to-peak, maximum solute

* Corresponding author. Tel.: +31-317-482778/485311; fax: +31-317-484885.
E-mail addresses: ger.derooij@users.whh.wag-ur.nl (G.H. de Rooij), frankst@deakin.edu.au (F. Stagnitti).
1 Tel.: +61-3-5563-3535; fax: +61-3-5563-3462.
fluxes, and total leaching varied more in high-leaching than in low-leaching compartments. This suggests a stochastic–convective transport process in the high-flow streamtubes, while convection–dispersion is predominant in the low-flow areas. $S$ can be viewed as a bivariate probability density function. Its marginal distributions are the BTC of all sampling locations combined, and the SSDC of cumulative solute leaching at the end of the experiment. The observed $S$ cannot be represented by assuming complete independence between its marginal distributions, indicating that $S$ contains information about the leaching process that cannot be derived from the combination of the BTC and the SSDC. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Solute transport; Unsaturated flow; Soil heterogeneity; Preferential flow; Lysimeter

### 1. Introduction

Our ability to predict movement of salts, nutrients, and pollutants in soils is hampered by the fact that soil heterogeneity and preferential flow cause considerable spatial variation of flow of water and solutes in soils (Nielsen et al., 1973; Biggar and Nielsen, 1976; Roth et al., 1991; Lennartz et al., 1997). Solute movement in natural soils thus causes solutes to spread out in time and space. Temporal solute spreading has received considerable attention in the past. It is usually characterized by the breakthrough curve (BTC), which describes the travel time distribution of solutes at a given depth (Jury and Roth, 1990; Lennartz et al., 1999). An analysis of the spatial redistribution of solutes was recently presented by Stagnitti et al. (1999) and de Rooij and Stagnitti (2000). The latter proposed the spatial solute distribution curve (SSDC) as the spatial equivalent of the BTC. They obtained a cumulative form of the SSDC by first sorting all sampling locations at a given depth in descending order of amounts of cumulative leaching, and then plotting the cumulative breakthrough as a function of location. A similar approach was presented by Quisenberry et al. (1994).

Experiments that seek to clarify the effect of soil heterogeneity often rely on the visualization of flow paths, either by the use of tracers (van Ommen et al., 1988; Flury et al., 1994; Forrer et al., 1999), or indirectly through detailed water content measurements (Ritsema et al., 1997). Even if quantitative data can be obtained from such trials, the data relate to resident concentrations, rather than flux concentrations (Parker and van Genuchten, 1984; Jury and Flühler, 1992).

A quantitative assessment of solute transport in soils requires measurement of water and solute fluxes. The need for flux data has prompted the development of devices that measure water and/or solute fluxes at a large number of locations at a given depth. Field experiments with water collectors that sampled the drainage water of 25 compartments of 0.090 m² total area were performed by Boll et al. (1992, 1997) and Stagnitti et al. (1998). The performance of similar single-cell sampling devices in the field was evaluated by Louie et al. (2000). Any desired number of these samplers can be installed in a field to provide data on the variability of fluxes. Laboratory experiments with monolith lysimeters having a sampling grid at the bottom were reported by Poletika and Jury (1994) (64 compartments, 0.64 m² total area), Wildenschild et al. (1994) (69 compartments, 0.071 m² total area), de Rooij (1996) (360 compartments, 1.00 m² total area), and Strock (2001) (81
compartments, 0.13 m² total area). Quisenberry et al. (1994) (100 compartments, 0.106 m² total area) placed the monolith on an outflow collection device that maintained a small suction at the drainage outlets. Buchter et al. (1995) placed a monolith of 0.0745 m² on 19 separate ceramic plates. An alternative approach is to perform leaching experiments on a large number of soil cores taken from the same soil (Sassner et al., 1994; Mallants et al., 1994, 1996; Lennartz and Kamra, 1998).

The objective of this paper is to combine the hitherto separate analyses of the temporal and spatial aspects of solute leaching into an integrated analysis of the spatio-temporal behavior of solute leaching. The analysis makes the sampling plane collapse onto a single spatial axis, thus allowing the leaching process in space and time to be efficiently represented by a curved leaching plane in a three-dimensional space. The mathematical relationships between this leaching plane, the BTC, and the SSDC are established. By studying suitable properties of the leaching plane, many quantitative characteristics about leaching behavior of the soil can readily be found, allowing much more information to be extracted from the available data than was previously possible. The leaching surface can be used to efficiently represent experimental observations and simulation results of multidimensional solute transport models.

The analysis is oriented towards the interpretation of observations of solute leaching in space and time that are typically produced by multisampler experiments. We also assess the usefulness of the BTC and the SSDC in characterizing the full spatio-temporal leaching process. The analysis will be applied to data of a chloride leaching experiment on a large lysimeter with 360 drainage compartments.

2. Theory

The solute flux density \( S_u \) [M L^{-2} T^{-1}] at a given depth is a function of the horizontal spatial coordinates \( x_1 \) and \( x_2 \) [L], and time \( t \) [T]. To facilitate the analysis of \( S_u(x_1, x_2, t) \), we collapse both spatial axes into a single \( x \)-axis [L^2] by ranking all individual sampling areas in descending order of cumulative leaching. This produces a curved plane \( S_u(x, t) \). This plane can be scaled to make the volume under the plane equal to one by dividing by the total amount of leaching:

\[
S(x,t) = \frac{S_u(x,t)}{\int_{t_0}^{\infty} \int_0^A S_u(x,t)dxdt}^{-1}
\]  

(1)

where \( S \) is the scaled solute flux density [L^{-2} T^{-1}], \( t_0 \) [T] is the solute application time (for solutes applied as a pulse), and \( A \) is the total sampling area [L^2].

For any location \( x^* \) the solute breakthrough curve at that location is the cross-section of \( S \) parallel to the \( t \)-axis at \( x^* \):

\[
\text{BTC}(t)|_{x^*} = S(x^*,t), \quad t \in [t_0, \infty)
\]  

(2)

Analogously, a cross-section of \( S \) parallel to the \( x \)-axis at time \( t^* \) represents the spatial solute distribution curve:

\[
\text{SSDC}(x)|_{t^*} = S(x,t^*), \quad x \in [0, A]
\]  

(3)
Thus, SSDC(\(x_i\)|\(t^*\)) describes the spatial distribution of solute leaching at time \(t^*\), and it is the spatial equivalent of the BTC.

Suitable integrations can yield other convenient expressions. The cumulative BTC (BTC_{cum} \(t^*/L^{-2}\)) at any point \(x^*\) is obtained by integrating \(S\) over time:

\[
\text{BTC}_{cum}(t)|_{x^*} = \int_{t_0}^{t} S(x^*, \tau) \, d\tau, \quad t \in [t_0, \infty)
\]  

where \(\tau\) is an integration variable. Integrating \(S\) over \(x\) yields the SSDC_{cum} \(x\) \([T^{-1}]\), which expresses the amount of leaching through the section \([0, x]\) of the sampling area at time \(t^*\):

\[
\text{SSDC}_{cum}(x)|_{t^*} = \int_0^x S(x, t^*) \, dx, \quad x \in [0, A]
\]  

Integrating over time yields the cumulative equivalent, BTC_{cum} \(x\):

\[
\text{BTC}_{cum}(x)|_{t^*} = \int_0^{t^*} S(x, \tau) \, d\tau, \quad x \in [0, A]
\]  

The SSDC of cumulative leaching at \(t^*\) is SSDC_{cum} \(t^*/[L^{-2}]\):

\[
\text{SSDC}_{cum}(t)|_{t^*} = \int_0^x S(x, t) \, dt, \quad x \in [0, A]
\]  

Integrating over \(x\) gives the total amount of leaching at \(t^*\) in the section \([0, x]\) of the sampling area, denoted by SSDC_{cum} \(x\):

\[
\text{SSDC}_{cum}(x)|_{t^*} = \int_0^x \int_0^{t^*} S(x, \tau) \, d\tau \, dx, \quad x \in [0, A]
\]  

Since \(S\) is scaled so that the total amount of leaching over all \(x\) and \(t\) is one, then BTC_{cum} \(x\) and SSDC_{cum} \(x\) are between 0 and 1. Stagnitti et al. (1999) and de Rooij and Stagnitti (2000) fit the cumulative Beta distribution function to curves resulting from Eq. (7b) with \(t^* = \infty\).

In analogy with the theory for multidimensional probability density functions (pdfs), we can view \(S(x, t)\) as a bivariate pdf, by virtue of the fact that the volume underneath it equals one. It then must have two marginal distributions associated with it, which are given by (Kendall and Stuart, 1969, p. 22):

\[
S_x(x) = \int_0^{t^*} S(x, t) \, dt, \quad x \in [0, A]
\]
\[ S_t(t) = \int_0^A S(x,t)dx, \quad t \in [t_0, \infty) \] (8b)

with \(S_x[L^{-2}]\) as the marginal distribution of \(S\) along the \(x\)-axis, and \(S_t[T^{-1}]\) as that along the \(t\)-axis.

Comparison of Eqs. (8a) and (8b) with Eqs. (6a) and (7a) shows that \(S_x\) is given by \(\text{SSDC}_{\text{cum}}(x)\), which is the SSDC of cumulative solute leaching when all solute has leached. \(S_t\) is given by \(\text{BTC}_{\text{cum}}x(t)[0,A]\), which represents the BTC of the entire sampling area \((A)\). Thus, experiments that either monitor solute leaching in time or record the spatial distribution of cumulative solute leaching, merely capture one of the two marginal distributions of the pdf that describes the full spatio-temporal leaching behavior.

If complete independence in the two marginal distributions is assumed, then by analogy to bivariate probability theory, solute leaching in space and time is simply the SSDC of cumulative leaching at the end of the experiment multiplied by the overall BTC (see Kendall and Stuart, 1969, p.22):

\[ S_{\text{ind}}(x,t) = \text{SSDC}_{\text{cum}}(x)_{\infty} \text{BTC}_{\text{cum}}x(t)[0,A] \] (9)

where \(S_{\text{ind}}[L^{-2}T^{-1}]\) represents the scaled solute flux density for independent spatial and temporal leaching characteristics.

3. Materials and methods

The experiments were performed on a lysimeter containing an undisturbed soil core of 0.56-m radius and 0.55-m height. The soil was a sandy mesic Typic Psammaquent (Soil Survey Staff, 1988) near Ouddorp in the south-western part of The Netherlands, and had a 0.2- to 0.4-m-thick water-repellent top layer. A dye tracer test and tensiometer measurements showed evidence of fingered flow in the top layer (de Rooij, 1996). The soil core was placed on a 0.35-m high grid of 300 drainage collection compartments of 0.05 \(\times\) 0.05 m, surrounded by 60 larger compartments at the edge. The grid was backfilled with sand taken from the same location as the soil core. It was sufficiently high to contain the capillary fringe above the drainage outlets. Artificial rain showers (20 mm at 246 mm day\(^{-1}\)) were applied every Monday, Wednesday and Friday by a rainfall simulator with 468 hypodermic needles that released droplets of water.

After a 6-month prewetting period, 6.4 mm of a 0.98 M CaCl\(_2\) solution was uniformly applied to the soil surface by sprinkling from 47 hypodermic needles mounted at 25-mm spacing in a PVC tube (1.235-m long, 24-mm i.d.) that was connected to a Mariotte vessel containing the tracer solution. The coefficient of variation of the flux from individual needles was about 5%. The tracer was applied by moving the tube back and forth over the lysimeter at a constant speed for approximately 85 min. Twenty collection cans of 30-mm radius were placed just outside the lysimeter. From the amount of tracer solution collected in the cans, the average applied amount (6.4 mm) and the population standard deviation (0.59 mm) were calculated.
Drainage was collected in flasks below the drainage compartments. Before every shower, the drainage collected since the start of the previous shower and its electrical conductivity (EC) were measured for each drainage compartment. For some compartments, the amount of leaching was too small to allow an accurate EC-measurement. For each sampling round, the water of these compartments was collected in a single container, and the EC of the pooled sample determined. The amount of chloride in each sample was determined from the EC. At the completion of the experiment, the amount of chloride still leaching was negligible. The total mass recovery was 102%, indicating all chloride was recovered. More details of the lysimeter, the rainfall simulator, and the chloride leaching experiment are given by de Rooij (1996) and de Rooij and Stagnitti (2000).

In the analysis below, we considered only the 300 inner drainage compartments (with a combined area of 0.75 m²) to avoid geometry effects caused by the various shapes and sizes of the outer compartments. The inner compartments captured 69.1% of the leached solute, 92% of the amount they should when the flow through the soil would be perfectly vertical throughout the lysimeter. We used the expressions developed in the theoretical section to describe the leaching process in space and time. In addition, we analyzed in detail the properties of the leaching peak. The combined information thus obtained allowed us to make inferences about the nature of the water flow and solute transport processes in this soil.

4. Results and discussion

Fig. 1 shows the spatial leaching pattern of two sampling rounds of de Rooij’s (1996) lysimeter experiment. A similar plot for the cumulative solute leaching is given by de Rooij and Stagnitti (2000). Fig. 2 shows the plane \( S(x,t) \) that summarizes the entire leaching experiment. The plane is constructed from 8700 data points, and noise has been smoothed out to preserve readability of the figure. In the following, we demonstrate how this figure can be used to guide the data analysis to target the most pronounced features of the leaching process. In doing so, we shall explore the scope of possibilities offered by the analysis of \( S \).

Fig. 2 shows a high peak for small \( x \) with a limited extent along the time axis: leaching is concentrated in a confined area with small values of \( x \) (compartments with high amounts of total leaching) and during a limited period of time. Compartments with lower amounts of total leaching had somewhat larger values of the time-to-peak \( t_p; T \), but overall, for most individual compartments the bulk of solute leaching occurred within a period of less than 12 days.

Fig. 3 gives the observed marginal distributions of \( S \), i.e., the BTC of all drainage compartments combined given by Eqs. (6a) and (6b) with \( x_a = 0 \) and \( x_b = A \) (Fig. 3a), and the SSDC (cumulative in time) at the end of the experiment, given by Eqs. (7a) and (7b) with \( t^* = \infty \) (Fig. 3b). The figures suggest a smoother, more evenly distributed leaching process than was actually observed. Still, Fig. 3a shows that most leaching occurred in about 15 days (compare cumulative leaching at day 15 and day 30), marginally larger than the period for the individual compartments.

To further investigate this we analyzed cross-sections of \( S \): BTCs for a number of individual compartments, and SSDCs at selected times. Fig. 4 presents BTCs of different
quantiles of $x$, with the 0.33% quantile being the first compartment in terms of total
amount leached and the 75% quantile the 225th compartment. Variation in fluxes and $t_p(x)$
was strongest for high-leaching compartments (small quantiles of $x$).

The SSDCs for different amounts of leaching show that leaching started at a few
compartments (Fig. 5a). These compartments all have small values of $x$, indicating a
significant correlation between the time on which leaching commences and the total
amount of leaching during the course of the breakthrough process. As time progressed,
more compartments contributed to leaching (Fig. 5b). Later still, solute passed through the
slowest compartments with low total amounts of leaching (large $x$), while solute fluxes
through the early compartments were already diminishing (Fig. 5c).

In Fig. 5, a clear distinction between areas of high and low leaching can only be made
during the onset of leaching. After some time ($t > 15.8$ days), the spatial distribution of
leaching becomes smooth. The SSDC of total leaching is equally smooth (Fig. 3b). This
suggests that, in this soil, diverging flow in the wettable soil below the fingers in the water-repellent top soil smoothed out sharp contrasts between fingers and surrounding areas (de Rooij, 1995; de Rooij et al., 2001; Cho and de Rooij, 1999).

The $t_p$-value quantifies the response time of fast and slow compartments. As such, it characterizes the solute travel time at every $x$. Fig. 6 shows there is considerable scatter in the relationship between $x$ and $t_p$, with the bulk of the compartments peaking after 22.84 days. Compartments with high amounts of total leaching (small values of $x$) have smaller $t_p$-values than compartments with lower amounts of total leaching: high total leaching is correlated with rapid leaching, although the compartment with the largest amount of cumulative leaching did not have the fastest leaching (Fig. 4).

The relationship between $x$ and the scaled maximum solute flux density $S_{\text{max}}(x)$ [$L^2 T^{-1}$] exhibits considerably less scatter (Fig. 7). As before, the scatter is largest for small $x$. The similarity between the SSDC at the end of the experiment (Fig. 3b) and Fig. 7 is striking. This suggests that the peak breakthrough flux rate can be an indicator for the total leaching from a given compartment and vice versa. We therefore determined $t_p(x)$, $S_{\text{max}}(x)$ and total leaching, $\text{SSDC}_{\text{cum}} f(x)_{\infty}$, for each compartment and used curvilinear regression to establish relationships between them. Linear, exponential, logarithmic and power relationships were fitted, and one of them selected on the basis of the $R^2$-value and visual inspection. The results (Table 1) show that total leaching and $S_{\text{max}}$ are indeed highly correlated. The other two relationships exhibit much more scatter. The range of $S_{\text{max}}$ for the smallest observed $t_p$ is particularly large (nearly one order of magnitude).
This increased degree of variation for rapidly leaching compartments is in line with the trends visible in Figs. 4–7: compartments with large amounts of leaching have more variation in their rates and amounts of solute transport than the remaining compartments. The decrease of variation among low-leaching compartments can only be partially explained by the fact that the solute amounts of the compartments with the smallest drainage quantities had to be determined from their combined leachate. We hypothesize that the solute transport in the high-leaching flow paths is so fast that most of the solute does not leave the stream tubes into which it entered upon infiltration at the soil surface, and as a result the transport process is predominantly stochastic–convective. This transport mode produces the observed erratic leaching behavior since there is no

Fig. 3. The observed breakthrough curve for all drainage compartments combined (a) and the observed distribution of total solute leaching at the end of the lysimeter experiment (b).
mechanism in operation to smooth the effect of the variation of travel times among the stream tubes. In the low-leaching flow paths, the solute has more time to travel between flow paths, and thus sample a wider variety of pore velocities. Consequently, the transport process there is mainly convective–dispersive (see Flühler et al., 1996 for a comprehensive discussion of the effect of solute exchange between streamtubes on the nature of the solute transport process). De Rooij (1996, pp. 196–199) gives further evidence for the importance of dispersion in the low-leaching flow paths. He observed that low-leaching compartments required a much smaller amount of cumulative drainage to reach their breakthrough peak than high-leaching compartments. He suggested that dispersion may have transferred a small fraction of the solutes carried by flow paths with rapid transport to neighboring slower flow paths.

It is often assumed that the transport process gradually changes from stochastic–convective close to the soil surface to convective–dispersive deeper in the soil, as solutes sample an increasing variety of pore water velocities while moving between stream tubes (Flühler et al., 1996). Possibly, this depth-dependence of the dominant transport process needs to be weakened to allow both processes to operate simultaneously at the same depth, with the local pore water velocity determining which process is dominant. Still, in the soil studied here, the bulk of the solute is transported through the stochastic–convective domain, and the transport process can best be described as convection-dominated, even though that domain may occupy a relatively small portion of the entire flow domain.

To gain additional insight in the dynamics of solute leaching, we grouped the drainage compartments according to their $t_p$-values. We then determined the fraction of the total area of each group of compartments, and the fraction of the total leaching transported through that group. We also determined the amount of leaching that each group transported in the drainage collection period during which the peak occurred. From the results in Table 2, it

![BTCs for different quantiles of x](image-url)

Fig. 4. Observed breakthrough curves for individual drainage compartments.
Fig. 5. Observed spatial distribution of $S$ at selected times.
appears that the fastest group transports 1.9 times the average amount of solute, while the slowest 6.3% (the slowest three groups combined) transport 0.88 times the average. The 71.3% of the compartments that peak after 22.84 days transport 0.79 times the average amount. The fastest 10.7% of the compartments leach 5.5% of the total during their peak sampling round. In comparison, the bulk 71.3% leach only less than twice that amount (9.6%) during their peak. This confirms the importance of the area with the most rapid leaching: not only does this area conduct 20.3% of total leaching, over 25% of this amount is delivered at 85-cm depth 7 days ahead of the overall peak (compare Fig. 3a).
de Rooij and Stagnitti (2000) interpreted the SSDC as a descriptor of the geometry of the flow paths. At the location where leaching is average ($x_{av}$), SSDC$_{cum t}$ ($x_{av}$) = $A/C0$. Locations with more-than-average total leaching ($0 < x_{av} < A$) were assumed to receive water from areas in the soil with converging flow paths, while the remainder of $A$ ($x_{av} < x < L$) received water from diverging flow paths. Figs. 2 and 3 suggest there is only a gradual difference between leaching from areas in the soil with converging flow and areas with diverging flow. To verify this we analyzed the areas of high and low leaching separately.

The average scaled total leaching of each of the 300 lysimeter compartments equals $1/300$. Fig. 3b indicates that $x_{av} = 0.2725$ m$^2$. SSDC$_{cum t}$ and SSDC$_{cum xt}$ were calculated for the high- and low-leaching regions from Eqs. (7a) and (7b) by varying $x$ over either region separately. Graphically, SSDC$_{cum t}$ and SSDC$_{cum xt}$ are represented by the sections of the curves in Fig. 3b on either side of the vertical separation line. The breakthrough curves of both regions are given by Eqs. (6a) and (6b), and are shown in Fig. 8. The low-leaching regions peaked 7 days after the high-leaching region and had more tailing. The high-leaching region transported 57% of the total solute through 36% of the sampling area.

The analysis above demonstrates the wealth of information that can be obtained from $S$ in addition to the conventional BTC$_{cum x}$. The data can be analyzed directly, without the need to apply any parameterization that may require assumptions about the underlying solute transport processes.

From the marginal distributions in Fig. 3, an artificial plane $S_{ind}(x,t)$ was generated according to Eq. (9). The plane (Fig. 9) has too much leaching for large $t$ and $x$ in comparison with the observed plane (Fig. 2). Note that $S_{ind}$ is virtually noise-free, unlike $S$. This hampers a direct comparison between Figs. 2 and 9. For instance, the smoothing makes

<table>
<thead>
<tr>
<th>$t_p$ (day)</th>
<th>Fraction of $A$</th>
<th>Fraction of total leaching transported through each group of compartments</th>
<th>Fraction of total leaching during the peak leaching period of each group</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.84</td>
<td>0.107</td>
<td>0.203</td>
<td>0.0552</td>
</tr>
<tr>
<td>18.84</td>
<td>0.0567</td>
<td>0.0835</td>
<td>0.0273</td>
</tr>
<tr>
<td>20.84</td>
<td>0.0600</td>
<td>0.0930</td>
<td>0.0229</td>
</tr>
<tr>
<td>22.84</td>
<td>0.713</td>
<td>0.565</td>
<td>0.0963</td>
</tr>
<tr>
<td>25.84</td>
<td>0.0400</td>
<td>0.0418</td>
<td>0.0109</td>
</tr>
<tr>
<td>27.84</td>
<td>0.00333</td>
<td>$1.18 \times 10^{-3}$</td>
<td>$1.57 \times 10^{-4}$</td>
</tr>
<tr>
<td>29.84</td>
<td>0.0200</td>
<td>0.0127</td>
<td>$2.05 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 1: Curvilinear regression relationships between three variables describing solute leaching from the individual drainage compartments.

<table>
<thead>
<tr>
<th>Relationship</th>
<th>$a$</th>
<th>$b$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{max}(x^<em>) = a[SSDC_{cum t}(x^</em>)]_\infty^b$</td>
<td>331.0 m$^2$ day$^{-1}$</td>
<td>1.388</td>
<td>0.940</td>
</tr>
<tr>
<td>SSDC$<em>{cum t}(x^*)</em>\infty = a[t_p(x^*)]_\infty^b$</td>
<td>3.448 m$^2$</td>
<td>$-2.295$</td>
<td>0.316</td>
</tr>
<tr>
<td>$t_p(x^<em>) = a \exp[bS_{max}(x^</em>)]$</td>
<td>24.13 days</td>
<td>$-0.7386$ m$^2$ day$^{-1}$</td>
<td>0.442</td>
</tr>
</tbody>
</table>

Table 2: Leaching characteristics of the drainage compartments grouped by their $t_p$-values.
the volume under $S$ appear smaller than that under $S_{\text{ind}}$, while both volumes are by definition equal to one. We therefore created a scatter diagram of observations vs. simulations of $S$ (Fig. 10). The 1:1 line was not at all approximated, and correlation was poor.

Fig. 8. Observed solute breakthrough for the areas with total leaching above and below the average.

Fig. 9. The simulated distribution of $S_{\text{ind}}$ in the $x,t$-plane if zero correlation is assumed between the spatial and temporal distribution of leaching. The simulation is based on the observed breakthrough curve of all drainage compartments combined and the spatial distribution of total solute leaching (Fig. 3).
Clearly, the assumption of zero correlation between location and velocity of leaching is invalid. Therefore, knowledge of the BTC of the entire sampling plane (BTC\textsubscript{cum}(x,t)|_{[0,A]}) and the SSDC of cumulative solute leaching at the end of the experiment (SSDC\textsubscript{cum}(x)|_{\infty}) combined is not sufficient to fully describe the spatio-temporal solute leaching process. Physically, the nonzero correlation between leaching velocity and location implies that locations with rapid leaching also tend to have larger amounts of total leaching. This is what would be expected, since locations with rapid leaching are inclined to carry larger flow volumes and therefore must receive their water and solutes from relatively large sections of the soil surface.

5. Conclusions

To facilitate the analysis of solute leaching at a given depth, we collapsed the two spatial axes of the sampling depth into one (x) by ranking the sampling locations in order of decreasing total leaching. By doing so, the spatio-temporal leaching process can be described by a curved surface $S(x,t)$. The ranking of the sampling locations ensures that the key features of the leaching process are highlighted in the shape of $S$. An analytical framework has been presented to comprehensively analyze $S$.

If $S$ is scaled to make the volume underneath it equal to one, it can be considered to be a bivariate pdf, with the conventional BTC and SSDC representing its marginal distributions. Analysis of $S$ instead of only these marginal distributions not only improves the description of solute leaching, but yields information about the nature of the transport process between the soil surface and the sampling depth that cannot be derived from the BTC or SSDC alone.
In this soil, the part of the flow domain with short solute travel times had predominantly stochastic–convective solute transport, while dispersion was more important in areas with slower solute transport. Most of the solute moved through the stochastic–convective domain. The fast and slow transport regions could not be clearly separated at the sampling depth, despite the occurrence of fingered flow. Finger dissipation in the wettable subsoil probably blurred any sharp boundaries between different flow domains.

The detailed information encapsulated by $S$ makes it a valuable tool to characterize observed leaching in multisampler solute transport experiments. $S$ can also serve as a benchmark to quantitatively evaluate the performance of multidimensional solute transport models (e.g., by comparing leaching surfaces calculated from simulations with an experimentally based $S$).

### List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Dimension</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$L^2$</td>
<td>Total sampling area</td>
</tr>
<tr>
<td>$a$, $b$</td>
<td></td>
<td>Regression coefficients</td>
</tr>
<tr>
<td>BTC</td>
<td>$T^{-1} L^{-2}$</td>
<td>Breakthrough curve</td>
</tr>
<tr>
<td>BTC$_{cum}$</td>
<td>$L^{-2}$</td>
<td>Cumulative breakthrough curve</td>
</tr>
<tr>
<td>BTC$_{cum}$$_x$</td>
<td>$T^{-1}$</td>
<td>Leaching from a section of $x$ as a function of time</td>
</tr>
<tr>
<td>BTC$<em>{cum}$$</em>{xt}$</td>
<td></td>
<td>Cumulative leaching from a section of $x$ as a function of time</td>
</tr>
<tr>
<td>$S$</td>
<td>$L^{-2} T^{-1}$</td>
<td>Scaled solute flux density</td>
</tr>
<tr>
<td>$S_{ind}$</td>
<td>$L^{-2} T^{-1}$</td>
<td>Simulated scaled solute flux density when $S_x$ and $S_t$ are assumed independent</td>
</tr>
<tr>
<td>$S_{max}$</td>
<td>$L^{-2} T^{-1}$</td>
<td>Maximum of $S$ as a function of $x$</td>
</tr>
<tr>
<td>$S_t$</td>
<td>$T^{-1}$</td>
<td>Marginal probability density function of $S$ along the $t$-axis</td>
</tr>
<tr>
<td>$S_u$</td>
<td>$M L^{-2} T^{-1}$</td>
<td>Solute flux density</td>
</tr>
<tr>
<td>$S_x$</td>
<td>$L^{-2}$</td>
<td>Marginal probability density function of $S$ along the $x$-axis</td>
</tr>
<tr>
<td>SSDC</td>
<td>$L^{-2} T^{-1}$</td>
<td>Spatial solute distribution curve</td>
</tr>
<tr>
<td>SSDC$_{cum}$$_t$</td>
<td>$L^{-2}$</td>
<td>Spatial solute distribution curve of cumulative leaching</td>
</tr>
<tr>
<td>SSDC$_{cum}$$_x$</td>
<td>$T^{-1}$</td>
<td>Spatial solute distribution curve, accumulated over $x$</td>
</tr>
<tr>
<td>SSDC$<em>{cum}$$</em>{xt}$</td>
<td></td>
<td>Total amount of leaching at a given time, as a function of $x$</td>
</tr>
<tr>
<td>$t$</td>
<td>$T$</td>
<td>Time</td>
</tr>
<tr>
<td>$t_0$</td>
<td>$T$</td>
<td>Solute application time</td>
</tr>
<tr>
<td>$t_p$</td>
<td>$T$</td>
<td>Time-to-peak</td>
</tr>
<tr>
<td>$t^*$</td>
<td>$T$</td>
<td>Location on the $t$-axis</td>
</tr>
<tr>
<td>$x$</td>
<td>$L^2$</td>
<td>Spatial axis of ranked sampling locations</td>
</tr>
<tr>
<td>$x_1$, $x_2$</td>
<td>$L$</td>
<td>Spatial coordinates</td>
</tr>
<tr>
<td>$x_a$, $x_b$</td>
<td>$L^2$</td>
<td>Lower and upper bounds of a section $[x_a, x_b]$ of $x$</td>
</tr>
</tbody>
</table>
Acknowledgements

The work of G.H. de Rooij has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences. This research was also in part supported by the Australian Research Council’s grants no. A10014154 and no. C00002301, and a RIRDC travel grant.

References


