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Indirect estimation of the Convective Lognormal Transfer function model parameters for describing solute transport in unsaturated and undisturbed soil

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Solute transport in partially saturated soils is largely affected by fluid velocity distribution and pore size distribution within the solute transport domain. Hence, it is possible to describe the solute transport process in terms of the pore size distribution of the soil, and indirectly in terms of the soil hydraulic properties. In this paper, we present a conceptual approach that allows predicting the parameters of the Convective Lognormal Transfer model from knowledge of soil moisture and the Soil Moisture Characteristic (SMC), parameterized by means of the closed-form model of Kosugi (1996). It is assumed that in partially saturated conditions, the air filled pore volume act as an inert solid phase, allowing the use of the Arya et al. (1999) pragmatic approach to estimate solute travel time statistics from the saturation degree and SMC parameters. The approach is evaluated using a set of partially saturated transport experiments as presented by Mohammadi and Vanclooster (2011). Experimental results showed that the mean solute travel time, μt, increases proportionally with the depth (travel distance) and decreases with flow rate. The variance of solute travel time σ²t first decreases with flow rate up to 0.4–0.6 Ks and subsequently increases. For all tested BTCs predicted solute transport with μt estimated from the conceptual model performed much better as compared to predictions with μt and σ²t estimated from calibration of solute transport at shallow soil depths. The use of μt estimated from the conceptual model therefore increases the robustness of the CLT model in predicting solute transport in heterogeneous soils at larger depths. In view of the fact that reasonable indirect estimates of the SMC can be made from basic soil properties using pedotransfer functions, the presented approach may be useful for predicting solute transport at field or watershed scales.

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1. Introduction

The solute transport is a key process determining the mass flow of chemical substances in soils once they are released in the soil solution. The transport process is a highly non-linear and space–time dynamic process for which predictive models are still poorly validated.

Solute transport in porous media is often conceptualized as being either a stochastic–convective or convective–dispersive process (Jury and Fluhler, 1992; Simmons, 1982). In a stochastic–convective process, the solute is assumed to move at different velocities in isolated stream tubes without any mixing of solute between tubes (Dagan and Bresler, 1979), whereas in a convective dispersive process perfect mixing between stream tubes is assumed to occur. Several field-scale solute
transport studies have shown that solute transport can be better modelled as stochastic–convective process, especially close to surface (Butters et al., 1989; Jury et al., 1982). Solute transport at core scale has also been described as a stochastic–convective process (Khan and Jury, 1990; Vancoloofter et al., 1995). The stochastic–convective solute transport process can appropriately be modelled by means of the Convective Lognormal Transfer (CLT) function model (Jury, 1982a, 1982b). For several field-scale (Butters et al., 1989; Jury et al., 1982) and lysimeter-scale (e.g., Vancoloofter et al., 1995; Vanderborght et al., 1997) solute transport experiments, the CLT model has been successfully used to predict observed Break Through Curves (BTCs).

When the solute transport process is modelled as a stochastic–convective process, solute transport can be predicted from knowledge of the partially saturated hydraulic properties. This is consistent with earlier experimental evidence showing that solute transport properties are related to other soil hydraulic related physical characteristics such as soil saturation degree or water content (Bejat et al., 2000; Krupp and Elrick, 1968; van Genuchten and Wierenga, 1977; van Genuchten et al., 1977), pore size distribution (Gist et al., 1990; Li and Chodrati, 1997), particle size distribution (Nielsen and Bigger, 1962) and pore geometry (Elrick and French, 1966; Skopp et al., 1981; Yule and Gardner, 1978). Wang et al. (2002) successfully used the Brooks and Corey (1964) hydraulic model to predict the shape of the solute breakthrough curve (BTC) in disturbed sand columns under saturated conditions. Similarly, Mohammadi et al. (2009) showed that the solute BTC of a step function miscible displacement experiment can be predicted from knowledge of soil hydraulic properties for small scale homogeneous soil cores under saturated conditions.

The original CLT model however assumes a vertically homogenous soil and may therefore not be applicable in soils having significant vertical heterogeneity, and hence when solute travel distances become larger (Barry and Parker, 1987; Javaux and Vancoolofter, 2004; Leij et al., 1991). The CLT model has therefore been generalized for different concentration modes and boundary and initial conditions by Jury and Scotter (1994). To compensate for the effect of vertically varying soil water content, Ellsworth and Jury (1991) introduced transformed depth coordinates in the CLT model. Using such transformed depth coordinates and a multi-domain flow model, Vanderborght et al. (2001) predicted the variance of the pore water velocity and apparent dispersivity from a non parametric description of the hydraulic conductivity curve (HCC) in undisturbed structured lysimeters. They were partially successful in predicting the apparent dispersivity for a wide range of soil types, but their approach did not take into consideration that the apparent dispersivity is not only a material constant, but also depends on the flow conditions, in particularly the flow rate. In addition, the use of non-parametric and empirical relationships between the HCC and apparent dispersivity does not allow explaining the relationships using clear conceptual considerations.

In this paper, we present a conceptual approach that allows predicting the geometric mean travel time of inert solute transport as modelled by means of the CLT model from knowledge of the Soil Moisture Characteristic (SMC), parameterized by means of the closed form model of Kosugi (1996). It is further assumed that in partially saturated conditions, the air filled pore volume act as an inert solid phase, allowing the use of the Arya et al. (1999) pragmatic approach to estimate the mean and variance of lognormally distributed solute travel time from the saturation degree and SMC parameters. The conceptual approach is further tested on a set of solute transport experiments as presented by Mohammadi and Vancoolorter (2011a).

2. Theory

2.1. Transport in a single pore

Following Hagen–Poiseuille’s equation (see e.g. Arya et al., 1999; Hillel, 1971), we conceptualize that the flow rate, $q_i$, within an individual soil pore can be calculated from:

$$ q_i = \frac{\pi r_i^2 \rho_w g \Delta H}{\eta} $$

where $r_i$ is the mean pore radius (L) for the ith pore fraction; $\rho_w$ is the density of water (ML$^{-3}$); $g$ is the acceleration due to gravity (LT$^{-2}$); $\Delta H$ is the pressure head difference across the flow path (L); $S$ is a shape factor (–); $\eta$ is the viscosity of water (ML$^{-1}$T$^{-1}$); and $l_i$ is the length of the flow path in ith pore (L). The term $(\Delta H/l_i)$ in Eq. (1) can be eliminated if flow occurs under a unit gradient. The exponent $x$ and the shape factor $S$ are dimensionless parameters. For cylindrical tubes of uniform diameter, $x=4$ and $S=8$. Soil pores, however are neither circular nor uniform nor straight. Therefore, an adjustment of the parameters $S$ and $x$ is necessary to adapt Eq. (1) for natural soils. Following Arya et al. (1999), we adopt a pragmatic approach, assuming a unit gradient and combining all factors except for pore size in a single empirical variable. As a result, Eq. (1) is modified to:

$$ q_i = c r_i^z $$

in which $c$ and $x$ can be evaluated empirically using experimental data. Eq. (2) is valid for a unit hydraulic gradient. In case no unit gradient applies, the eventual bias will be lumped within the empirical terms $c$ and $x$. Considering $q_i = \frac{A_l}{t}$, where $A_l$ is the pore cross section area and $l$ is the distance, and suggesting Laplace equation as $r_i = \beta / \psi_s$, where the $\beta$ is a constant depending on temperature and water-soil contact angle and is 0.15 cm$^2$ for 20 °C, $\psi_s$ is the matric suction of ith pore, Eq. (2) can be expressed as:

$$ t = C \psi_s^\frac{1}{2} $$

where $t$ is the travel time (T), and $C$ is constant and depends on temperature, pore cross section shape and travel distance. The empirical constant $C$ is defined for unit hydraulic gradient. For experimental conditions, it can be adjusted for any hydraulic gradient. If we consider pure convective solute transport within each pore then, we may postulate that the $t$ in Eq. (3) can be defined as the non-reactive solute travel.
time in a single pore subjected to a Dirac delta function boundary condition.

2.2. Transport in a saturated pore system

Following a stochastic convective solute transport concept and based on the linear impulse response theory, Jury (1982a) proposed the travel time probability density function (pdf) of the convective lognormal transfer function model (CLT):

\[ f(t) = \frac{1}{\sqrt{2\pi} \sigma_t} \exp \left[ -\frac{(\ln t - \mu_t)^2}{2\sigma_t^2} \right] \]

(4)

The parameters of the CLT model scales with depth according (Jury and Roth, 1990):

\[ \sigma_z = \sigma_l \quad \text{and} \quad \mu_z = \mu_l + \ln(z/l) \]

(5)

where \( \mu_l \) and \( \mu_s \) are the mean travel time at a calibration distance \( l \) and a distance of interest \( z \) from the inlet, respectively, and \( \sigma_l \) and \( \alpha_z \) are the standard deviations of \( \ln(t) \) at these distances. Assuming flow in a single pore domain occurs as described in previous section and taking the logarithm of Eq. (3) yields:

\[ \ln(t) = \ln(C) + (x-2) \ln(\psi_i) \]

(6)

The distribution of matric head (pore sizes) in natural soils is often expressed by means of a lognormal distribution (Kosugi, 1994; Kosugi, 1996). Hence, \( \ln(\psi_i) \) is normally distributed and the mean (\( \mu \)) and variance (\( \sigma^2 \)) of \( \ln(t) \) can be calculated from the statistical moments of \( \ln(\psi_i) \) (e.g. Abramowitz and Stegun, 1970):

\[ \mu_{\ln(t)} = \ln(C) + (x-2)\mu_{\ln(\psi)} \]

(7.1)

\[ \sigma^2_{\ln(t)} = (x-2)^2 \sigma^2_{\ln(\psi)} \]

(7.2)

The mean (\( \mu_{\ln(\psi)} \)) and variance (\( \sigma^2_{\ln(\psi)} \)) of matric head distribution are linked to the soil moisture characteristic (SMC) by means of the Kosugi (1996) model as follows:

\[ Se = \frac{1}{2} \text{erfc} \left[ \frac{\ln(\psi) - \mu_{\ln(\psi)}}{\sqrt{2}\sigma_{\ln(\psi)}} \right] \]

(8)

where \( \text{erfc} \) is the complementary error function, \( S_e = (\theta - \theta_r) / (\theta_s - \theta_r) \) is the effective saturation degree, and \( \theta_r, \theta_s \) the normal, residual and saturated volumetric water content (L² m⁻²). The geometric mean of matric head \( \mu_{\ln(\psi)} \) can be converted to geometric mean of pore radius by means of the Laplace equation. Hence, a-priori knowledge of the SMC model (e.g. Mohammadi and Vanclooster, 2011b) can be used to estimate the statistical moments of the matric head distributions and further the CLT travel time parameters. For simplification, hereafter, the \( \mu_{\ln(t)}, \sigma^2_{\ln(t)}, \mu_{\ln(\psi)} \) and \( \sigma^2_{\ln(\psi)} \) will be denoted by the \( \mu_z, \sigma^2_z, \mu_\psi \) and \( \sigma^2_\psi \) respectively. Eqs. (7.1) and (7.2) reveal that CLT parameters can be estimated from SMC data if the two empirical coefficients, \( x \) and \( C \), are known. The mean of matric head distribution, \( \mu_\psi \) is defined by (e.g. Abramowitz and Stegun, 1970):

\[ \mu_\psi = \int_0^\infty \psi f(\psi) d\psi \]

(9)

where \( f(\psi) \) is the matric head distribution function of a pore system equal to the first derivative of the SMC, and \( a = \psi_x \) is the bubbling pressure, which can be related to the \( r_{max} \) the maximal pore size, by the Laplace equation. See also Fig. 1.

2.3. Transport in a partially saturated pore system

In partially saturated conditions, air filled pores do not contribute to flow and transport. So, the statistical moments

---

**Fig. 1.** Schematic of the Soil Moisture Characteristics (SMC) curve (A) and matric head distribution function (\( f(\psi) \)) (B), for a partially saturated soil system. The water filled pores are represented by the dotted area in both curves. \( S_e = \frac{\theta_i - \theta_r}{\theta_s - \theta_r} \) where, \( \theta_s \) and \( \theta_r \) are the saturated and residual volumetric water content respectively.
and CLT parameters must be calculated for the water filled pores only. Hence:

$$
\mu_{\text{in}}(t) = \ln(C' + (x-2)\mu_{\phi})
$$

(10.1)

$$
\sigma^2_{\text{in}}(t) = (x-2)^2 \sigma^2_{\phi}
$$

(10.2)

where $\sigma^2_{\phi}$ and $\mu_{\phi}$ are the variance and mean of the matric head distribution of the water filled pore system respectively. The mean of the matric head distribution of the water filled pores yields:

$$
\mu_{\phi} = \int_a^b \psi g(\psi) d\psi
$$

(11)

where the $g(\Psi)$ is the matric head distribution function of water filled pores, i.e. the part of matric head distribution function ranged from $\Psi = \infty$ to the soil matric suction, $b$ and $b > \Psi_e$. The parameter $b$ is related to soil matric suction or saturation degree in experiments. Hereafter, $g(\Psi)$ is defined by:

$$
g(\psi) = \frac{f(\psi)}{\int_b^\infty f(\psi) d\psi}
$$

(12)

Replacing the $g(\Psi)$ in Eq. (11) with the right hand side of Eq. (12) gives:

$$
\mu_{\phi} = \int_b^\infty \psi \frac{f(\psi)}{\int_b^\infty f(\psi) d\psi} d\psi
$$

(13)

The denominator of right hand side of Eq. (13) is a constant for a given soil. Hence, Eq. (13) can be expressed as:

$$
\mu_{\phi} = \frac{1}{\int_b^\infty f(\psi) d\psi} \int_a^b \psi f(\psi) d\psi
$$

(14)

The denominator of Eq. (13), $\int_b^\infty f(\psi) d\psi$ is equal to the $S_e$, with $S_e$ the effective saturation degree. Hence, Eq. (14) becomes:

$$
\mu_{\phi} = \frac{1}{S_e} \int_a^b \psi f(\psi) d\psi - \int_a^b \psi f(\psi) d\psi
$$

(15)

Substituting Eq. (9) in Eq. (15) and numerical approximation of the second term in right hand side of Eq. (15) yields:

$$
\mu_{\phi} \approx \frac{1}{S_e} \left[ \mu_{\phi} \frac{a + b}{2} \int_a^b f(\psi) d\psi \right]
$$

(16)

Since $\int_a^b f(\psi) d(\psi) = S_e$, Eq. (16) can be expressed as:

$$
\mu_{\phi} \approx \frac{1}{S_e} \left[ \mu_{\phi} \frac{a + b}{2} \int_a^b f(\psi) d\psi \right] = \frac{a + b}{2} \mu_{\phi} - \frac{a + b}{2} (1 - S_e)
$$

(17)

The variance of matric head distribution, $\sigma^2_{\phi}$ is defined by (e.g. Abramowitz and Stegun, 1970):

$$
\sigma^2_{\phi} = E(\psi^2) - \mu_{\phi}^2
$$

(18)

where the $E(\psi^2)$ is the mathematical expected value of $\psi^2$. Consequently, the variance of matric head of water filled pores, $\sigma^2_{\phi}$ can be defined as:

$$
\sigma^2_{\phi} = E(\psi^2) - \mu_{\phi}^2
$$

(19)

where, $E(\psi^2)$ is the mathematical expected value of square of matric head of water filled pores and is defined as:

$$
E(\psi^2) = \int_a^b \psi^2 f(\psi) d\psi
$$

(20)

Eq. (20) can be expressed as:

$$
E(\psi^2) = \frac{1}{S_e} \int_a^b \psi^2 f(\psi) d\psi \bigg[ \frac{b}{b} \int_a^b \psi f(\psi) d\psi \bigg]
$$

(21)

The first term in the right hand side of Eq. (21) is the definition of $E(\psi^2)$. The second term can be estimated numerically. Hence, Eq. (21) becomes:

$$
E(\psi^2) \approx \frac{1}{S_e} \left[ E(\psi^2) - \frac{a^2 + b^2}{2} \int_a^b f(\psi) d\psi \right]
$$

(22)

Since $E(\psi^2) = \sigma^2_{\phi} + \mu_{\phi}^2$ and $\int_a^b f(\psi) d(\psi) = S_e$, Eq. (22) can be written as:

$$
\sigma^2_{\phi} \approx \frac{1}{S_e} \left[ \sigma^2_{\phi} + \mu_{\phi}^2 - \frac{a^2 + b^2}{2} (1 - S_e) \right] = \frac{a^2 + b^2 - S^2}{2} (1 - S_e)
$$

(23)

$\sigma^2_{\phi}$ and $\mu_{\phi}$ are the variance and mean of matric head distribution corresponding to water filled pores. These parameters can therefore be obtained from the SMC parameters and soil saturation degree, $S_e$.

3. Solute transport experiments

For validating the conceptual modelling approach, use was made of a set solute transport experiments performed on an undisturbed inceptisol. The experiments are described in detail by Mohammadi and Vanclooster (2011a).
experimental details of the set-up are also given in Abbasi et al. (2006). In short, we sampled a 80 cm diameter and 1 m high undisturbed soil core from an inceptisol. We fully equipped the soil core in the laboratory for monitoring water flow (tensiometers and TDR probes) and inert solute transport during controlled transport experiments. The experimental design allowed measuring local soil water and inert solute concentration at 10 different positions in the soil monolith. Nine steady state solute partially saturated transport experiments were performed at different flow rates ranging from 9.5 to 75 cm d\(^{-1}\) allowing to analyse transport properties in terms of different flow rates (Ks = 75 cm d\(^{-1}\)).

At the end of the transport experiment, 80 undisturbed kopecky ring samples were collected within the monolith (7–10 samples for each 5 cm layer) and were used to characterize the particle size distribution and organic matter content of the material as well as soil moisture characteristics (SMC) curve, using standardized soil physical techniques (Dane and Topp, 2002). Details of particle size distribution at different depths are given in Mohammadi and Vanclooster (2011a). Kosugi’s (1996) SMC model was fitted to the experimental data. Parameters were estimated using a least square fitting programme and are summarized in Table 1.

4. Results and discussion

4.1. Flow rate-moisture content relationships

Fig. 2 shows the saturation degree, S\(_{sat}\), distribution within the soil monolith in terms of the applied flow rate. The S\(_{sat}\) increases with flow rate in all soil regions. This supports the conceptual idea that more and larger pores contribute to flow and transport throughout the monolith when flow rate increases. The measured hydraulic gradient as a function of depth for different flow rates are presented in our previous paper (Fig. 2b of Mohammadi and Vanclooster, 2011a). As expected, the absolute values of hydraulic gradient are larger for the low flow rates, in particular in the topsoil.

The geometric mean, \(\mu'_{\psi_{w}}\), and standard deviation, \(\sigma'_{\psi_{w}}\), of the matric suction of water filled pores were calculated using Eqs. (17) and (23) and are shown as a function of depth and flow rate in Fig. 3.

### Table 1

<table>
<thead>
<tr>
<th>TDR probe number</th>
<th>Position within the soil monolith</th>
<th>SMC parameters (Kosugi (1996) model)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Depth (cm)</td>
<td>Direction(°)</td>
</tr>
<tr>
<td>1</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>0</td>
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<td>0</td>
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<td>40</td>
<td>240</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>240</td>
</tr>
</tbody>
</table>

The mean of water filled pores matric suction (\(\mu'_{\psi_{w}}\)) is maximum at lowest flow rate and depth, it decreases with both depth and flow rate, and is inversely related to S\(_{sat}\) (Fig. 2). The standard deviation of water filled pores matric suction (\(\sigma'_{\psi_{w}}\)) is maximum at the lowest depth and at saturated conditions (Fig. 3). At saturated conditions (q = Ks), the variation of \(\sigma'_{\psi_{w}}\) for different depths is only related to variation of Kosugi SMC parameters (Table 1). For other flow rates, both SMC and \(\sigma'_{\psi_{w}}\) influences variation of \(\sigma'_{\psi_{w}}\).

4.2. Flow rate-solute travel time relationship

Fig. 4 shows the fitted CLT model parameters, \(\mu_{\psi_{w}}\) and \(\sigma_{\psi_{w}}\), as a function of flow rate and depth, as estimated by fitting Eq. (1) to the observed BTCs. The mean of solute travel time \(\mu_{\psi_{w}}\), increases with depth (travel distance) and decreases with flow rates. In general \(\sigma_{\psi_{w}}\) decreases with flow rate (up to 0.4–0.6 Ks) and rises to reach the saturated condition which result in a U shaped function representing the variation of \(\sigma_{\psi_{w}}\) with flow rate, with a minimum at about 0.4 Ks especially in the topsoil. This is inconsistent with what would be expected from the conceptual model represented in theoretical section of the paper. The U shaped function of the solute travel time variability in terms of flow rate can be explained by two different mixing regimes (Mohammadi and Vanclooster, 2011a): at low flow rates (q<0.4 Ks) flow mainly occur in the soil matrix, while at higher flow rates,
preferential flow through macropores is activated. Activation of preferential flow at higher flow rate in this inceptisol has been confirmed by the dye staining experiment as presented by Mohammadi and Vanclooster (2011a).

4.3. Estimating $C'$ and $x$ parameters

Eqs. (7.1) and (7.2) for saturated flow conditions, and [10.1] and [10.2] for partially saturated flow conditions, link the statistical moments of the solute travel time to the statistical moments of the pressure head. The latter can be inferred from the parameters of the SMC. These equations can only be used in a predictive mode, if the two remaining empirical constants, $C'$ and $x$ are known. The empirical constants $C'$ and $x$ were estimated from the data presented in Figs. 3 and 4 respectively.

Table 2 shows the results of the predicted relationship between the geometric mean of solute travel time and water filled pores matric suction. The average value of $R^2$ (0.885) supports the validity of Eq. (10–1) for predicting the geometric mean of solute travel time for any saturation degree (Table 2).

In contrast to this, the geometric standard deviation of solute travel time ($\sigma_t$) and water filled pores matric suction ($\sigma_\psi$) do not obey the relationship as presented by Eqs. (10.2). Indeed, $\sigma_t$ exhibits a U-shape variation with flow rates at all soil depths (Fig. 4), whereas $\sigma_\psi$ varies nearly linearly with flow rates at all locations of the soil monolith (Fig. 4).

4.4. Prediction of solute transport

In order to evaluate the predictive capacity of the conceptual model (Eq. (10.1)), parameterized with the generic data inferred from Tables 1 and 2, solute transport in the inceptisol was predicted and compared with predictions with the classical CLT model. With the classical CLT model, BTC data measured at a single depth are used to estimate the travel time moments, $\mu_t$ and $\sigma_t$, using Eq. (1). Subsequently, these travel time moments are used to predict solute transport at deeper depths. With the presented conceptual model, $\mu_t$ is estimated using measured soil moisture data, data from the SMC and empirical relations derived in previous section. Since only Eq. (10.1) could be appropriately validated, we only calculated $\mu_t$ using generic data, keeping $\sigma_t$ to the calibrated values. This approach, that calculates $\mu_t$ from generic data, is further referred to as the adjusted CLT modelling approach. The Root Mean Square Error (RMSE) of predicted versus observed relative concentration ($C/C_0$) was used as an index to assess the prediction capacity of the modelling approach.

Fig. 5 shows the comparison between the classical and adjusted CLT model in predicting solute transport in the soil monolith. Both models have been calibrated using data observed in the upper 30 cm of the monolith. For the classical CLT model, both $\mu_t$, $\sigma_t$ are calibrated, while for the adjusted
model only $\sigma_t$ is calibrated. The character above any graph shows significant difference ($\alpha = 5\%$) in Dunken test. Fig. 5 clearly shows that the prediction capacity of the CLT model is smaller than for the adjusted CLT model. With increasing interval distance between calibration and prediction depth, the prediction capacity of the classical CLT decreases but remains appropriate for the adjusted CLT model, showing that the adjusted CLT model is more robust.

The improved goodness of fit of the adjusted CLT model is further illustrated for 4 different flow rates and observation depths in Fig. 6. The experimental BTCs which are used for calibrating the CLT model are shown in the right hand side small box within each figure. Fig. 6a, b shows the observed and predicted BTCs at the location of observation probe number 11 (depth 70 cm and direction 240°) when flux rates of 0.127 Ks and 0.35 Ks were used. In this cases, the CLT model was calibrated using BTC at a depth of 40 cm. Fig. 6c, d shows the observed and predicted BTCs at the location of observation probe number 1 (depth 85 cm and direction 0°) when flux rates of 0.127 Ks and 0.35 Ks were used. The CLT model was calibrated using BTC at a depth of 25 cm.

The adjusted CLT model outperforms in predicting all BTCs, as compared to the classical CLT. This is expected as the adjusted CLT model calculates $\mu_t$ from SMC and soil moisture data. The current approach allows integrating this soil mapping and soil moisture data in a better prediction of chemical transport in the soil.

Yet, there remains still some lack of fit due to inaccuracy in $\sigma_t$ prediction. The classical CLT model overestimates significantly the mean solute travel time, in particular when distance increases. Indeed the probability of introducing considerable vertical heterogeneity increases when depth increases. This limits the use of CLT parameters inferred from observations at shallow soil depths for predicting solute transport at the larger scale. In contrast, the adjusted CLT model incorporates vertical heterogeneity in the parameter structure through variable SMC and saturation degrees in the profile.

The adjusted CLT model remains therefore more reliable for predicting solute transport deeper in the soil profile. The gain in predictive power of the adjusted CLT model is partially due to the physical concepts introduced in the model. The predictive conceptual solute transport model is based on matrix flow only. Hence, only the transport experiments with flow rates $q$<0.4 Ks should be considered for model assessment. The proposed conceptual model considers that a portion of soil pores is completely water filled whereas larger pores are completely empty. The distribution of water filled pores is determined from the SMC and the saturation degree of the soil, and relies only on capillarity theory. The conceptual model ignores the role of water included in water-filled corners, pendular spaces and thin water films coating the exposed particle surfaces (Derjaguin et al., 1987; Lebeau and Konrad, 2010; Nitao and Bear, 1996; Tokunaga, 2009; Tuller

Table 2
The relationship of the geometric mean of solute travel time (day) and water filled pores matric suction (cm) at different locations of the soil monolith. For any location within the monolith, each pair of parameters ($\ln(\mu_t)$ and $x-2$) was obtained from observations at different flow rates. Each value is shown together with its 95% confidence interval.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Direction</th>
<th>$\ln(\mu_t)$</th>
<th>x − 2</th>
<th>$R^2$</th>
<th>RMSE (day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>0</td>
<td>−12.81 ± 1.875</td>
<td>2.2844 ± 0.3255</td>
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Fig. 5. Comparison of the RMSE of prediction of the classical CLT and adjusted CLT model in predicting experimental BTCs. (#: the BTC at this location has been calibrated at a depth of 25 cm).
Fig. 6. Comparison of experimental BTCs at different depth and flow rates in an undisturbed sandy subsoil and prediction results of classical CLT and adjusted CLT models. The geometric mean, $\mu_t$ and standard deviation, $\sigma_t$ of solute travel time used for predicting of breakthrough curve with CLT and adjusted CLT models are shown on top of the calibrating and predicted BTCs respectively.
and Or, 2001, 2002, 2005; Tuller et al., 1999). Goss and Madliger (2007) found that capillarity based models are successful for estimating the soil hydraulic properties, except for very dry conditions. The shortcomings in the proposed model for estimating $\sigma_0$ may partially be attributed to the ignoring of soil-water flow in thin films. Such thin water film may decrease the water flow path tortuosity and/or act as medium for molecular diffusion which result in reduction of $\sigma_0$ with flow rate when soil water content decrease (Maraga et al., 1997; Matsubayashi et al., 1997; Vanderborght et al., 2001). In summary, the CLT model, as the base of proposed approach, does not include lateral pore scale diffusion and the travel time variance is related to the macro-dispersion. The modelling approach may therefore underestimate the total dispersion. However, we hypothesize that for small flow rates (in our case $q \leq 0.4$ Ks) the total dispersion is mainly determined by macro dispersion and that the lateral pore scale diffusion is negligible.

5. Conclusion

The current study showed that the solute transport in unsaturated flow conditions can be predicted using the Convective Lognormal Transfer function theory with parameters inferred from the Soil Moisture retention Curve (SMC) as modelled by means of the Kosugi model. With the conceptual model, it is assumed that, in unsaturated conditions, the air filled pores acts as an inert solid phase which allows calculating the mean and variance of the solute travel time from the saturation degree and SMC parameters. The conceptual model is evaluated on a set of solute transport experiments. In these experiments, the geometric mean of observed solute travel time, $\mu_t$, increases proportionally with depth (travel distance) and decreases with flow rates. The variance of the solute travel time, $\sigma_t$, however, decreases with flow rate up to 0.4–0.6 Ks and increases again at saturation, which result in a U shaped variation of $\sigma_t$ with flow rate. This last observation impedes the use of the conceptual model in predicting $\sigma_t$ from SMC and saturation degree for these experiments. Notwithstanding this, inserting indirect estimated $\mu_t$ improves considerably the prediction capacity of the CLT model. This opens new perspectives for indirect estimations of solute transport parameters from basic soil data and describing solute transport at the larger scale. Yet, further testing of this approach on more solute transport data sets is needed to evaluate the transferability of the approach at the larger scale.

References


