Non-Fickian transport in homogeneous unsaturated repacked sand

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Abstract

It is commonly assumed, *a priori*, that solute-transport experiments conducted in homogeneously repacked laboratory columns can be described by the advective-dispersive (AD), with the modification of a single-rate mobile-immobile (MIM) transport model. To investigate this, non-reactive transport through macroscopically homogeneous, repacked unsaturated sand was studied at two water contents using laboratory columns of diameter 11cm and lengths 10, 20 and 40cm. Non-Fickian behavior was found to dominate solute transport at this small scale, with long breakthrough curve (BTC) tailing persistent over the range of column lengths tested. Measured BTC tails could be well described by the single-rate MIM model at each depth.; However over the range of travel distances studied, BTC tailing was better explained by stochastic-convective (SC) transport, or continuous time random walk (CTRW). The SC model was applied using the probability density function of the BTC measured at 10cm to make predictions to subsequent depths. The spreading parameter (β) of CTRW model remained approximately constant across the range of both travel distances and water contents considered. It is concluded that the assumption of a single-rate MIM model cannot be made *a priori* for macroscopically homogeneous unsaturated sands. In this case, variability between replicates prevented identification of whether a SC transfer function or CTRW provided the best description of transport. These results demonstrate the variability in transport as a result of heterogeneities in column packing, even for macroscopically homogeneous sand, and emphasize the importance of studying transport over a range of travel distances in order to allow prediction of transport.

Introduction

To characterize solute transport through porous media, the rate of solute spreading with depth must be determined. For repacked, laboratory columns of macroscopically homogeneous media, it is generally assumed that transport is well described by an advective-dispersive (AD) process, with a single-rate mobile-immobile (MIM) model to better handle local, pore-scale heterogeneities. These models of transport have often been assumed *a priori*, without verification across a range of travel distances, and used in subsequent laboratory experiments to determine reactive transport parameters (e.g. Hoffman and Rolston 1980, Gaston and Selim 1990, Spurlock et al. 1995, Kookana and Naidu 1998). For systems of greater complexity, such as intact columns and field soils, application of the AD -MIM model has often been shown to result in a scale effect (e.g. Khan and Jury 1990, Ellsworth et al. 1996). To model such preferential transport, a stochastic-convective (SC) model may be appropriate, with the assumption that solutes move through isolated streamtubes with negligible lateral mixing. This is commonly referred to as channeling, or preferential flow. While the importance of considering several travel distances in order to determine the appropriate model of transport has been demonstrated (Jury and Roth 1990) this is frequently neglected, thereby constituting a limitation to interpretation of many studies of solute transport.

For heterogeneous soils, a number of alternative models exist. These attempt to capture the effects of heterogeneity on break through curves (BTC). Multiple-rate MIM models have been proposed as a means of accounting for multiple, simultaneous mass transfer processes, such as slow diffusion into and from immobile zones of a range of sizes, and rate-limited sorption (Haggerty and Gorelick 1995, 1998, Haggerty et al. 2000). In this work, “MIM” is used to denote the single-rate mobile-immobile model (van Genuchten and Wierenga 1976), and “multiple-rate MIM” to denote the recent extensions of the MIM model which are capable of accounting for multiple mass-transfer processes. The continuous time random walk (CTRW) model (Montroll and Weiss 1965, Scher and Lax 1973, Berkowitz et al. 2000, Berkowitz et al. 2001, Berkowitz and Scher 2001) also has the potential to simulate a range of transport behaviors. CTRW models transport as a series of particle jumps, which removes the assumption of characteristic time and/or space scales of particle motion. The joint density of particle motion size and duration is arbitrary and specified by the modeler. The CTRW model is able to encompass the AD representation, for both single-rate and multiple-rate MIM transport models (Dentz and Berkowitz 2003). We sought to assess solute transport in repacked sands and to evaluate the nature of the transport by predicting breakthrough curves at column lengths of 20 and 40 cm based on model parameters that were determined at a column length of 10 cm for a number of well-established models.

Theory

Details of the models used can be found in Bromly and Hinz (2004) (not in references). Here we only describe the features of the continuous time random walk. The CTRW visualizes solute transport as a series of particle jumps or transitions, and allows for waiting between jumps. Various transport processes may be explained by using a broad distribution of particle waiting times and modeled as a continuous time random walk (CTRW) process (Berkowitz and Scher 1995, 1998, Berkowitz et al. 2001, Kosakowski et al. 2001). The joint probability density function $\psi(\mathbf{s},t)$ describes each particle transition over a distance and direction $\mathbf{s}$ in time t, with a power-law tail for $\psi(\mathbf{s},t)$ at large time. Particle migration is coupled in time and space, thus accounting for particle transitions that extend over short and long distances, and short and long times (Levy and Berkowitz 2003). Whereas the AD and SC models assume complete and zero lateral mixing respectively, CTRW allows for any degree of mixing between these extremes.

Using the model and notation of Berkowitz and Scher (1995), the fitted parameter β characterizes the dispersion behavior (Berkowitz et al. 2001). The case $0< \beta <1$ describes dispersion during transport where both the mean position and size (related to velocity and dispersion, respectively) of the solute plume are scaled as a power law with time. This is described by the first passage time distribution (FPTD)

$$FPTD = -\frac{1}{\pi\tau}\sum_{j=0}^{\infty}(-x)^j \sin(\pi j\beta)\frac{\Gamma(j\beta+1)}{\Gamma(j+1)} \text{ with } x = b/\tau^{\beta}\ ,\ b = b_{\beta}L/\langle l\rangle \qquad 1$$

where β characterizes dispersion, x_{shift} [T] describes the mean effective time for tracer particles to reach distance L, τ is dimensionless time, $<l>$ is the average length of a single particle transition and b_{β} is a dimensionless constant. When $1 < \beta < 2$ the plume velocity is constant in time, while the standard deviation retains power-law scaling. This is given by

$$FPTD = -\frac{1}{\pi\beta\langle t\rangle b^{1/\beta}}\sum_{j=0}^{\infty}(-h)^j \frac{\Gamma((j+1)/\beta)}{\Gamma(j+1)}\sin\frac{\pi(j+1)}{\beta} \qquad 2$$

with $h = (1-\tau)/b^{1/\beta}\ ,\ b = lb_{\beta}\ ,\ l = L/\langle l\rangle\ , b_{\beta} = c_{\beta}/\langle t\rangle^{\beta}$

where t_{mean} is related to mean residence time, c_{β} and b_{β} are dimensionless constants, and $<t>$ is the mean transition time for $<l>$. The case of $\beta >2$ corresponds to Fickian transport.

It has recently been shown that for multi-rate, or power-law waiting times, CTRW models are equivalent to MIM representations (Dentz and Berkowitz 2003, Schumer et al. 2003), when the transition length and time distribution density decouple (Dentz and Berkowitz 2003). Both the multi-rate MIM and CTRW models can simulate the density of waiting times that are observed. The former builds a density through a linear combination of exponentials (see Haggerty et al., (2000)) The latter empirically employs a user-defined density, for example a Levy-type density of waiting times. The single-rate MIM model is a subset of the CTRW model.

Methods and Materials

Miscible displacement experiments were carried out by Grasser and Sitta (1993). For completeness, experimental details are summarized here. Laboratory studies were conducted in plexiglass columns of 10, 20 and 40cm length, with internal diameter 11cm. A medium sand was used, with 1% of particles less than 0.1mm, 17% in the range 0.1-0.315mm, 38% 0.315-0.5mm, 36% 0.5-0.71mm, and 8% larger than 0.71mm. Columns were packed incrementally using a tube to deliver the sand for packing, using the sequence of sieves described by Stauffer and Dracos (1986). Vertical Columns were supported by porous plates at their bases in order to apply suction. The sand was kept unsaturated under unit gradient using tensiometers as described by Koch and Flühler (1994).

A rotating irrigation head was used at the top of the column to deliver the background and pulse solutions across the column area. The columns consisted of two halves, allowing excavation and the study of longitudinal cross-sections of the sand after the BTC experiments, in order to check that the packing was sufficiently homogeneous to create a homogeneous flow field. Dye (Brilliant Blue FCF, color index

42090) was injected into the soil column either across the column area or by syringe at the column centre at the top.

For each column length, experiments were performed at two water contents, as described in Table 1The suffixes *a* and *b* in Runs 5.3 and 6.2 denote replicates of the same experiment; in all other cases the column was re-packed for each run. Two different lissamine FF (color index 56205) concentrations were used, 1 and 3*g/L*, as shown in Table 1. Absorbance measurement was calibrated to concentration by $A = 12.79\ C + 0.04$.

Each of the models considered was fitted to the measured data and used to investigate the parameter dependence on depth and water content, providing an indication of the applicability of the model. Secondly, the averaged fitted parameters for the 10cm columns were used to predict the first BTC measured for both a 20 and 40cm columns (i.e. Runs 6.1 and 7.1).. Further detail can be found in Bromly and Hinz (2004).

Table 1. Experimental setup and mass balances of measured BTCs

Run	Length cm	q cm.min^{-1}	v cm.min^{-1}	θ -	Pulselength s	Pulse conc gL^{-1}	Mass balance -	First moment min	Variance* min^{2}
5.1	10	0.042	0.186	0.24	140	3	0.89	63.78	686.93
5.2	10	0.048	0.204	0.24	126	3	0.89	62.69	354.57
5.3a	10	0.042	0.174	0.23	157	1	0.97	68.16	460.72
5.3b	10	0.042	0.174	0.23	157	1	0.93	67.38	496.28
6.1	20	0.042	0.228	0.20	143	3	0.96	110.72	1469.07
6.2a	20	0.042	0.210	0.21	141	3	0.91	126.14	4229.14
6.2b	20	0.042	0.216	0.21	142	3	0.97	119.23	2054.50
7.1	40	0.042	0.228	0.18	107	3	0.92	232.47	5369.49
7.2	40	0.048	0.270	0.18	128	3	1.09	216.56	7579.43
10.1	10	0.186	0.588	0.32	20	3	1.04	21.53	103.29
11.1	20	0.180	0.600	0.30	28	3	1.07	38.16	105.41
11.2	20	0.180	0.606	0.30	24	3	0.83	41.19	110.46
12.1	40	0.186	0.690	0.27	24	3	0.84	80.36	448.19
12.2	40	0.180	0.636	0.28	28	3	0.98	70.37	- *

q [cm.min^{-1}]: flowrate, *v* [cm.min^{-1}]: pore water velocity; θ [-]: water content

[*] missing value due to inadequate measurement of BTC tail

[*] variance: centered second temporal moment

Results and Discussion

Figure 1 shows the measured BTC for Run 5.1, fitted to the AD, MIM, CLT and CTRW models. The MIM and CTRW models provide fits to the data significantly better to those of the AD and CLT models. The first and centered second temporal moments for each BTC are shown in Table 1. From this it is seen that the AD centered second temporal moment does not increase linearly with travel distance, as would be expected asymptotically for AD transport, providing a model-independent indication of non-Fickian transport. It is noted that there is a large degree of variability between the BTCs obtained from columns of the same length, as seen considering the first and centered second temporal moments for the measured BTCs (Table 1). This will have implications for predictions from one depth to another, as discussed later.

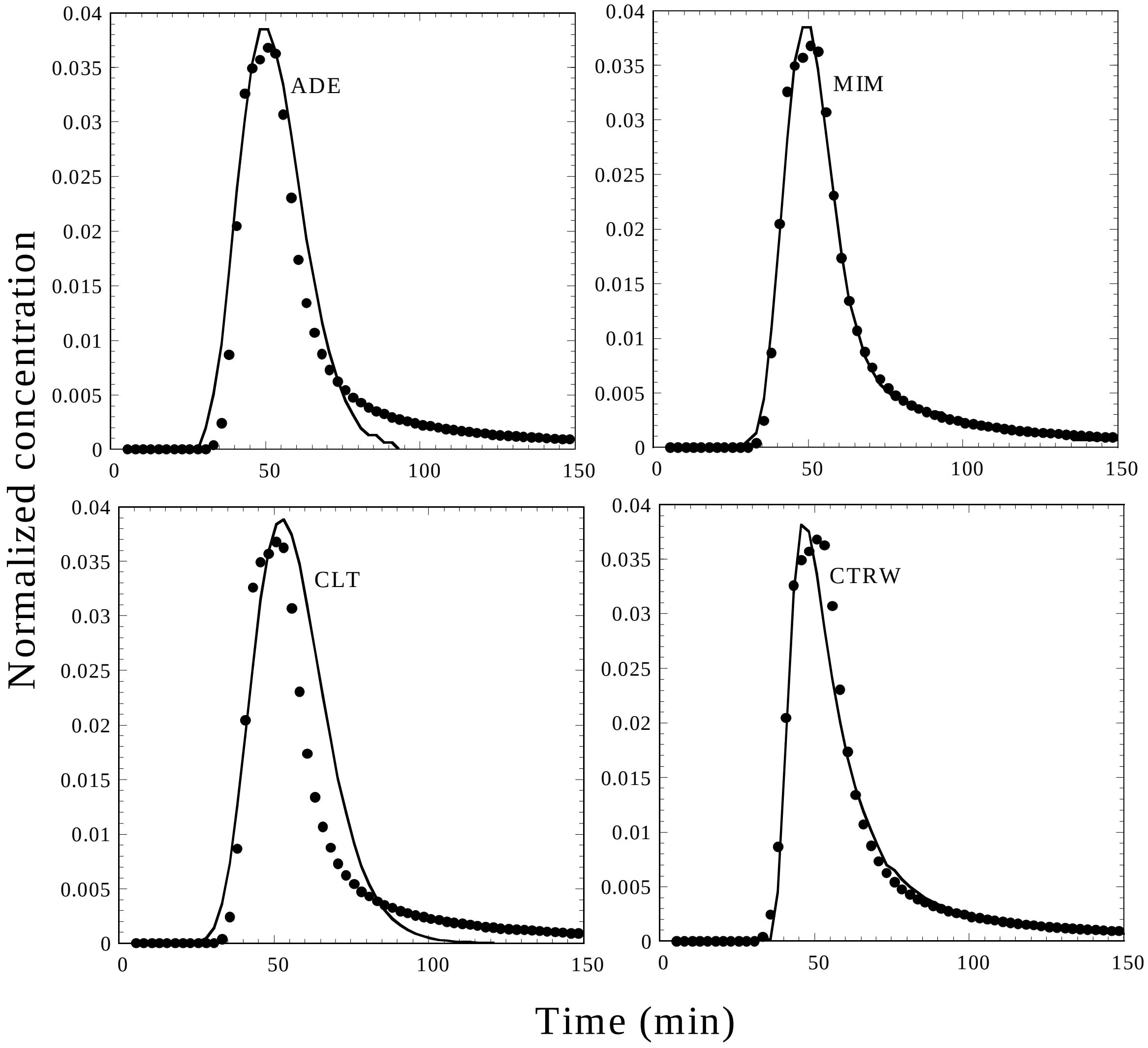

Figure 1. Measured 10cm column BTC (Run 5.1) fit to the AD, MIM, CLT and CTRW models

Details of AD, MIM and SC models fits and results can be found in Bromly and Hinz (2004). The CTRW model was fit to the data for both ranges $0 < \beta < 1$ and $1 < \beta < 2$, however β values $1 < \beta < 2$ were not able to fit the long tails of these distributions. For the range $0 < \beta < 1$ an example of the fitting of the CTRW model to the data is shown Figure 1 (for Run 5.1). The x_{shift} parameter varies with both column length and water content. From the values obtained, it cannot be conclusively determined whether β is independent of water content, or has decreased slightly with water content. The fitted β values, being $0 < \beta < 1$, are indicative of highly anomalous transport, with the concentration peak moving more slowly than for Fickian transport and a longer forward advance of particles (Kosakowski et al. 2001). This indicates multiple timescales of transport, consistent with the recent literature review and experiments by Haggerty et al. (2004).

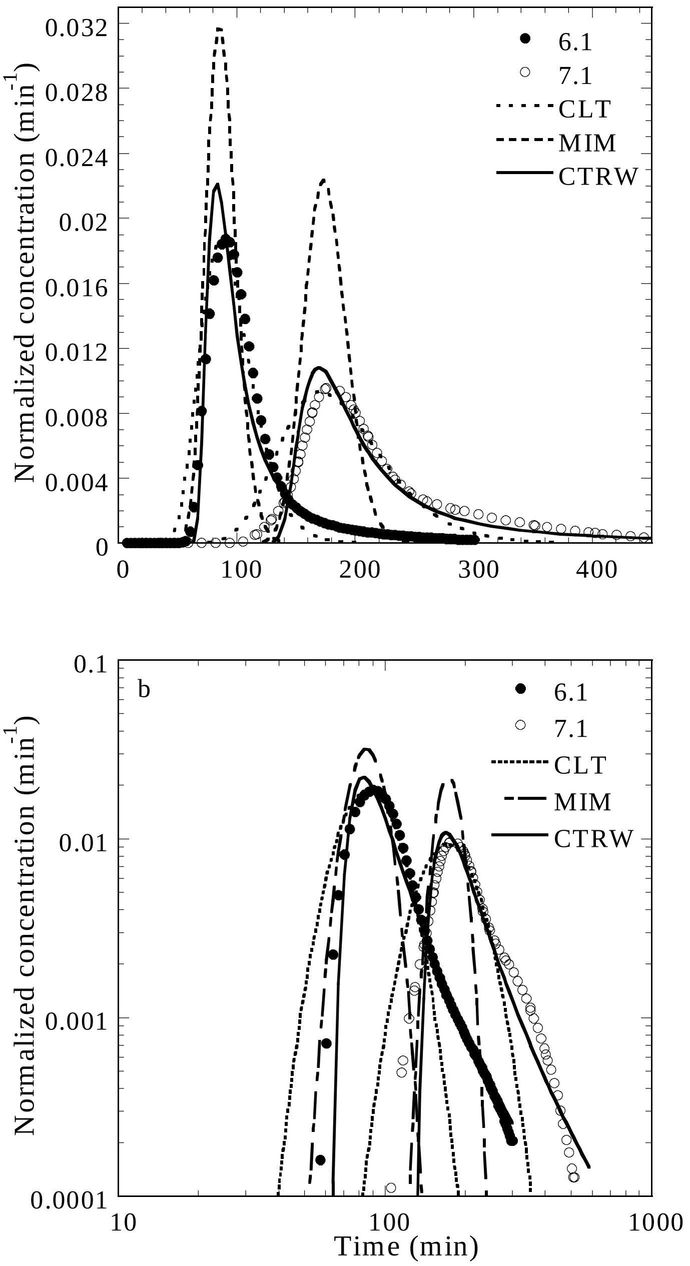

Figure 2. Measured low-water content 20cm column (Run 6.1) and 40cm column (Run 7.1) BTCs, and predicted BTCs using averaged 10cm low-water content column parameters for CLT, MIM and CTRW models (a) linear axes, (b) log-log axes.

Plotting the fitted x_{shift} values as a function of $L^{1/\beta}/v$, gives the line of best fit

$$x_{shift} = 0.943\left(\frac{L^{1/\beta}}{v}\right) \tag{3}$$

across both water contents, with correlation coefficient $r^2 = 0.986$. Taking the average β value across all runs for both water contents ($\overline{\beta} = 0.903$, SE = 0.0053), Equation 3 was used to predict x_{shift} given the column length and experimental velocity. BTCs predicted at the lower water contents (Runs 6.1 and 7.1) are shown in Figure 2 These plots demonstrate that the CTRW predictions capture both the evolution of the plume with distance, and tailing of the BTC.

In visualizing solute transport as a series of particle jumps (Section 2), it appears that a single-rate description with exponential waiting times, as provided by the MIM, is unsuitable. Instead, the greater flexibility of the CTRW model, allowing multiple rates of transport with a power-law tail of waiting times, provides an adequate description of the observed transport.

To compare the SC and CTRW models, the CTRW software was used to predict the first measured BTC in the 20 and 40cm columns (Runs 6.1 and 7.1) using each of the measured BTCs from 10cm. As was done for the SC model predictions, BTCs were scaled for mass balance to remove the area normalization used in the earlier predictions.

Conclusions

Unsaturated laboratory column experiments were conducted through macroscopically homogeneous sand at two different water contents in columns of diameter 11cm. The columns were of lengths 10, 20 and 40cm. Measured breakthrough curves (BTCs) were highly asymmetric, with long BTC tailing persistent over the range of column lengths tested. Solute transport was shown to be non-Fickian, with little lateral solute mixing during transport. Transport through unsaturated homogeneous media has previously been attributed to single-rate mobile-immobile transport using the MIM; however these findings suggest that this transport model should not be assumed *a priori*.

The stochastic-convective (SC) model without parameterization was shown to provide good predictions of transport using BTCs obtained from the 10cm columns as probability density functions for extrapolation of transport to 20 and 40cm. Similarly, predictions using the continuous time random walk model (CTRW) showed a high correspondence with measured BTCs. The CTRW spreading parameter β was essentially independent of water content and travel distance for the experimental parameters tested, indicating that further investigation of this model is warranted for a greater range of transport conditions. It was not possible to identify whether the CTRW or SC model provides a better description of the observed solute transport. The variability between runs, following re-packing of the same column, did not allow for discrimination between these models. This emphasizes the importance of column packing in influencing the derived parameters of solute transport. It therefore remains unclear whether there is a significant immobile water fraction during transport in this soil, as implied by the CTRW model, or whether the simple ‘black box’ approach of the SC transfer function provides an adequate description of transport. The major implications of this work are that (a) small variations in column packing, even in macroscopically homogeneous media, may have a significant impact on the resulting solute transport regime, (b) *a priori* assumption of a solute transport model or mechanism may not be possible, and should not be made, without investigation of the transport across a range of distances, and (c) caution should be exercised in investigating relationships between the model parameters and soil physical properties, particularly when transport is measured at one depth.

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