

Nonreactive chemical transport in structured soil: The potential for centrifugal modelling

L. Li & D.A. Barry

Centre for Water Research and Department of Civil and Environmental Engineering, University of Western Australia, Nedlands, W.A., Australia

P.J. Hensley

Department of Civil and Environmental Engineering, University of Western Australia, Nedlands, W.A., Australia

K. Bajracharya

Centre for Water Research, Australia

ABSTRACT: Centrifugal model scaling of chemical transport in soils is carried out by identifying the dimensionless transport equations of the model and prototype. The possibility of centrifugal modelling of nonreactive chemical transport with nonequilibrium physical sorption is discussed. It is demonstrated that, with suitable scaling of the sorption rate, centrifugal modelling is feasible in theory. Results from laboratory experiments indicate that the required scaling is achieved, suggesting that this transport process may be modelled approximately using a centrifuge.

1 INTRODUCTION

Geotechnical centrifuges have been used to model nonreactive chemical transport in soil, as reported, for example, by Cooke and Mitchell (1991) and Hensley and Schofield (1991). It has been shown also that chemical transport with linear equilibrium sorption in soils can be successfully modelled by a centrifuge (Celorie et al., 1989). This type of modelling is possible due to similarity between a prototype soil mass under the earth's gravity and a model soil mass in a small, $1/N$ (notation is collected at the end of the paper), length scale model, experiencing a centrifugal force of Ng (Fig. 1). In Fig. 1, we see that the soil prototype length (L) is reduced by a factor of $1/N$ in the model. The rotation of the centrifuge with angular velocity, w , produces the centrifugal acceleration: $Ng = rw^2$, where r is the rotation radius. If the product of depth times acceleration is the same in the model and the corresponding prototype, the stress distribution in the model soil will be geometrically similar to that of the prototype soil. Further, similarity of chemical transport between centrifugal model soils and prototype soils can be achieved as long as the grain Peclet number is controlled in the model (Hensley, 1987).

As a result of the increase in acceleration imposed by the centrifuge, the seepage velocity will increase by N times, i.e., $V_m = NV_p$. This relationship gives the velocity scaling. The

length scale is also known, i.e., $L_m = L_p/N$. The time scale for the fluid flow in the model is then $t_m = L_m/V_m = N^2L_p/V_p = N^2t_p$. This time scale therefore applies to any passive tracer moving with the soil water. However, it doesn't necessarily follow that this is the time scale for any time-dependant chemical reactions that are taking place, since the chemical transport process in soils is not wholly an advective process.

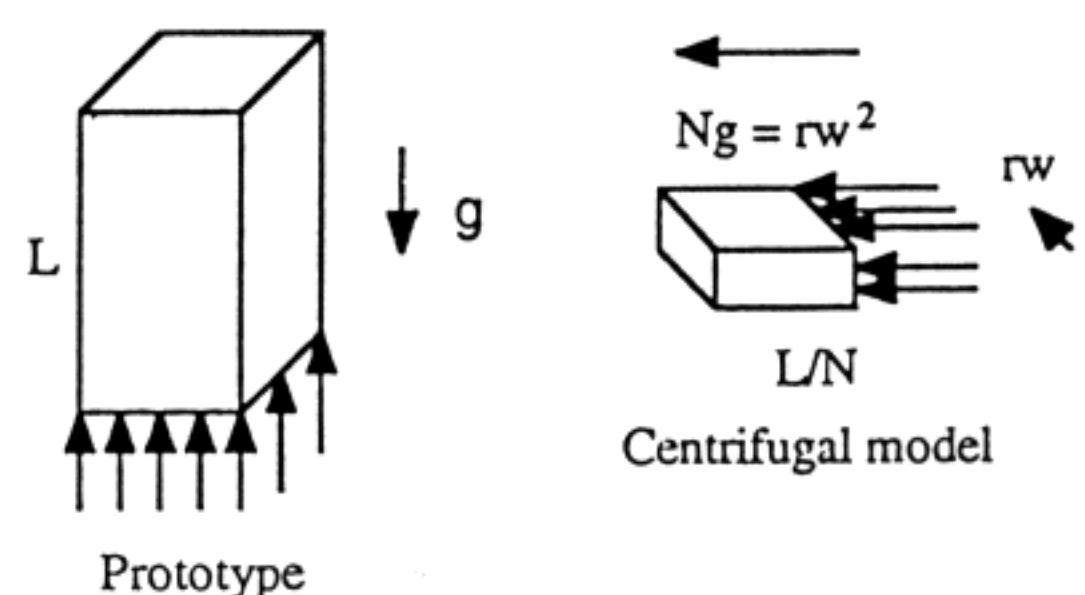


Fig. 1. Centrifugal model and prototype (after Schofield, 1980).

1.1 Scaling for Equilibrium Sorption

The governing equations describing chemical transport in the model and prototype soils with linear equilibrium sorption (without solute decay or sink terms; the LEA model) are, in dimensionless form (e.g., van Genuchten and

Alves, 1982):

$$R_m \frac{\partial C_m^*}{\partial T} = \frac{1}{P_m} \frac{\partial^2 C_m^*}{\partial X^2} - \frac{\partial C_m^*}{\partial X}; T = \frac{t_m V_m}{L_m}, X = \frac{x_m}{L_m} \tag{1a}$$

and

$$R_p \frac{\partial C_p^*}{\partial T} = \frac{1}{P_p} \frac{\partial^2 C_p^*}{\partial X^2} - \frac{\partial C_p^*}{\partial X}; T = \frac{t_p V_p}{L_p}, X = \frac{x_p}{L_p} \tag{1b}$$

where $P (= VL/D)$ is the column Peclet number and $C^* = C/C_0$ (see notation list).

Observe that by writing the governing transport equations for the model and prototype in dimensionless form, it is clear that similarity exists in the space and time scales. Hensley (1987), amongst others, has shown that, in the absence of reactions, scaling between model and prototype is achieved if the grain Peclet number is suitably small, e.g., smaller than 1. Thus, the transport process in each situation will be similar if the retardation factor, R , is identical in model and prototype. If the initial and boundary conditions for both equations are the same then their solutions are identical, i.e., $C_m^*(T,X) = C_p^*(T,X)$; or, in dimensional form, $C_m(t_m,x_m) = C_p(t_p,x_p)$, where $x_m = x_p/N$ and $t_m = t_p/N^2$.

These results can be summarised as shown in Table 1. The entries in the table show the scalings necessary for similarity between model and prototype for transport with instantaneous reactions (Arulanandan et al., 1984).

Table 1. Scaling for time-independent reactions

Model	Prototype
$g^* = Ng$	g
$X_m = X_p/N$	X_p
$t_m = N^2/t_p$	t_p

1.2 Scaling for Nonequilibrium Sorption

Many experiments (e.g., Brusseau and Rao, 1989) have shown that the assumption of equilibrium sorption is not always satisfied. Indeed, Barrow (1989) suggested that the occurrence of equilibrium sorption is relatively infrequent in natural soils. Time-dependant sorption is sometimes called nonequilibrium sorption. It is therefore of considerable

practical interest to investigate centrifugal modelling of chemical transport with nonequilibrium sorption. Nonequilibrium sorption can be the result of either chemical or physical phenomena. In this paper, the possibility of centrifugal modelling of nonreactive chemical transport coupled with the latter case, i.e., physical nonequilibrium sorption, will be analysed theoretically. The results of analysis are then compared with laboratory experimental data.

2 THEORY

2.1 Nonreactive chemical transport with physical nonequilibrium sorption in soils: The two-region model

A common model including physical nonequilibrium sorption is that based on a two-region soil structure. This is the NEA model, and is usually assumed to operate in aggregated soils where it is supposed that there are large pores between aggregates and small pores within aggregates. Water in the small pore region is considered to be stagnant. Basically, the chemical transport process in such soils can be thought to consist of longitudinal (in the mean flow direction) and lateral transport. Longitudinal transport, which takes place in the large pore (or mobile) region, is due to advection and dispersion. Lateral transport is due to inter-region transport between the mobile and immobile (small pore) regions. This is clearly a time-dependant process, so-called physical nonequilibrium sorption (De Smedt and Wierenga, 1979).

The following model describes nonreactive chemical transport with physical nonequilibrium sorption (Coats and Smith, 1964):

$$\theta_1 \frac{\partial C_1}{\partial t} + \theta_2 \frac{\partial C_2}{\partial t} = \theta_1 D \frac{\partial^2 C_1}{\partial x^2} - \theta_1 V \frac{\partial C_1}{\partial x} \tag{2a}$$

$$\theta_2 \frac{\partial C_2}{\partial t} = \alpha (C_1 - C_2) \tag{2b}$$

In dimensionless form, these equations can be written as (Parker and van Genuchten, 1984):

$$\frac{\partial C_1^*}{\partial T} + \frac{(1-\beta)}{\beta} \frac{\partial C_2^*}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1^*}{\partial X^2} - \frac{\partial C_1^*}{\partial X} \tag{3a}$$

$$\frac{(1-\beta)}{\beta} \frac{\partial C_2^*}{\partial T} = \omega(C_1^* - C_2^*) \quad (3b)$$

$$\text{where } \omega = \frac{\alpha L}{V\theta_1}, \beta = \frac{\theta_1}{\theta_1 + \theta_2}, T = \frac{tV}{L}, X = \frac{x}{L}$$

$$P = \frac{VL}{D} \text{ and } C^* = C/C_0.$$

2.2 Centrifugal modelling and scaling

We use the same modelling approach as was used in the case of the equilibrium sorption process. The length and acceleration scales remain unchanged, i.e., $L_m = L_p/N$, $g^* = Ng$. For the model, we have:

$$\frac{\partial C_{1m}^*}{\partial T} + \frac{(1-\beta_m)}{\beta_m} \frac{\partial C_{2m}^*}{\partial T} = \frac{1}{P_m} \frac{\partial^2 C_{1m}^*}{\partial X^2} - \frac{\partial C_{1m}^*}{\partial X} \quad (4a)$$

with

$$\frac{(1-\beta_m)}{\beta_m} \frac{\partial C_{2m}^*}{\partial T} = \omega_m(C_{1m}^* - C_{2m}^*) \quad (4b)$$

while, for the prototype, the corresponding equations are

$$\frac{\partial C_{1p}^*}{\partial T} + \frac{(1-\beta_p)}{\beta_p} \frac{\partial C_{2p}^*}{\partial T} = \frac{1}{P_p} \frac{\partial^2 C_{1p}^*}{\partial X^2} - \frac{\partial C_{1p}^*}{\partial X} \quad (5a)$$

and

$$\frac{(1-\beta_p)}{\beta_p} \frac{\partial C_{2p}^*}{\partial T} = \omega_p(C_{1p}^* - C_{2p}^*) \quad (5b)$$

Given that the grain Peclet number is small, as mentioned above, then (4) and (5) are identical if $\beta_m = \beta_p$ and $\omega_m = \omega_p$. In other words, these conditions must be satisfied for exact centrifugal modelling of nonreactive chemical transport with physical nonequilibrium. If this is the case, the centrifuge test results are directly transferable to the prototype, i.e., in dimensional form,

$$C_m(t_m, x_m) = C_p(t_p, x_p)$$

where $x_m = x_p/N$ and $t_m = t_p/N^2$. It is, not surprisingly, the same scaling as we have for equilibrium process.

Let us look more closely at the implication of the equality of (4) and (5). For the same soil it is clear that β will be identical in model and prototype. The condition of $\omega_m = \omega_p$ requires that the inter-region transfer rate (α) in the model increases by a factor of N^2 . Thus,

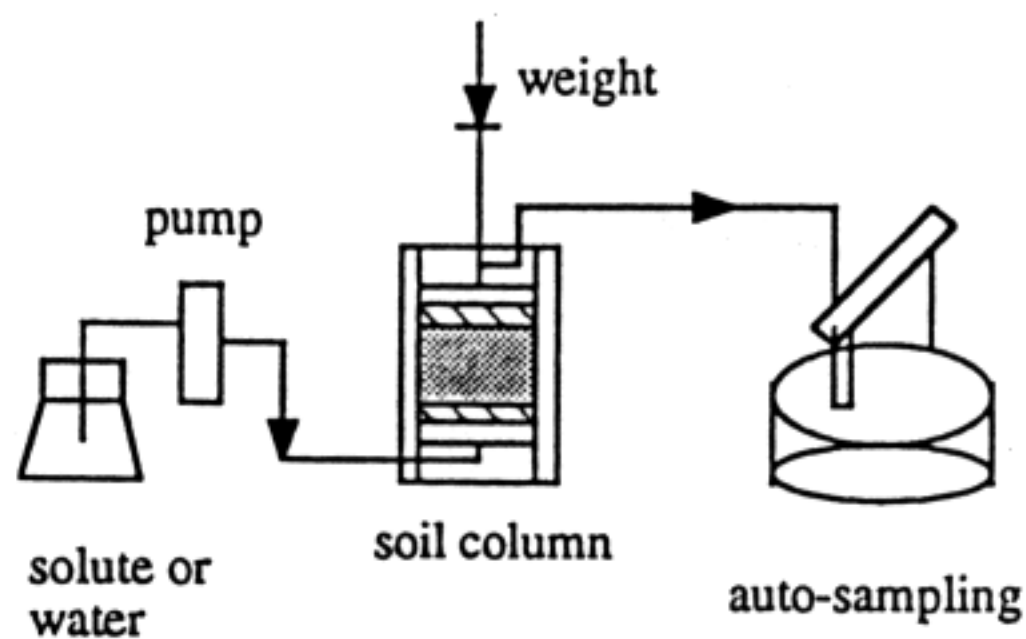


Fig. 2. Laboratory experimental apparatus.

modelling is dependant on the scaling of α , i.e., if the scale of α , $N_\alpha (= \alpha_m/\alpha_p)$, equals to N^2 , modelling is possible. It is yet to be determined whether this condition will hold, since the change of α is dependent on the inter-region transport process, the details of which are not well understood.

At the heart of the question of whether physical nonequilibrium sorption can be modelled is the variation of α as V changes, i.e., $N_\alpha = N_V^2$ ($N_V = V_m/V_p = N$ in the model) is required for centrifugal modelling. We report below on an experiment that was carried out to investigate directly changes of α with V .

3 EXPERIMENT

3.1 Apparatus

The main components of the apparatus consisted of a plastic column shell, a pump and an auto-sampling instrument as shown schematically in Fig. 2.

In all experiments, the flow direction is upward in the soil column. Each sample was consolidated prior to starting the flow. The flux through the soil was controlled by a peristaltic pump.

3.2 Simulation of the two regions in the soil column

Cylinders made of a fine porous polyethylene material (Diameter 13.5 mm \times Length 10 mm cylinders) were used to simulate the two-region soil structure. This material was mixed with silt in predetermined proportions, p_r (the volume of polyethylene to the whole volume, the column's size is Diameter 139 mm \times

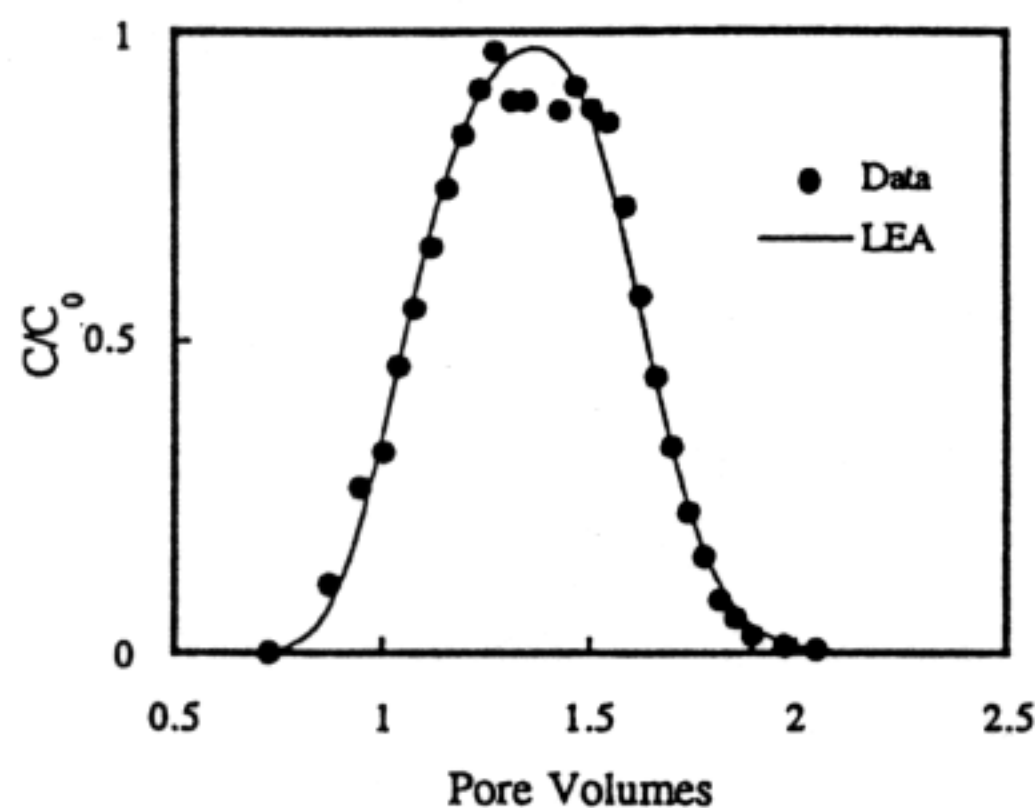


Fig. 3. Breakthrough curve for experiment 1 ($p_r = 0$).

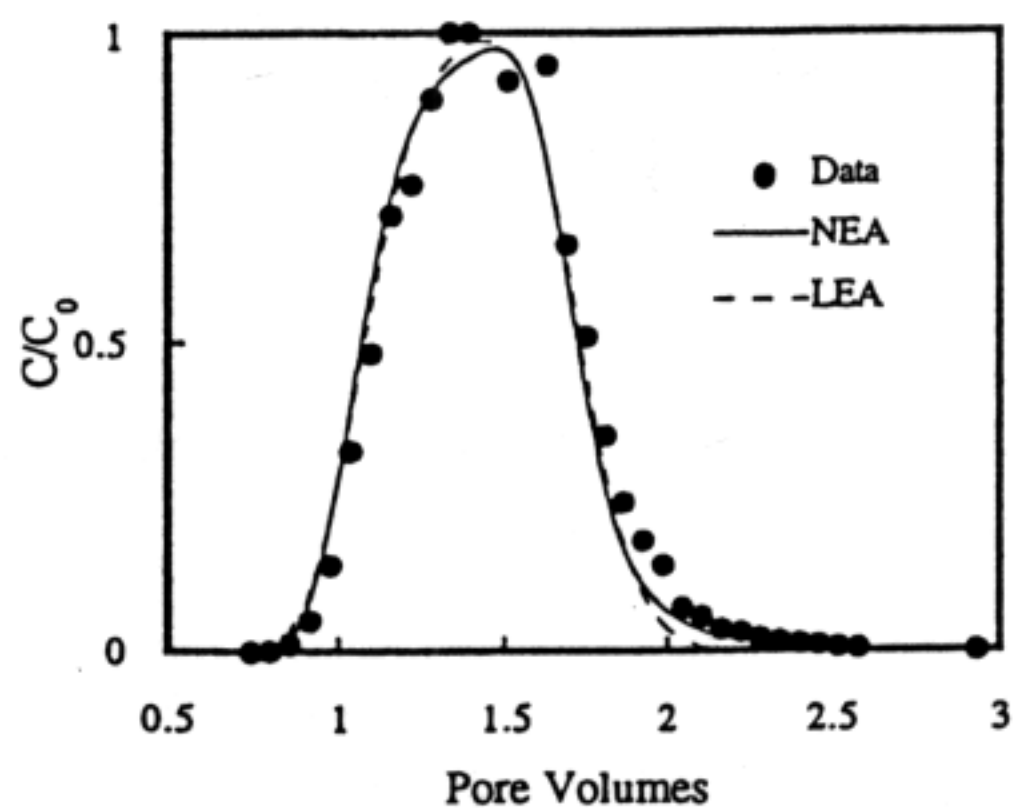


Fig. 4. Breakthrough curve for experiment 2 ($p_r = 0.056$).

Length 55 mm). Sodium Chloride was used as the nonreactive chemical tracer. Tests with three proportions of polyethylene ($p_r = 0, 0.056, 0.177$) were carried out. The columns were initially saturated with solute-free water, followed by a pulse of solute. The experimental data were fitted to the appropriate solution of (3) using the fitting package from Parker and van Genuchten (1984). The parameters obtained by fitting are listed in Table 2, while the breakthrough (BTC) curves for experiments 1, 2 and 3a are shown in Figs. 3 - 5 (other fits are similarly good).

The parameters values for experiment 1 are given by the simulation of the LEA model [linear equilibrium model with $R = 1$, see (1)]. For experiments 2 and 3a, we used both the LEA and NEA [nonequilibrium model, see (3)] models to simulate the experimental data (Figs. 3 - 5). The values listed in Table 2 for experiment 1 were obtained by unconstrained fitting of the model parameters. In experiments 2 and 3a the appropriate pore water velocity was obtained using $V = V_1/\beta$ (V_1 is the velocity for experiment 1). The other parameters for experiments 2 and 3a were obtained by fitting. In the curve fitting for Experiments 3b-e, we changed the velocity according to the change of flux, and fixed D and β .

The simulation results clearly showed that, with increasing p_r , the NEA model was more appropriate. The values of β are reasonably correlated with p_r , as shown in Table 2, which suggests that this polyethylene-silt mixture can simulate the two-region soil structure quite well.

With the last column ($p_r = 0.177$), the experiment was repeated with five different velocities. We investigated the change of α with V by plotting the experimental (α, V) data and the pairs (α, V) necessary for exact similarity. For this purpose, we used the point (α_a, V_a) of experiment 3a as the reference point (α_{ref}, V_{ref}) ; then we calculated the pairs $(\alpha_{si}, V_i; i = b, c, d, e)$ for experiments 3b-e as follows: $\alpha_{si} = N_\alpha \alpha_{ref} = N_V^2 \alpha_{ref} = (V_i/V_{ref})^2 \alpha_{ref}$. The results (Fig. 6) show that the experimental data are reasonably close to the computed points, which suggests that the scaling relationship, $N_\alpha = N_V^2$, can be achieved to some extent.

4 DISCUSSION

As a working hypothesis, we assume that solute transport with physical nonequilibrium sorption in soils is a two time-scale process. There is an advective time scale at which the solute travels through the soil, and a local, point time scale at which inter-region transport occurs. The advective time scale is of the order of L/V , whereas the local point time scale is of the order of $1/\alpha$. In the centrifugal model, the advective time scale is shortened by a factor of N^2 . If the local point time scale is also shortened by N^2 times (which requires $N_\alpha = N^2$, or $\alpha_m = N^2 \alpha_p$), then the chemical transport time scale will change to the same degree, i.e., $t_m = t_p/N^2$. Because L/V can be controlled, the possibility of centrifugal modelling is thus dependant on how the inter-region transport behaves under fluid velocity changes.

There exist three main factors which

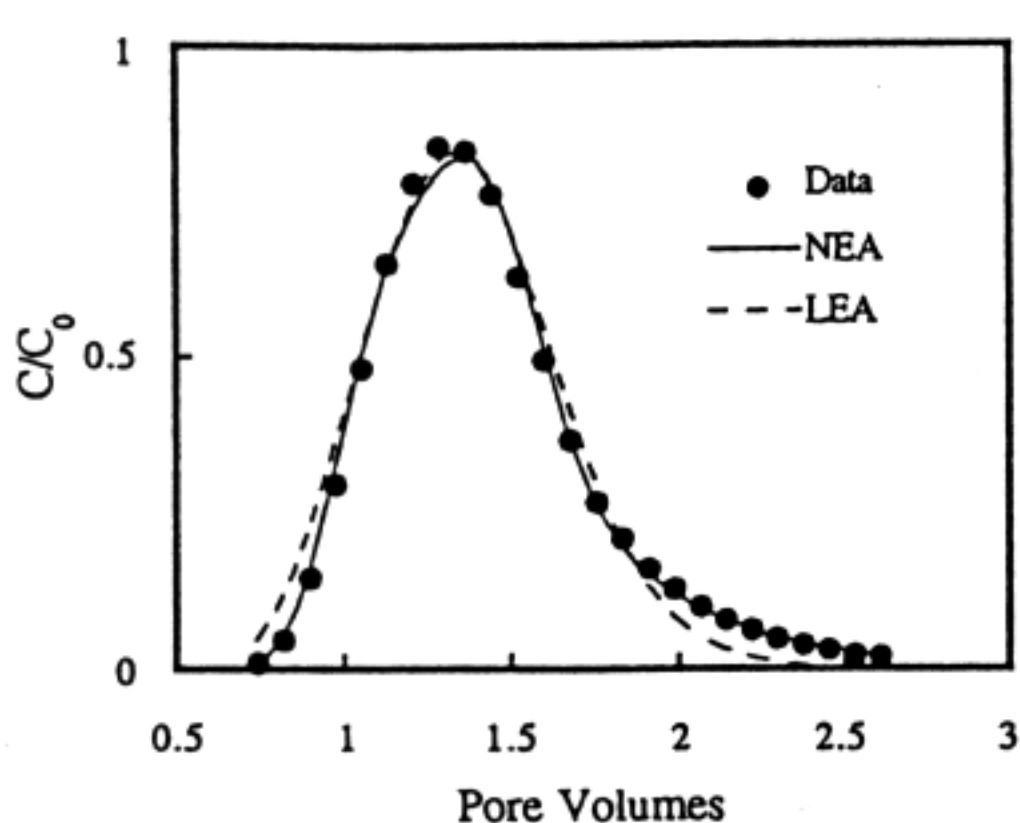


Fig. 5. Breakthrough curve for experiment 3a ($p_r = 0.177$).

influence the inter-region transport process: solute diffusion, local velocity variations between the regions, and the relative surface area of the immobile region. The relevant parameters are therefore D , the diffusion coefficient, V , characterising the velocity variations, and ϕ , which is the surface area per unit volume of the aggregates.

These three parameters can be combined into the two dimensionless groups:

$$\frac{D\phi^2}{\alpha}, \frac{V^2}{D\alpha}$$

If the second group, $V^2/D\alpha$, remains constant as V is varied, i.e., if $\alpha \propto V^2/D$, then because D is constant, the inter-region transport rate is predominantly influenced by the factor of V^2 . The scale of α is related to the velocity scale by the equation: $N_\alpha = N_V^2$. In the centrifuge model, $N_V = N$, so $N_\alpha = N^2$, i.e., $\alpha_m = N^2\alpha_p$. In such cases centrifugal modelling is feasible.

In our experiments, the velocities ranged from 0.05 cm/min to 0.2 cm/min. The results in Fig. 6 show that $N_\alpha \approx N_V^2$, or, $\alpha \propto V^2/D$. This relationship accords with the dimensionless analysis, and suggests that centrifugal model can be used to simulate nonreactive solute transport with physical nonequilibrium sorption, at least in the range of flow rates tested.

In the centrifuge model, the flow rate is likely to be higher than those in our experiments. This, however, could just lead to velocity variations dominating the inter-region transport. In this situation, we suggest that the scaling relationship, $N_\alpha = N_V^2$, will still hold.

It is reasonable, on the other hand, to assume that when the velocity becomes very small,

Table 2. Simulation of the experiments

Experiment Number	V cm/min	D cm ² /min	β	$\alpha \times 100$ 1/min	P_r
1	0.0469	0.0038	1	0	0.00
2	0.0491	0.0039	0.954	0.051	0.056
3a	0.0536	0.0024	0.875	0.26	0.177
3b	0.0803	0.0024	0.875	0.50	0.177
3c	0.1071	0.0024	0.875	1.10	0.177
3d	0.1608	0.0024	0.875	1.92	0.177
3e	0.2144	0.0024	0.875	3.33	0.177

diffusion will be the dominant factor, and thus we lose the required local point time scaling for centrifugal modelling. Physically, this situation must occur eventually because in the limit of $V = 0$ there are obviously no velocity variations within the medium. In such cases, centrifugal model results cannot be scaled directly to the prototype. Further experiments need to be carried out to investigate scaling at both low and high flow rates.

Even in the flow rate range of our experiments, the scale number reached 4 (between experiments 3a and 3e). The change in time scale will then be $1/N^2 = 1/16$, which means that in the centrifuge model, we can replicate experiment 3a in 1/16 less time than it took initially. This significant change can speed up chemical transport investigation in soils, which can take an unacceptably long time in laboratory. However, the model is then 1/4 of the prototype length, which is not a large reduction in the length scale.

5 CONCLUSION

Exact centrifugal modelling of chemical transport with physical nonequilibrium in soils is predominantly dependant on whether the local inter-region transport time ($1/\alpha$) scales correctly. Two possibilities exist: First, if the inter-region transport is controlled mainly by local velocity variations, then the scaling between model and prototype is exact and modelling is feasible in theory; second, if the inter-region transport is controlled mainly by diffusion, then direct scaling of model results is not possible.

Our initial experimental results suggest that where the flow rate is not too low, the velocity variations are always the dominant factor

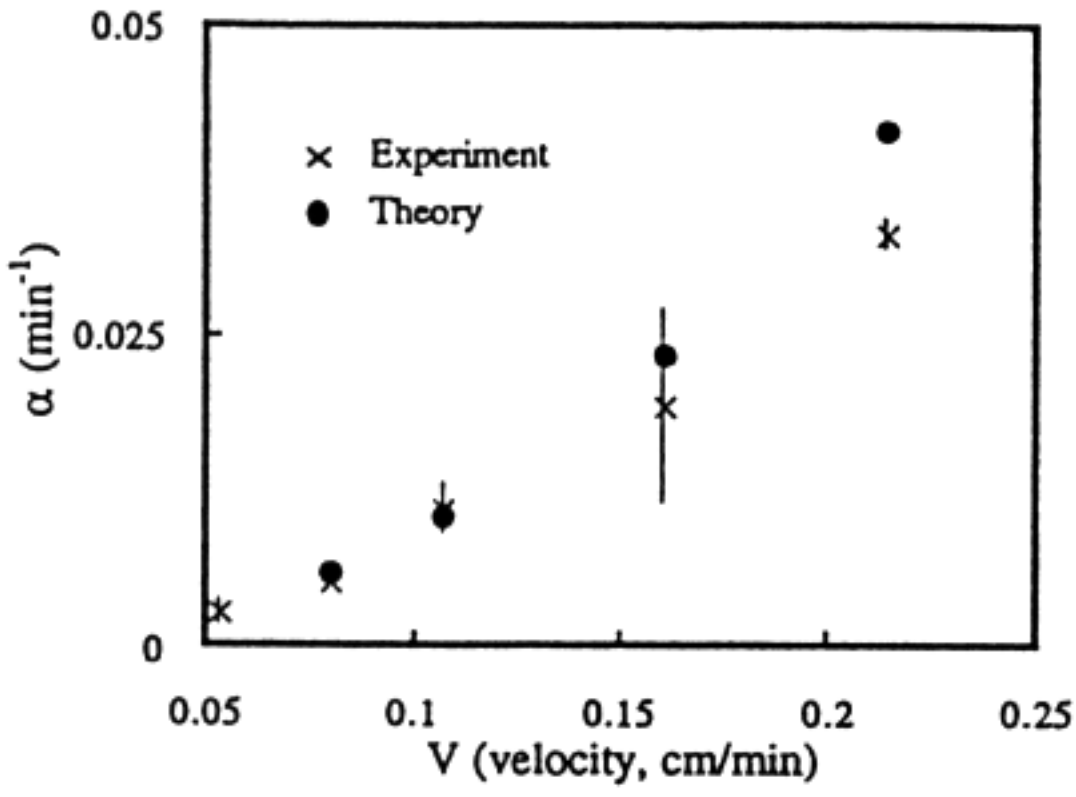


Fig. 6. Comparison between the experimental (x) and theoretical (•) results. The bars on each experimental datum are the 95% confidence intervals for the estimate.

affecting transport process. These findings indicate that centrifugal modelling may have application as a practical technique for predicting chemical transport with physical nonequilibrium sorption in soils.

NOTATION

C_1	mobile region solute concentration [ML ⁻³]
C_2	immobile region concentration [ML ⁻³]
C^*	dimensionless concentration, C/C_0
C_0	source concentration [ML ⁻³]
g	gravitational acceleration [LT ⁻²]
g^*	centrifugal acceleration, Ng [LT ⁻²]
L	length of soil column [L]
LEA	linear equilibrium model
m	model
N	scale factor
NEA	nonequilibrium model
p	prototype
p_r	proportion of polyethylene
P	column Peclet number
r	centrifuge radius [L]
R	retardation factor
t	time [T]
T	pore volumes, Vt/L
V	velocity [LT ⁻¹]
w	angular velocity [RadiansT ⁻¹]
x	distance [L]
X	dimensionless distance, x/L
θ_1	water content in mobile region
θ_2	water content in immobile region
β	ratio of mobile region to whole volume

α	inter region transport rate [T ⁻¹]
ω	dimensionless transport rate, $\alpha L/V\theta_1$
ϕ	surface area per volume of aggregate [L ⁻¹]

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