
SIMULATING THE 1-D BROMIDE TRANSPORT IN A DEFORMING STAGNO-VERTIC CAMBISOL UNDER MECHANICAL LOADING SEQUENCES

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Abstract

The tri-axial compression of a soil matrix under 1-D steady-state water (phase) flow conditions and the transport behavior of a conservative bromide tracer (component) under incremental mechanical stress was investigated. The momentum mass balance equations incorporated an Advection-Diffusion term and took into account the Dispersion coefficient $D$, changing porosity, $\Theta$, velocity $u$, of the non-compressible Newtonian pore fluid, the Mobility Index $MI$, and the parameters $\beta$ and $\omega$ of the solute transport in a deforming porous medium. Simulated results demonstrated that the longitudinal dispersivity $\delta_L$ and $MI$ of the single component was influenced by the magnitude of applied load. Statistical results also demonstrated that the influences of incremental mechanical loading on the bromide mobility index $MI$ and mass transfer terms $\alpha$ were significant with bromide mass recovery rates at 70%, 52% and 48% for 0, 10 and 40 kPa respectively.

Keywords: Mobility Index $MI$, longitudinal dispersivity, mass recovery, creep, mechanical load

Introduction

Simulating water flow or solute transport in soils has often involved perceiving the soil as a porous medium consisting of rigid incompressible solid particles randomly distributed and fixed in space. Under such circumstances, spatial and temporal functions have no considerations on water flow or solute transport and so the Darcy velocity of water flow or Dispersion coefficient of solute transport is entirely a function of the hydraulic gradient. However, particle rearrangement and reduction in pore space as effected by porous medium deformations can lead to unsteady and reduced solute transport velocities as in resin membranes (Mackie and Meares, 1955); as of large molecules in liquid filled
pores, (Deen 1987) and water flow as well as influence solute-solid matrix interactions as in the case of soft tissues or cells (Albro et al., 2007; Gu et al., 2004) or even induce active solute transport in smaller pores during dynamic loading (Albro et al., 2008). Strain induced alterations may influence permeability and diffusivity as in articular cartilages (Quinn et al., 2001; Mansour and Mow, 1976; Quinn et al., 2000; Gu et al., 2003). Some examples of the effects of deforming porous medium on solute transport include those through a clay liner during waste-filling operations (Smith, 2000) and solute transport in cartilage under mechanical load (Zhang and Szeri, 2005). (Smith, 2000) derived a one-dimensional theory of contaminant migration based on a small strain analysis of a consolidating soil, while (Peters and Smith, 2000) extended the previous model of (Smith, 2000) for transient solute transport within a deformable porous medium for both small and large deformations.

The overall objective of this study was to determine the effects of incremental mechanical load or stress on the transport behavior of a conservative bromide tracer. Specifically, the objective was to quantify and qualify compaction of a stagno-vertic Cambisol and how this impacted on bromide transport.

**Theory of water flow in soils**

The one-dimensional movement of non-interactive solute in a rigid non deformable, homogenous porous medium is commonly expressed by means of the Richards equation. The model assumes that the solute mass flux during steady state flow conditions may be expressed as the sum of two terms: a mass flow term describing the convection of the dissolved solute within the mobile soil solution, also considered as the mechanical dispersion, and the random mixing of the solute by diffusion within the moving soil solution. Hereby, the model further assumes that the solute pathways do not act as sources or sinks and that the solute concentration in the direction of flow is a constant. The model however fails to adequately characterize solute transport under unsaturated, transient flow conditions within an aggregated, multimodal pore system (van Genuchten and Wierenga, 1977; Gaudet et al. 1977). For a homogenous, isotropic porous medium under deformational forces, a series of constitutive equations with several dependent variables must first be formulated.

i) **The constitutive equation of motion of water flow in a rigid porous medium:**

\[
\frac{\partial (\phi \rho)}{\partial t} = -\nabla \cdot \left( \frac{\rho}{\mu} \mathbf{k} (\nabla \rho - \rho \varphi \nabla \mathbf{x}) \right) + \mathbf{q}
\]  

(1)

Where \( \phi \) is the actual porosity at the given load and assumed to be time invariable, \( \mathbf{k} \) is the absolute permeability tensor of the medium, \( \rho \) is the atmospheric pressure, \( \mu \) is the water viscosity \( \varphi \) is the magnitude of gravitational acceleration, \( \mathbf{x} \) is the depth, and \( \nabla \) is the gradient operator, \( \mathbf{q} \) water flux.
ii) **Mass balance equation of a component in a single fluid phase**

Following (Peters and Smith, 2002) the solute transport equation in a one-dimensional deforming porous medium may be expressed as:

$$\frac{\partial \phi_s C_i}{\partial t} + \frac{\partial ((1-\phi) C_i)}{\partial t} = -\frac{\partial}{\partial x} \left[ n \phi_r \left( -D \frac{\partial C_i}{\partial x} + u_f C_i \right) + (1-\phi) u_s C_i \right]$$

\hspace{1cm} (2)

where $\phi$ is the porosity of the porous medium at a given mechanical load, $C_f$ and $C_s$ are the concentrations of the solute in the fluid and solid phases, respectively; $\phi_r$ the degree of soil saturation, $D$, the hydrodynamic dispersion coefficient, $u_f$ is the average fluid velocity and $u_s$ the velocity of the solid.

For simplicity however, general assumptions will have to be made of which:

1- The solid particles of the porous medium as well as the fluid phase are incompressible and that deformation is entirely a function of particle rearrangement
2- Pore-water pressure and the subsequent consolidation due to likely dilatation of the solid particles are negligible
3- There are no sink and source points for the single component during transport process
4- No volumetric changes occur due to creep effects (Creep implies the deformational processes occurring at very low rate and at constant load).
5- The principal axial strain $|\varepsilon_v|$ is absolute and is only influenced by the vertical stress $\sigma_v$ (assuming that $\sigma_h$ produces no lateral strain, i.e. $|\varepsilon_h|=0$ and is consistent with $K_0$-conditions).

Here the transport of bromide ion (as a component) in a fluid phase (water) that occupies the entire void space is considered. It is assumed that, for each 24-hour loading sequence, the porosity $\phi$, attained is invariable with time and that each porosity $\phi$, has a direct influence on the nature of solute transport within the porous medium as this would otherwise contradict assumption 3 on consolidation.

The mass balance equation of the component in the fluid phase (Chen et al., 2006) is given by:

$$\frac{\partial (\varphi^C \rho C)}{\partial t} = - \nabla \cdot (C \rho u - \rho D \nabla C) - \sum_i q_1^{(i)} (x^{(i)}, t) \delta (x - x^{(i)}) (\rho C)(x,t)$$

$$\hspace{1cm} + \sum_j q_2^{(j)} (x^{(j)}, t) \delta (x - x^{(j)}) (\rho C)(x,t)$$

\hspace{1cm} (3)

where $C$ is the concentration of the component, $D$ is the diffusion-dispersion tensor, $q_1^{(i)}$ and $q_2^{(j)}$ are the production and injection rates (or specific discharge) at source and sink points $x^{(i)}$ and $x^{(j)}$ respectively, and $C^{(j)}$ the concentration at source points. However, if the effects of chemical reactions
between the component in the fluid phase, the chemical decay of the component and the absence of any sinks and sources are considered, then the above equation reduces to:

$$\frac{\partial (\varphi \rho C)}{\partial t} = -\nabla \cdot (C\rho u - \rho D\nabla C)$$  \hspace{1cm} (4)

Implying therefore, that $D$ is entirely a function of the Darcy flow $u$ in the porous medium. In theory, the mass balance equation of a single component should add up to zero. However, part of the single component may be retained by sinks within the porous matrix or may decay due to chemical transformation. In the case of bromide as conservative tracer, the amount of single component contained in the effluent relative to the input pulse or concentration is described as the “recovery rate” of that component. This may be rewritten in a form as in Eqn. (3) as:

$$\frac{\partial (\varphi \rho C)}{\partial t} = -\nabla \cdot (C\rho u - \rho D\nabla C) - \sum_i q_i^{(i)} \delta(x - x^{(i)})(\rho C)(x, t) + \phi^* \rho C \Gamma$$  \hspace{1cm} (5)

Whereas the 1st and 2nd terms at the r.h.s of Eqn. (5) denotes the amount of solute recovered in the effluent and the 3rd term denotes the amount of the solute retained within the matrix of the porous medium.

The erratic one-dimensional movement of non-interactive solute in a rigid non-deformable, homogenous porous medium is commonly expressed by means of the deterministic Convection Dispersion Model (CDM). The model also known as the One Region Model (ORM) assumes that the solute mass flux occurs within a unimodal pore system during steady state flow conditions and may be expressed as the sum of two terms: a mass flow term describing the convection of the dissolved solute within the mobile soil solution, also considered as the mechanical dispersion, and the short random mixing of the solute by diffusion within the moving soil solution. Hereby, the model further assumes that the solute pathways do not act as sources or sinks and that the solute concentration in the direction of flow is a constant. The model however fails to adequately characterize solute transport under unsaturated, transient flow conditions within an aggregated, multimodal pore system (van Genuchten and Wierenga, 1977; Gaudet et al., 1977).

With the aforementioned assumptions, analytical solutions to one-dimensional solute transport of a single component within a fluid phase under isothermal, steady-state water flux conditions by van Genuchten and Wierenga, (1977) are considered. For this case, neglecting the adsorption isotherm of the bromide ions, eqn. (4) may be rewritten as:

$$\left(1 + \frac{\rho m}{\theta} \right) \frac{\partial C_m}{\partial t} = R \frac{\partial C_m}{\partial x} = D \frac{\partial^2 C_m}{\partial x^2} - u \frac{\partial C_m}{\partial x}$$  \hspace{1cm} (6)

where:
\[ R = 1 + \frac{\rho_b K_D}{\theta} \]  

is the retardation factor. Dividing each side of Eqn. (5) with \( R \), we then obtain:

\[ \frac{\partial C_m}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} - u_R \frac{\partial C_m}{\partial x} \]  

where \( D_R = D/R \) is the dispersion coefficient of the solute retarded by adsorption, and \( u_R = u/R \) solute velocity retarded by adsorption. Owing to the non-adsorbable character of the bromide ions, and assuming that the coefficient for linear adsorption, \( K_D = 0 \), then the quotient on the r.h.s of Eqn. (6) reduces to \( R = 1 \). Characterizing solute transport under steady state flow conditions using the CDM, would require the use of the mean pore water velocity \( u \) and \( u_R \) as fitting parameter during optimization. The ratio of the measured velocity \( u \) to the fitted pore water velocity \( u_R \) was the equivalent of that approximated by (Lennartz and Kamra, 1998) as the Mobility Index, \( MI = u/u_R \).

Model-II (herein referred to as the Mobile-Immobile Water Model, MIM). (Coats and Smith, 1964; van Genuchten and Wierenga, 1976, 1977; van Genuchten, 1980) conceptualizes the bimodality of the porous medium whereof solute transport by mass flow is localized in the mobile region \( \theta_m \), while the immobile region \( \theta_{im} \) is presumed to have stagnant water and solute transport is essentially diffusive between both regions. For an inert, non-reactive bromide tracer and assuming constant water flux \( J_w \), \( \theta_m \) and \( \theta_{im} \):

\[ \theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} - J_w \frac{\partial C_m}{\partial x} \]  

The lateral diffusion or solute exchange between both regions depends on the concentration gradient expressed in a simplified dimensionless form as follows:

\[ \theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \]  

where \( \alpha \) is the first order mass transfer coefficient between mobile/immobile (\( d^{-1} \)) regions and the subscripts \( m \) and \( im \) refer to mobile/immobile regions respectively. Analytical solutions to the equations for ORM and TRM are given by (van Genuchten, 1981). The tracer concentration at the entry surface is a third-type or Dirac delta function \( c_0(t) = 0 \), whereby the initial and boundary conditions can be generally expressed as: 

\[ c_0(t) = 0 \]
\[ \mathbf{C}(x, 0) = 0 \quad (11) \]
\[ \mathbf{C}(0, t) = \mathbf{C}_0(t) \mathbf{D} \mathbf{u} \cdot \frac{\partial \mathbf{C}}{\partial x} \quad (12) \]
\[ \mathbf{C}(\infty, t) = 0 \quad (13) \]

iii) **Mass balance and stress-strain equations of solid matrix**

Assuming that displacement or strain \( |\epsilon| \) of the solid matrix is a function of the effective stress which is related to the applied pressure \( p \), then the porosity \( \phi = \phi(\sigma_e) \) becomes directly a function of effective stress. This is combined with the specific discharge of the fluid phase as the porosity changes as:

\[ \frac{\partial |\epsilon|}{\partial t} = -\nabla \mathbf{q} + \phi \frac{\partial p}{\partial t} \quad (14) \]

Taking the r.h.s of Eqn. (1) on the motion of water flow and replacing the \( p \) with \( p_e \), the pressure due to increased mechanical load:

\[ \frac{\partial |\epsilon|}{\partial t} = -\nabla \left( \frac{\rho}{\mu} \mathbf{k}(p_e + \rho \phi \nabla \mathbf{x}) \right) + \phi \frac{\partial p_e}{\partial t} \quad (15) \]

where \( \Theta \) is the coefficient of compressibility of the solid matrix and is given as \( \Theta = \frac{1}{\phi \frac{\partial \phi}{\partial p}} \). Observing Eqn. (4) and Eqn. (14), the strain experienced during mechanical loading may be directly correlated to porosity and concentration of solute within porous medium.

\[ \frac{\partial |\epsilon|}{\partial t} = -\nabla \mathbf{q} + \phi \frac{\partial p}{\partial t} \leftrightarrow \frac{\partial (\phi \rho \mathbf{C})}{\partial t} = -\nabla (\rho \mathbf{C} \rho - \rho \mathbf{D} \nabla \mathbf{C}) \]

Where:

\[ \frac{\partial |\epsilon|}{\partial t} = \frac{\partial (\phi \rho \mathbf{C})}{\partial t} \quad (16) \]
Materials and Methods

Measurements were carried out on undisturbed samples from an arable topsoil of a stagno-vertic Cambisol or loamy sand soil (Ap-horizon of a Braunerde-Pseudogley) on a site located about 7 km North West of Kiel, Germany (Table 1).

Table 1. Mechanical and physical features of a stagno-vertic Cambisol.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC(µS/cm 20°C)</td>
<td>70.2</td>
</tr>
<tr>
<td>Org. matter (C₀rg)</td>
<td>2.68</td>
</tr>
<tr>
<td>Plastic Limit</td>
<td>21-28%</td>
</tr>
<tr>
<td>Liquid Limit</td>
<td>68-70%</td>
</tr>
<tr>
<td>Specific gravity (gm/cm³)</td>
<td>2.63</td>
</tr>
<tr>
<td>Dry bulk density (gm/cm³)</td>
<td>1.52</td>
</tr>
<tr>
<td>Specific surface (cm²/gm)</td>
<td>111.1</td>
</tr>
<tr>
<td>Sand (2-0.2mm; cS-fS)</td>
<td>60.1%</td>
</tr>
<tr>
<td>Silt (0.2-0.063mm; cU)</td>
<td>33.8%</td>
</tr>
<tr>
<td>Clay (&lt;0.002mm; T)</td>
<td>6.1%</td>
</tr>
<tr>
<td>vol. water content (cm³/cm³)</td>
<td>0.422 (at saturation)</td>
</tr>
</tbody>
</table>

The lower and upper surfaces of the 10 cm in diameter and 12 cm in height sample core were trimmed smooth to reduce the likely effects of bifurcation and then mounted onto the base pedestal and top cap within a modified tri-axial cell as in (Figure 1) (Günther, 1991). The soil sample was then subjected to confining pressure, $\sigma_3$ (pneumatic pressure P5 HBM, with maximum loading range 500 kPa) and sheared with axial pressure, $\sigma_1$ (pneumatic pressure PN 1 HBM, with maximum loading range 500 kPa) applied to the cap through the loading piston. The axial head displacement of the soil sample during deformation was measured by an inductive height sensor (W20TK) and read out from the computer. At a given mechanical load, distilled water was then let to flow into the soil core through the top cap and out through the base pedestal that both contained porous ceramic plates ($P42$ KPM, pore size 3µm, diameter 12cm, width 7mm) until stationary water flow conditions at matric suction -30 hPa was reached (soil sample still under saturated conditions). At this given load, 0.25PV from a solute concentration of 50 mg/l of bromide tracer was applied and the effluents collected by a programmed auto-fraction collector. Consistent with the principle of miscible displacement, and after application of the pulse volume, tracer-free distilled water was immediately applied to about 2-4 pore volumes until the effluents collected were assumed free from any detectable tracer amounts. The displaced effluents were collected and received by programmed auto-fraction collector with a chosen sampling time-interval. The receiving test tubes from the auto-fraction collector were later on taken for analysis on the levels of bromide concentrations.
For practical purposes and in order to investigate the effects of induced mechanical loading on solute transport parameters, the same sample core at 0 kPa was used for the different loading sequences at 10 and 40 kPa. Each subsequent loading sequence was maintained for 24 hours, and a 0.25PV of bromide tracer applied under steady-state water flow conditions until all effluents were assumed to be tracer-free prior to a further incremental loading sequence. Such was done at the 0, 10 and 40 kPa pressures.

**Figure 1: Diagrammatic representation of the modified tri-axial cell and its components.**

1) Lateral pressure line (σ); 2) air vent; 3) matric suction sensors; 4) soil sample; 5) support framework; 6) pneumatic system for axial pressure (σ); 7) loading pressure transducer; 8) inductive height sensor; 9) loading ram; 10) Perspex cylinder; 11) inflow line; 12) ceramic plates 13) mini-tensiometers; 14) rubber membrane; 15) drainage line; 16) Mariotte’s flask; 17) electronic balance; 18) adjustable plate; 19) pressure control unit; 20) data logger; 21) computer; 22) auto-fraction sampler.

**Analysis**

The analytical solution to the One Region Model (ORM) contains two independent parameters, D and \( u_R \) while the Two Region Model (TRM) contains three: D, \( \beta \) and \( \omega \). The nonlinear curve-fitting program CXTFIT of (van Genuchten, 1981) was employed to estimate the model parameters. In ORM, both D and \( u_R \) were variable parameters \( R \) held constant during each optimization run. In TRM, D, \( \beta \) and \( \omega \) were let to vary for each optimization run. The sum of squared residuals (SSQ) was used as a measure for the goodness of fit between the measured data and the estimated values upon convergence to its lowest value.
Results and Discussion

Figure 2 shows individual breakthrough curves observed during steady flow conditions under incremental mechanical loading. At 0 kPa, the curve showed asymmetry and tailing reflecting consistent preferential transport behavior with relative peak concentrations of the tracer between 0.6-0.8 at about 0.5 PV and relative mean pore water velocity of 29 cm/d. Incremental 10 and 40 kPa loading, the curves showed reduced peak concentrations with rather greater values of the pore volumes. The shape and skewness of the BTC’s were generally influenced by loading sequences.

The relatively lower MI and β values (Table 2) at the 0 kPa implied that only a smaller portion of the total soil water enhanced solute transport, with the immobile water content ($\theta_{im}$) at 56% which as estimated from $\theta_{im} = 1 - \theta_m$. High $\theta_{im}$ values of over 50% on columns packed with large oxisol aggregates 2-4.7 mm ((Nkedi-Kizza et al., 1983); on aggregated, gravelly oxisols (Anamosa et al., 1989), and on unsaturated sand at around 36% (De Smedt et al., 1986).

Under the chosen test conditions by e.g. 10 kPa, there was less time for diffusive The estimation of the tracer recovery rate or mass recovery, usually an approximated value, is expressed as a percentage of the normalized effluent concentrations (mg/l) collected. A more accurate estimation of this value would require determining the concentration of each individual effluent across the entire pore volume spectrum. As shown in Figures 2a, c and e, the recovery rate for the BTC’s decreased with decreasing pore water velocity. This was about 70% at $u=29$ cm/d (0 kPa) to about 55% at $u=22$ cm/d (10 kPa) and finally to about 48% at $u=13$ cm/d (40 kPa). This was not to be expected, and would imply that the number of effective pores accounting for rapid solute transport was either reduced and hence a reduction of the average-solute flux, or that the loading effects enhanced pore truncation with the subsequent increase of the solute in the immobile regions.
Figure 2: BTC’s of some Ap-soil samples during increasing mechanical load with the fitted parameters.

a) Model-I: $D = 165.1 \text{cm}^2/\text{d}$ ; Model-II: $D = 84.82 \text{cm}^2/\text{d}$ $MI = 0.58$; $u = 28 \text{cm/d}$; $\beta = 0.36$; $\omega = 0.52$

b) Model-I: $D = 149.98 \text{cm}^2/\text{d}$ ; Model-II: $D = 63.27 \text{cm}^2/\text{d}$ $MI = 0.659$; $u = 28.7 \text{cm/d}$; $\beta = 0.41$; $\omega = 0.48$

c) Model-I: $D = 87.34 \text{cm}^2/\text{d}$ ; Model-II: $D = 10.97 \text{cm}^2/\text{d}$ $MI = 0.98$; $u = 23 \text{cm/d}$; $\beta = 0.50$; $\omega = 1.16$

d) Model-I: $D = 9.57 \text{cm}^2/\text{d}$ ; Model-II: $D = 9.00 \text{cm}^2/\text{d}$ $MI = 1.01$; $u = 18 \text{cm/d}$; $\beta = 0.98$; $\omega = 3.43$

e) Model-I: $D = 4.62 \text{cm}^2/\text{d}$ ; Model-II: $D = 4.28 \text{cm}^2/\text{d}$ $MI = 0.92$; $u = 12.5 \text{cm/d}$; $\beta = 0.89$; $\omega = 0.01$

f) Model-I: $D = 8.4 \text{cm}^2/\text{d}$ ; Model-II: $D = 7.56 \text{cm}^2/\text{d}$ $MI = 1.16$; $u = 11.9 \text{cm/d}$; $\beta = 0.81$; $\omega = 0.1$
The BTC in Figure 2 at the 0 kPa range was markedly asymmetrical and skewed to the left, characterizing early breakthrough with extensive tailing. On loading (10 kPa), the BTC was characterized by less asymmetry and tailing (Figure 2 c and e). This implied a reduction in density of the larger pores transporting the solute toward apparently smaller and more uniformly distributed pore sizes. From 0 kPa to 10 kPa mechanical loading, both MI and \( \beta \) increased, with a reduction in the immobile water (\( \theta_{im} \)) \( u \) or from about 59% to about 49%. Such results under unsaturated conditions were also mentioned by Lennartz and Meyer-Windel (1995) working on haplic Cambisols. Similarly, at the 40 kPa pressure range with subsequent reductions in \( u \), both MI and \( \beta \) increased. Under such test conditions, the solute transfer between the two regions owing to the increased solute residence time was greatly enhanced (Table 2). However, given the crumby structure and absence of distinct aggregates in the studied soil, much of the immobile water involved in solute exchange mechanism can be assumed to be localized within the dead-ends of truncated pores or isolated inter-particle pores within the soil matrix.

Table 2: Comparison between the porosity, and solute transport parameters under variable mechanical loading of a Ap-samples.

<table>
<thead>
<tr>
<th>Mobile water content (( \theta_m ))^2</th>
<th>Transport parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model - I</td>
</tr>
<tr>
<td></td>
<td>( f ) fitted, ( D )</td>
</tr>
<tr>
<td></td>
<td>(cm²/d)</td>
</tr>
<tr>
<td></td>
<td>(MI)</td>
</tr>
<tr>
<td></td>
<td>( \alpha ) (d^-1)</td>
</tr>
<tr>
<td>0.145(0.312)</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>118.87± 34.46</td>
</tr>
<tr>
<td></td>
<td>87.6±11.19^1</td>
</tr>
<tr>
<td>0.116(0.202)</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>53.84± 8.39</td>
</tr>
<tr>
<td></td>
<td>40.76±10.61</td>
</tr>
<tr>
<td>0.09(0.137)</td>
<td>19.9</td>
</tr>
<tr>
<td></td>
<td>50.11±12.16</td>
</tr>
<tr>
<td></td>
<td>36.17±9.71</td>
</tr>
</tbody>
</table>

1) ± 95% confidence interval  
2) \( \theta_m = (\theta)\beta \) \( \theta \) in parenthesis is soil water content under stationary flow conditions  
3) \( u \), pore water velocity, cm/d  
4) \( \phi \), porosity  
5) \( \alpha = (\omega u \ast \theta_m)/L \) \( \omega \) in parenthesis is transfer coefficient

**Dispersivity, \( R_L \)**

The underlying assumption consistent to the CDM is that mechanical dispersion is the largest mechanism contributing to dispersive flux of the solute. This, however, would require the setting of a threshold value of the mean pore velocity, under which the mechanical dispersion is valid. The assumption is that under this threshold mean pore velocity, depending on the porous medium under study the axial, film and intra-particle diffusions play significant roles in the total solute dispersion or spreading. Brissaud et al., (1983) investigated the significance of these additional sources of diffusions at different mean pore velocities and their operational ranges. For that matter, the tracer-derived dispersion and therefore the dispersivity (\( D/\dot{u} = R_L \)) may be assumed as „lumped parameter“
consisting of the aforementioned components. Much of the discussions here have focused on the contribution of variable mean pore water velocities due to loading on longitudinal dispersivity.

Table 3: Dispersivity $\alpha_L$ (cm) and the mass recovery (%) values of Ap samples during loading.

<table>
<thead>
<tr>
<th>Applied load in (kPa)</th>
<th>Model I</th>
<th>Model II</th>
<th>Recovery rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.48</td>
<td>3.31</td>
<td>70.0</td>
</tr>
<tr>
<td>10</td>
<td>2.38</td>
<td>1.77</td>
<td>52.3</td>
</tr>
<tr>
<td>40</td>
<td>2.52</td>
<td>1.82</td>
<td>47.6</td>
</tr>
</tbody>
</table>

Table 3 shows that the 1-D longitudinal dispersivity for the Ap soil samples was load dependent. Generally, the $\alpha_L$ decreased with increasing mechanical load and decreasing $u$. Similar results by (Biggar and Nielsen, 1967) showed that the $\alpha_L$ was approximately proportional to the average pore water velocity $u$. Much of the solute travel pathways were either constricted or truncated due to incremental loading thereby reducing solute dispersivity within the soil matrix. Inspection of the data revealed that the $\alpha_L$ in Model-I was greater than $\alpha_L$ in Model-II under incremental loading. Both models give $\alpha_L$ values that are within the range investigated on sandy loam by (Ellsworth et al., 1989; Brissaud et al., 1983); on sand by (van Wesenbeeck and Kachanowski, 1991); loamy sand by (van Ommen et al., 1989).

For the soil samples, the net reduction in $\alpha_L$ for Model-I due to loading from 0-10 kPa was about 49% and this was about 40% from 10-40 kPa. An explanation to that effect is that incremental loading apparently increased pore constriction along the flow path, thereby reducing the net dispersive flux. Furthermore, deformation of the initially vertical pores due to incremental loading led to a reorientation in the direction of flow. The effects were more significant under unsaturated conditions, where certain pores were apparently truncated into dead ends leading to isolated immobile regions within the soil matrix. Pore truncation could be the result of localized depositional processes occurring during the dynamic shearing of the grain particles at higher loading sequences.
Figure 3 shows that the Retardation Factor \( R \), varied on average between 0.4 to 0.7 at 0 kPa gradually increasing to between 0.5 to 0.9 at 10 kPa and to 0.8 to 1.0 at 40 kPa with a decrease in the pore water velocity during each loading sequence as best described by the exponential function

\[ R = A \exp(\beta u) \]

where \( A \) and \( \beta \) are material constants. Conversely, the dispersion coefficient \( D \), within the soil sample decreased with reduction of the pore water velocity \( u \) resulting from incremental mechanical loading and was best described using the polynomial function of the \( D = A u^2 - B u + C \) where \( A \), \( B \) and \( C \) are material constants. The results showed that reduction in solute spreading within the soil matrix due to incremental loading must have enhanced both pore truncation and reduction in the pore radii of larger pores. It was however, not possible to quantify the net extent of pore truncation or pore size reduction as influenced by each individual loading sequence. As shown in Table 2, the
average net D reduction due to incremental loading from 0 to 10 kPa was about 55% while this only about 7% from 10 to 40 kPa. This would indicate that D reduction at 10 kPa was predominantly reduction in size of the larger primary pores. Meanwhile, the mobile fraction β of the bromide decreased with decrease in the pore water velocity u, as more pores were either truncated or reduced in radius as a result of increased loading.

Figure 4: The effect of variable porosity φ as influenced by increasing mechanical load on the dispersion coefficient, D

Figure 4 shows the effects of increased loading characterized by variable porosity φ, on the solute transport parameter D using Model-I and II with values of the Model-I generally greater than those of Model-II. This was to be expected since the Model-I assumed the uni-modality of the pore system thereby lumping together D as opposed to the Model-II that assumed the bimodality of the pore system.

The first order mass transfer coefficient α here derived as (ou*θm)/L, showed some consistent trend or descriptive functional relationship within the individual experiments. Referring back to Table 2 showed that α increased with increasing mechanical load. The α increase from 0-10 kPa was about 21%. The increase of α as a function of mechanical load was to be expected consistent with the equation: (ou*θm)/L whereby α inversely correlated with the effective path length. This implied that under increased mechanical stress conditions, the effective path length for bromide ion transport increased with subsequent increase of both the solute mass transfer between the mobile/immobile regions and a corresponding decrease in the mobile fraction, β (Figure 5).
Figure 5: The effects of variable porosity $\varphi$ as influenced by incremental mechanical load on the mobile fraction $\beta$ of the bromide solute.

Statistical analysis of transport parameters

Given the textural nature of the $Ap$ samples, it could easily be presumed that the herein derived deformation state variable $\varphi$ and solute transport parameters $MI$, $D$, $\beta$ and $\omega$ are invariable at each loading sequence. A simple statistical test of significance for differences of the solute transport parameters was carried out by comparing two sample variances of 5 independently chosen $Ap$ soil samples. The F-Test was used to determine the equality of means of each of the investigated transport parameters under given axioms or hypothesis at the $\alpha=0.05$ level of significance. The Null Hypothesis ($H_0$) asserts that there were no significant differences in the solute transport parameters of $Ap$-samples as a result of loading sequences.

Table 4: Influence of loading sequences on the solute transport parameters: $MI$, $D$ and $\beta$ of some $Ap$ soil samples.

<table>
<thead>
<tr>
<th>soil sample</th>
<th>statistical variable</th>
<th>$MI$</th>
<th>$D'$ (cm²/d)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ap</td>
<td>MStr</td>
<td>0.163</td>
<td>8769.426</td>
<td>0.062</td>
</tr>
<tr>
<td>MSE</td>
<td></td>
<td>0.0114</td>
<td>2786.89</td>
<td>0.0187</td>
</tr>
<tr>
<td>F-Test</td>
<td></td>
<td>14.326*(S)</td>
<td>3.15 (NS)</td>
<td>3.32 (NS)</td>
</tr>
</tbody>
</table>

1) dispersion coefficient using Model-I; *$^*$ significant at $\alpha = 0.05$ with the critical value ($F_{crit}$) of $3.81$; S = Significant; NS = Not Significant; F-Test >$F_{crit}$ = S (reject $H_0$); whereas F-Test <$F_{crit}$ = NS (accept $H_0$)

NOTE: degrees of freedom, 2 and 13 for the error and treatment respectively
Consistent with the $H_0$ null hypothesis, the results in Table 4 generally showed that, the differences due to loading effects at the $\alpha=0.05$ level in the Ap soil samples especially for the MI was significant than for both $D$ and $\beta$. A visual inspection of the breakthrough curves also reasserts this assumption that there were changes as shown by the asymmetry and tailing of the curves at maximum loading of 0 kPa. The non-significant differences in the solute transport parameters $D$ and $\beta$ during loading sequences may be attributed to the presence of relatively larger proportion of smaller conducting pores at 10 and 40 kPa that enhanced bromide transport and which appeared less affected by the magnitude of the induced load. Larger part of the solute transport parameters $D$ (Figure 4 with e.g. $D=50, 36.2 \text{cm}^2/\text{d}$ at 40 kPa and $D=54, 40 \text{ cm}^2/\text{d}$) and $\beta$ appeared to be enhanced within the smaller pores that were more stable against any loading sequences suggesting the less homogenizing effects of mechanical load in reducing the pore diameter from the large conducting to smaller and uniformly sized pores. Note that the natural overburden pressure of the Ap samples was about 15 kPa, even at this pressure range, there were still abundant and stable biopores.

**Conclusion**

In this study, the transport of bromide as a single component within water as fluid phase under incremental load was investigated. Results showed that the influences of incremental mechanical loading on the mobility index $MI$ and mass transfer terms $\alpha$ were significant. However, the effects on dispersion coefficient $D$, longitudinal dispersivity $\mathcal{R}_L$ and mobile fraction $\beta$ were significant in some soil samples. The parametric analysis investigated both breakthrough and advective-dispersion of bromide ions, and the results indicated that the lower mechanical load led to more advective bromide transport due to greater water velocity, and that higher loading to increased mass transfer coefficient. Furthermore, it highlighted the need to integrate tortuosity that must have influenced path flow in all considerations while interpreting breakthrough curves and the effects of porous medium deformation on solute transport.

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References


