

CHLORIDE TRANSPORT PARAMETERS PREDICTION FOR A LACONIAN ALLUVIAL CLAY-LOAM SOIL COLUMN

BOURAZANIS G.¹ and NIKOLAOU N.²

¹Department of Rural Economy and Veterinary of Regional Government of Laconia, Sparta, Laconia, 23100, Greece, ²Department of Marine Sciences, School of the Environment, University of the Aegean, Mytilene, Lesvos
E-mail: gbourazanis@windtools.gr

ABSTRACT

Water scarcity in arid and semi arid regions makes treated wastewater an unavoidable supplementary irrigation water source. At the same time treated municipal wastewater quality depends on the fresh water quality and usage and on the wastewater treatment plant's degree (primary secondary, tertiary, etc) and efficiency. The main recipient of all chemical compounds contained in this effluent, via irrigation, is soil. The pathways that these compounds are following are due to four processes which are the advection (refers to the moving of the solutes with the flowing water) dispersion (represents the spreading of the solute about a mean position) phase changes (meaning sorption, volatilization, etc.) and reaction (chemical, physical or microbial degradation or production). The fate of each compound is the resultant of these processes depending on the soil and compound properties. It is also determines the risks of polluting the aquifer by passing the solute through the soil profile under saturated or unsaturated conditions and so intruding the aquifer's body. This solute movement continues in the aquifer governed by the same processes but in different scales. Models have been developed to predict factors involved in this phenomenon. From all the chemical compounds contained in the reused effluent, chloride which is an excipient produced by the disinfection process is much of a concern as a conservative pollutant. In this work we forced a solution of potassium chloride to go through a loam packed soil column by applying pressure head and so breakthrough curves (BTCs) were determined. After this the BTCs were analysed with the one dimensional advection dispersion equation (ADE) by exploiting the CXTFIT code to obtain estimates of the solute transport parameters. These parameters are depending on the soil and chemical compound characteristics and by the processes prevailing throughout the soil column. The comparisons between experimental and calculated results were satisfactory. At the same time useful conclusions derived about the flow conditions in the soil column and its uniformity. Also comparisons made between predicted values of the model parameters and limits cited in the literature.

Keywords: Loam alluvial soil, Chloride breakthrough curve, CXTFIT code, STANMOD software, flow parameters prediction.

1. Introduction

Chemical fate and transport through soil is a complex task involving four major processes advection, dispersion, interphase mass transfer and reaction or transformation (Brusseau, 1994). For characterising the solute fate and transport, experiments (miscible displacement experiments) may be conducted, where a solute is applied at a specific point of the soil and its' evolution is monitored versus time and distance. These are the most important methodological approaches among others for investigating the involved phenomena (Alvarez-Benedi, et. al., 2005). Two are the main constrains of such experiments: (i) spatial variability of soils and (ii) scale dependencies (Winton & Weber, 1996). Although laboratory experiment results with soil columns could not be extrapolated to field scale, they are useful for isolating and studying each factor affecting the evolution of the phenomenon. (Alvarez-Benedi, et. al., 2005).

Our experiment was conducted in a repacked clay loam soil column by using a chloride solution in order to investigate the prevailing mechanisms and their magnitude.

2. Materials and methods

2.1. The theory

The simplified equation describing the nonvolatile no reacting and no adsorbing chemical compound movement in a homogeneous porous medium is (Jury & Horton, 2004):

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (1)$$

$$D = D_e / \theta \quad (2)$$

$$v = J_w / \theta \quad (3)$$

$$D_e = D_l^s + D_{lh} \quad (4)$$

$$D_{lh} = \lambda v \quad (5)$$

$$D_l^s = \xi_1(\theta) D_l^w \xrightarrow{\xi_1(\theta) = \frac{\theta^{7/3}}{\theta_s^2}} D_l^s = \frac{\theta^{7/3}}{\theta_s^2} D_l^w \quad (6)$$

Where J_w and v are the macroscopic and the pore water flow velocity respectively, D_e , D_l^s and D_{lh} are the effective dispersion, diffusion and hydrodynamic dispersion coefficients respectively, λ is the dispersivity, D_l^w is the diffusion coefficient of the chemical compound in water and ξ is the tortuosity factor ($\xi(\theta) < 1$) used to incorporate the presence of solid and air phases resulting to a reduction of the diffusion coefficient's value in water.

Furthermore we investigated the effects of structure on solute transport assuming that part of the pore volume water was flowing (mobile water) and another part was stagnant (immobile water) which is a physical non equilibrium situation, (Coats & Smith, 1956). For this case Mobile-immobile (MIM) the driving equations are:

$$\theta_m + \theta_{im} = \theta \quad (7)$$

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = D \frac{\partial^2 C_m}{\partial z^2} - v \frac{\partial C_m}{\partial z} \quad (8)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (9)$$

Where θ_m and θ_{im} are the portions of soil water content θ assumed mobile and immobile respectively. C_m and C_{im} are the chemical compound concentrations in mobile and immobile water respectively and α is a rate coefficient.

2.2. Experimental Device

The experimental device consisted of two Mariotte tubes (deionized water (DW) and KCl solution (CIS)) (Fig 1a). By these two Mariotte devices it was achievable to maintain steady head conditions (Fig 1b). The soil column's dimensions were 7 cm diameter (D_{sc}) and 25 cm long (L) (Fig. 1c). At each end of the porous medium an inlet and outlet chamber existed (Fig. 1d). Each chamber had a valve for diaeration (Fig. 1e). A combination of metallic and cloth sieve (Fig. 1f) was used to separate the chambers from the column. By using three way valves (TWV) (Fig. 1g) the inlet chamber could be connected with the two liquids (DW and CIS). The outlet chamber was connected via a tube with the sampler container (Fig. 1h).

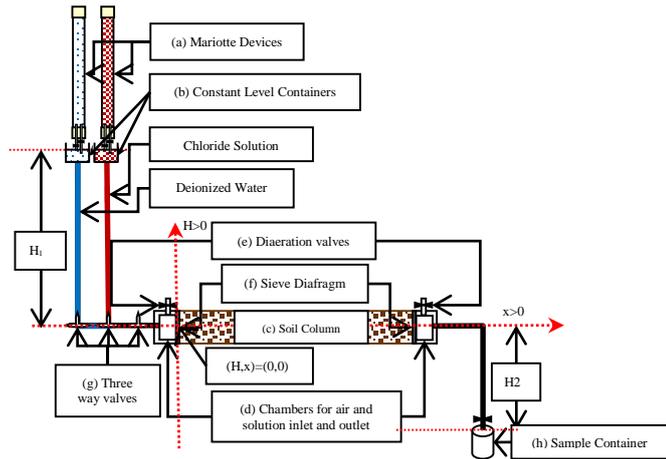


Figure 1: Schematic diagram showing the experimental device.

2.3. Experimental Procedure

Disturbed soil sample was taken from the upper 30 cm of an olive orchard placed in Evrotas river alluvial field. The sample was air-dried, ground and sieved through a 2 mm sieve. Soil particle-size distribution of the <2 mm fraction was determined by the Bouyoucos hydrometer method (Gee & Bauder, 1986).

The soil was packed uniformly via vibrating machine in a 25 cm long Perspex tube until the bulk density was representative for a clay-loam soil. The packed dry soil column was weighted it (B_{cd}) and afterwards the saturation procedure with DW was conducted with an upright column position from the bottom to the top and a very small inlet pressure head and hence small water velocity to avoid possible soil column “cut” and air entrapment. The saturated column was weighted (B_{cs}) and so by subtraction we estimated the soil column water content by taking in mind also the volumes of the two chambers (V_{ch}). So the characteristics of the porous medium were given from the equations 10 and 11

$$d = \frac{m}{V} \Leftrightarrow d = \frac{m}{\frac{\pi \cdot D_{sc}^2 \cdot L}{4}} \Leftrightarrow d = \frac{4 \cdot m}{\pi \cdot D_{sc}^2 \cdot L} \quad (10)$$

$$\Theta_s = \frac{B_{cs} - (B_{cd} + 2 \cdot (V_{ch} \cdot \rho_{H_2O(20^\circ C)}))}{\frac{\pi \cdot D_{sc}^2 \cdot L}{4}} \Leftrightarrow \Theta_s = 4 \cdot \frac{B_{cs} - (B_{cd} + 2 \cdot (V_{ch} \cdot \rho_{H_2O(20^\circ C)}))}{\pi \cdot D_{sc}^2 \cdot L} \quad (11)$$

Afterwards the column was put at a horizontal position and the predetermined pressure head was applied. The saturated hydraulic conductivity (K_s) was determined by using the constant head permeameter method (Klute & Dirksen, 1986). The experimental results were the volume of the water collected with time when a constant hydraulic head gradient was applied. The macroscopic velocity was calculated by $V(t)$ data (eq. 12) and by Darcy's law (eq. 13)

$$u_x = \frac{4 \cdot V(t)}{\pi \cdot D_{sc}^2 \cdot t} \quad (12)$$

$$u_x = K_s \frac{H_2 + H_1}{L} \quad (13)$$

$$(eq. 12), (eq. 13) \Rightarrow K_s = \frac{4 \cdot V(t) \cdot L}{\pi \cdot D_{sc}^2 \cdot t \cdot (H_2 + H_1)} \quad (14)$$

$H_1=200\text{cm}$ and $H_2=50\text{cm}$ are water and solution inlet and outlet heights respectively, imposing a constant hydraulic gradient ($\frac{\partial H}{\partial x} = \frac{H_1 - (-H_2)}{x_1 - x_2} = \frac{200 - (-50)}{0 - L} = \frac{250}{-47.9} = -5.22$) and hence steady water flow velocity from the left to the right of the column (Figure 1).

Afterwards the CIS was allowed to infiltrate the soil column by turning properly the TWV. This signaled the initiation for the experimental determination of the break through curve (BTC) with initial condition ($t=0$ and $C_o=0$). Samples were taken every 15 minutes or more until $C_{Cl-inlet} = C_{Cl-outlet}$. Then again by using the TWV the chloride washout experiment started and samples were taken from the outlet every 60 minutes until $C_{Cl-inlet} = C_{Cl-outlet}$. The samples' chloride concentration was determined by titration with silver nitrate ($AgNO_3$) in presence of potassium chromate ($KCrO_4$) as indicator (Dhaliwal, *et al.*, 1985).

2.4. STANMOD software, CXTFIT code

For making all the calculations and predicting the chloride break through parameters the Stanmod software was used (Simunek, *et. a.*, 1999). This software package includes an updated version of the CXTFIT code (Toride, Leij, & van Genuchten, 1995) for estimating solute transport parameters using a nonlinear least-squares parameter optimization method. Three different one-dimensional transport models are considered: (i) the conventional CDE; (ii) the chemical and physical nonequilibrium CDEs; and (iii) a stochastic stream tube model based upon the local-scale equilibrium or nonequilibrium CDE. This code may be used to solve both inverse and direct or forward problems. For our needs the conventional CDE and the physical non equilibrium CDE (MIM) models were used.

3. Results and discussion

Table 1 shows the characteristics of the packed clay loam soil column and of the chloride solution

Table 1 Characteristic of the packed clay loam soil and the chloride solution

Soil column characteristics	$V_{out}(t)$
Diameter (cm)	7
Length (cm)	25
Dry soil Weight (gr)	1356.6
Bulk density d (gr/cm^3)	1.41
Water content at saturation (ml) (V_{sat})	490.68
Θ_s (cm^3/cm^3)	0.51
Darcy velocity (J_w) (cm/min)	0.030
Pore volume velocity (v) (cm/min) ($v=J_w/\Theta_s$)	0.059482
C_o (chloride) (meq/l)	1500

By following the experimental procedure BTCs were determined for both chloride infiltration through the soil column (Figure 2(a)) and chloride washout (Figure 3(a)). The experimental values ($V_{out}(t)$ and $C_{out}(t)$) were converted to dimensionless by dividing with V_{sat} and C_o respectively. Also fitted values were calculated for both BTCs via CXTFIT code assuming deterministic equilibrium-average flux concentration conditions and deterministic physical non equilibrium (MIM) average flux concentration conditions (Figures 2 & 3).

The larger the dispersivity values the more dispersed the solute front will be as a result of a wide range of pore size distribution (Radcliffe & Simunek, 2010). λ values for laboratory experiments with packed soil columns are between 0.5 and 2 cm and for intact soil columns or field experiments are between 5 and 20 cm (Jury & Horton, 2004) so from our λ values (table 3) is obvious that in our soil column a wide range of pore size distribution existed and hence varying pore water velocities resulted to a dispersed solution front. At the same time the fact that at pore volume 1 the C/C_o value was 0.6 and not 0.5 (Figure 2(b)) illustrates the earlier than expected arrival of our tracer due to its' negative charge in a porous medium with negative charges in its' structure (anion exclusion effect) (Marshall, *et. al.*, 1996). A non symmetrical shape of BTCs, like our case, also indicates a wide range in the distribution of pore water velocities (Alvarez-Benedi, *et. al.*, 2005), They also reported that large holdback area (the area between the BTC and the V/V_o axes up to pore volume 1) indicates difficult displacement and the tailing or large holdup area (area between BTC and $C/C_o=1$ from pore volume 1 until end of experiment) indicates large amount of solute that was stored. The same curve characteristics are recognized also at the washout experiment (Figure 3 (b)) and led to relevant conclusions.

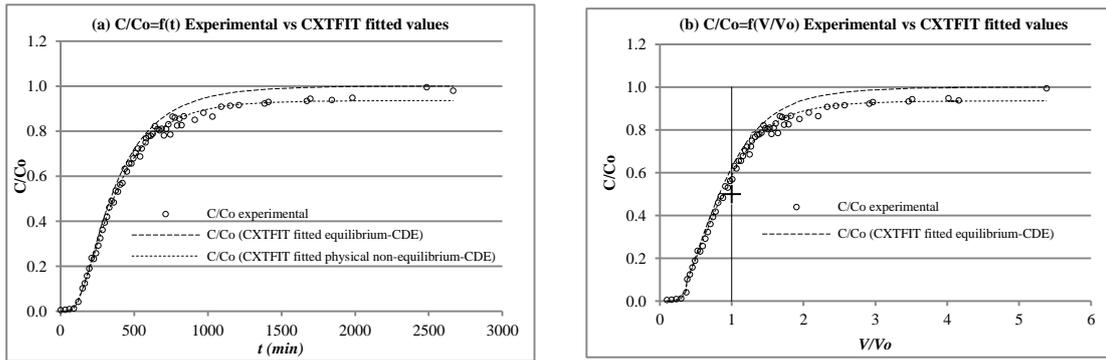


Figure 2: Chloride BTC experimental and fitted results (under equilibrium and physical non equilibrium assumptions)

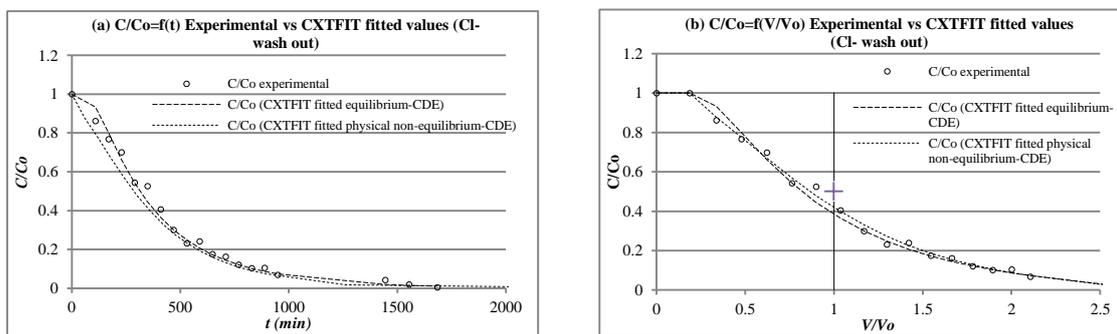


Figure 3: Chloride washout BTC experimental and fitted results (under equilibrium and physical non equilibrium assumptions)

Generally R^2 values showing that the assumption of the deterministic physical non equilibrium solution of CDE (MIM) describes better the experimental results for both cases ($R^2_{eq}=0.9765 < 0.9959=R^2_{n-eq}$ and $R^2_{eq}=0.9892 < 0.9951=R^2_{n-eq}$). Furthermore the shape of the experimental BTC (figure 2(b)) implies that the chloride is spread as a result of the hydrodynamic dispersion (Alvarez-Benedi, et. al., 2005). The magnitude of the D_e is determined mainly by the D_{lh} and hence the D_l^s can be ignored. This is due to the value of the D_l^s which according to equation (6) is equal to the D_l^w reduced as the $\xi(\theta)$ imposes. In saturated conditions $\xi(\theta)=\theta_s^{\frac{7-6}{3}}=\theta_s^{\frac{1}{3}}=\sqrt[3]{\theta_s}$ and so $D_l^s=\sqrt[3]{\theta_s}\cdot D_l^w \rightarrow D_l^s=\sqrt[3]{0.51}\cdot 2.06\cdot 10^{-9} \rightarrow D_l^s=1.646\cdot 10^{-9} \text{ cm}^2/\text{min}$.

($D_l^w(Cl_{25^\circ C})=2.06\cdot 10^{-9} \text{ cm}^2/\text{min}$) (Appelo & Postma, 1996). λ could be calculated by equations (4) and (5) (Table 2).

Table 2: Predicted values of D and λ for the experimental results assuming equilibrium CDE and physical non equilibrium (mobile-immobile) chloride displacement

Soil solution displacement by Chloride solution			
	V (cm/min)	D (cm ² /min)	$\lambda=D/v$ (cm)
CXTFIT fitted equilibrium-CDE	0,059482	0.365	6.14
CXTFIT fitted physical non-equilibrium-CDE	0,059482	0.319	5.36
Chloride displacement by deionized water			
	V (cm/min)	D (cm ² /min)	$\lambda=D/v$ (cm)
CXTFIT fitted equilibrium-CDE	0,059482	0.514	8.64
CXTFIT fitted physical non-equilibrium-CDE	0,059482	0.359	6.04

4. Conclusions

This work demonstrates the ability of low cost but laborious and time consuming laboratory experiment to recognize and describe soil solute transport processes. Additionally by such monofactorial laboratory experiments it is possible to describe the influence of each factor to BTC characteristics. At the same time this work showed the usefulness of tools such as the CXTFIT (STANMOD) for solving and understanding such complex processes.

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