

SOLUTE DISPERSION COEFFICIENTS IN HETEROGENEOUS POROUS MEDIA AS RELATED WITH THE MIGRATION OF PESTICIDES IN GROUNDWATER

CHRISTOS TSAKIROGLOU¹, DIMITRA TZOVOLOU¹, CHRISTOS AGGELOPOULOS¹,
MARIA THEODOROPOULOU², THEODORA DALKARANI², KONSTANTINOS
PIKIOS²

¹ *Institute of Chemical Engineering and High Temperature Chemical Processes – Foundation for Research and Technology, Stadiou str., Platani, P.O.Box 1414, GR-26504 Patras, Greece*

² *Technological Educational Institute of Patras, Department of Mechanical Engineering, Megalou Alexandrou 1, Koukouli, GR-26334 Patras, Greece*

ABSTRACT

Breakthrough curves of miscible displacement experiments performed on long columns of disturbed soils are employed to estimate the longitudinal dispersion coefficient as a function of the Peclet number and pore-scale heterogeneity. A 2-D numerical simulator of the transport / sorption / biodegradation of organic compounds in porous media is built and used to examine the transient spreading pattern of three pesticides (glyphosate, phorate, 2,4-D) in a macroscopically heterogeneous porous medium. The macrodispersion and flow channelling, associated with micro-scale heterogeneities, are reflected in the small and large thickness of the macroscopic pesticide dispersion front.

1. INTRODUCTION

The application of various types of pesticides to plants and soils is the main source of diffuse pollution for groundwater. There is variety of transport processes through which the organic chemicals of pesticides migrate in the subsurface environment (Weber and Miller, 1989) such as sorption, advection, dispersion, etc. In addition, the fate of organic compounds in the subsurface is closely related with the kinetics of chemical transformation processes such as the biodegradation, abiotic hydrolysis, photochemical reactions, etc.

The numerical simulation of the transport of pesticides in underground aquifers is complicated by the spatial and temporal variations of the physicochemical and biological characteristics of the soil (Aden et al., 2000; Stagnitti et al., 2001). For this reason, the macroscopic modeling of pesticide fate at the field scale is commonly based on assumptions (e.g. local equilibrium assumption, porous medium homogeneity, 1st order kinetics of biodegradation, etc), the validation of which requires consideration of the processes at the microscopic level (Harmon et al., 1989). In spite of the great deal of attention that has been paid on the assumptions related to sorption, biodegradation, and diffusion (Bouchard et al., 1989), the hydrodynamic dispersion has been overlooked. Experimental (Theodoropoulou et al. 2003; Tsakiroglou et al., 2005) and theoretical studies (Bruderer and Bernabe, 2001) of solute dispersion pore network models have revealed that both the longitudinal and transverse

dispersion coefficients (as well as the corresponding dispersivities) vary non-linearly with the Peclet number. One of the problems arising from such microscopic studies is to find out how important is the specific law relating the dispersion coefficient with Peclet number for the spreading of pesticide at the macroscopic scale.

In the present work, datasets of miscible displacement experiments performed on soil columns are employed to estimate the variation of the longitudinal dispersion coefficient with Peclet number for two soils: one with broad and another with narrow grain size distribution. These two different relationships are used as input data in a finite element numerical code that simulates the sorption / biodegradation / advection / dispersion of pesticides dissolved in water in a macroscopically heterogeneous porous medium. In this manner, the effects of the longitudinal dispersivity on the transient pattern of the pesticide spreading over the porous medium are clarified. The numerical code is employed to simulate the spreading pattern of three pesticides (glyphosate, phorate, and 2,4-D) in groundwater.

2. ESTIMATION OF DISPERSION COEFFICIENTS

2.1 Miscible displacement experiments on soil columns

The longitudinal dispersion coefficient was determined as a function of Peclet number by performing miscible displacement experiments on disturbed soil columns and monitoring the electrical conductance at 2-3 cross-sections along the column (Aggelopoulos and Tsakiroglou, 2005). The total length of the soil column is $L=30$ cm and its diameter $D=5$ cm. Two soil samples were tested: (1) a well-sorted commercial sand (S1) with narrow grain size distribution ($D_g=125-250$ μm), porosity $\phi=0.40$ and permeability $k=35.8$ Da; (2) a sandy soil (S2) with broad grain size distribution ($D_g=50-1400$ μm), porosity $\phi=0.36$ and permeability $k=21.8$ Da.

Miscible displacement experiments of a low NaCl concentration solution by a high NaCl concentration solution were performed on the sandy soils S1 and S2 at varying values of the Peclet number defined by

$$Pe = u_p \langle D_g \rangle / D_m \quad (1)$$

where $u_p = q/(\phi A)$ is the pore velocity, ϕ is the porosity, $\langle D_g \rangle$ is the mean grain diameter, and D_m is the NaCl-H₂O bulk diffusion coefficient ($D_m = 1.6 \times 10^{-9}$ m²/s). For the soil S1 ($\phi=0.4$, $\langle D_g \rangle=200$ μm) the solute concentration breakthrough curves were measured at two distances from the column inlet, whereas for the soil S2 ($\phi=0.36$, $\langle D_g \rangle=350$ μm) the solute concentration breakthrough curves were measured at three distances from the column inlet (Aggelopoulos and Tsakiroglou, 2005).

2.2 Dispersion coefficients

The non-linear Bayesian estimator of GREGPLUS solver of ATHENA software package was used to fit the experimental breakthrough curves to the analytic solution of the one-dimensional advection-dispersion equation (Tsakiroglou et al., 2005) and estimate

simultaneously the mean pore velocity, and the longitudinal dispersion coefficient, D_L (Fig.1a,b).

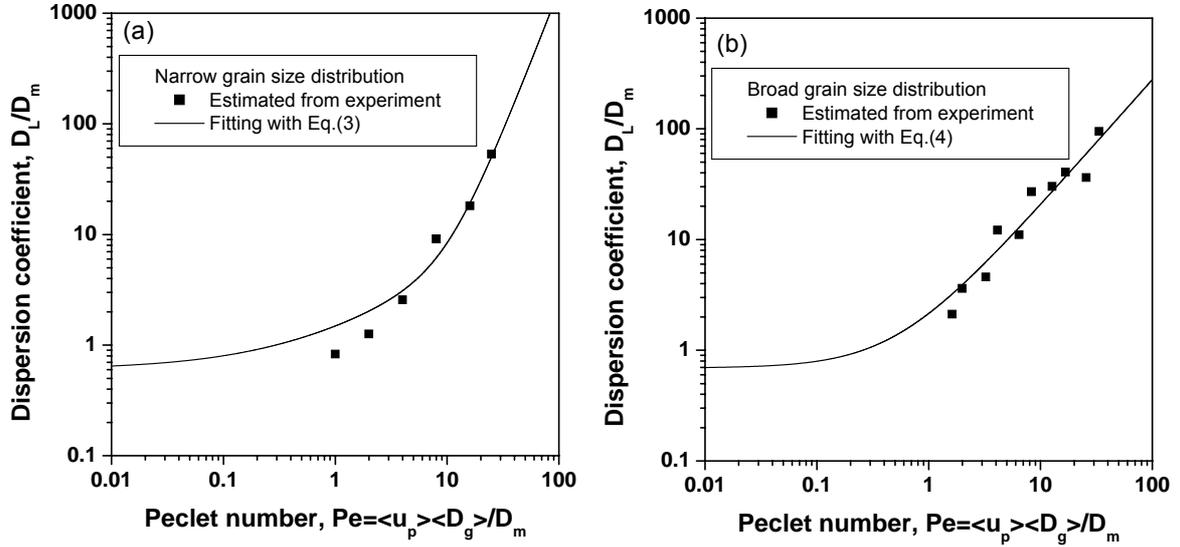


FIGURE 1. Longitudinal dispersion coefficient for soil with (a) narrow grain size distribution and (b) broad grain size distribution.

Concerning the soil S1, the breakthrough curves were reproduced perfectly whereas the estimated pore velocity was almost identical to its actual value calculated at each flow rate. However, we were unable to fit satisfactorily the breakthrough curves of soil S2 by using only one set of pore velocity and dispersion coefficient at a given Pe value. Because of the broad particle size distribution, the porous medium can be regarded as a dual one with the convective-dispersive process being controlled by two pairs of parameters. In this manner, two dispersion coefficients and two pore velocities were estimated simultaneously and were used to calculate the relationship $D_L(Pe)$ (Fig.1b). Moreover, it is assumed that at vanishing flow rates (as $Pe \rightarrow 0$) $D_L \rightarrow D_{eff}$, where D_{eff} is the effective diffusion coefficient and can be calculated from the measured values of the electrical formation factor, F and porosity (Sahimi, 1995). The estimated D_L of soil S1 was fitted with the model (Fig. 1a)

$$D_L/D_m = D_{eff}/D_m + b_1 Pe^m + b_2 Pe^l \quad (2)$$

where $D_{eff}/D_m = 0.6$ and produced the parameter values: $b_1 = 0.88$, $b_2 = 0.01$, $m = 0.64$, $l = 2.6$. Respectively, the estimated D_L of soil S2 was fitted with the model (Fig.1b)

$$D_L/D_m = D_{eff}/D_m + b_0 Pe^m \quad (3)$$

where $D_{eff}/D_m = 0.69$, and produced the parameter values: $b_0 = 1.46$, $m = 1.14$.

Given that Pe depends not only on the pore velocity but also on the average grain size, Eq.(1), it is crucial to define how these two parameters are interrelated. It is well-known from empirical relationships that $\langle D_g \rangle \propto k^{1/2}$, presuming that the porosity is kept constant.

Therefore, $\langle D_g \rangle$ and k can be interrelated through the simple scaling law

$$\langle D_{g2} \rangle = \langle D_{g1} \rangle (k_2/k_1)^{1/2} \quad (4)$$

3. SIMULATION OF CONTAMINANT FATE IN GROUNDWATER

The steady flow of groundwater that has already been contaminated by dissolved organic chemicals (pesticides) and can be regarded as a miscible displacement process where, the porous medium is initially ($t < 0$) occupied by an aqueous solution of solute concentration, $C_i = 0$, and at time $t = 0$, a solution of finite and constant solute concentration, $C_i = C_0$ is injected. The sorption of a pesticide on the solid surface is a strong function of the soil organic content and hydrophobicity of the solid surface and is correlated to the octanol/water partition coefficient (Eweiss et al., 1998). For the sake of simplicity we adopt the local equilibrium assumption (LEA) by considering sorption as an instantaneous process that is quantified by a distribution coefficient, K_d , and retardation factor, R_d given by (Harmon et al. 1989)

$$R_d = 1 + \rho_g K_d \quad (5)$$

where ρ_g is the solid grain density. The biological decomposition (biodegradation) of organic compounds depends in a complex manner on soil factors such as microbial species and population density (Eweis et al., 1998). When microbial biomass is optimum, it is common to express the biological breakdown of a compound as a 1st order reaction of the form

$$dC/dt = -\lambda C \quad (6)$$

where, λ is a rate coefficient that is related to the half-life time $t_{1/2}$ by

$$t_{1/2} = \ln 2/\lambda \quad (7)$$

The advection-dispersion, sorption, and biodegradation of an organic compound in a 2-D dimensional porous medium is described by the dimensionless mass balance

$$R_d \frac{\partial C^*}{\partial \tau} + u_\xi \frac{\partial C^*}{\partial \xi} + u_\zeta \frac{\partial C^*}{\partial \zeta} = \frac{\partial}{\partial \xi} \left(D_{\xi\xi} \frac{\partial C^*}{\partial \xi} + D_{\xi\zeta} \frac{\partial C^*}{\partial \zeta} \right) + \frac{\partial}{\partial \zeta} \left(D_{\xi\zeta} \frac{\partial C^*}{\partial \xi} + D_{\zeta\zeta} \frac{\partial C^*}{\partial \zeta} \right) - \lambda \frac{W^2}{D_m} C^* \quad (8)$$

The steady incompressible flow of a liquid with a density independent of the solute concentration is described by the continuity equation

$$\frac{\partial u_\xi}{\partial \xi} + \frac{\partial u_\zeta}{\partial \zeta} = 0 \quad (9)$$

whereas, ignoring gravity effects, the Darcy law is written

$$u_\xi = -\frac{f(\xi, \zeta)}{\phi} \frac{\partial P^*}{\partial \xi} \quad u_\zeta = -\frac{f(\xi, \zeta)}{\phi} \frac{\partial P^*}{\partial \zeta} \quad (10)$$

where the scalar function $f(x, y)$ represents the heterogeneity of a porous medium, regarded as a spatial variation of the local permeability from its average value $\langle k \rangle$. The dimensionless variables and parameters involved in the foregoing relations are defined by

$$\tau = tD_m/W^2 \quad \xi = x/W \quad \zeta = y/W \quad C^* = (C - C_0)/(C_i - C_0) \quad (11)$$

$$u_j = (W/D_m)u_i \quad i = x, y \quad j = \xi, \zeta \quad (12)$$

$$P^* = P\langle k \rangle/(\mu D_m) \quad (13)$$

$$D_{kl} = D_{ij}/D_m \quad i, j = x, y \quad k, l = \xi, \zeta \quad (14)$$

In addition, the components of the dimensionless dispersion tensor may be given by the approximate relationships (Bruggeman, 1999)

$$D_{\xi\xi} = D_{eff}/D_m + (a_T/W)(u_\xi^2 + u_\zeta^2)^{1/2} + [(a_L - a_T)/W]u_\xi^2 / (u_\xi^2 + u_\zeta^2)^{1/2} \quad (15a)$$

$$D_{\zeta\zeta} = D_{eff}/D_m + (a_T/W)(u_\xi^2 + u_\zeta^2)^{1/2} + [(a_L - a_T)/W]u_\zeta^2 / (u_\xi^2 + u_\zeta^2)^{1/2} \quad (15b)$$

$$D_{\xi\zeta} = D_{\zeta\xi} = [(a_L - a_T)/W]u_\zeta u_\xi / (u_\xi^2 + u_\zeta^2)^{1/2} \quad (15c)$$

The PDEs (8) - (10) coupled with the adequate initial and boundary conditions are solved along with the algebraic Eqs.(11)-(15) to determine the flow and solute concentration fields over a porous medium.

3.1 Numerical solution of transport equations in a heterogeneous porous medium

One of the most common characteristics of shallow aquifers is that high permeability sand lenses may be embedded within an otherwise homogeneous and low permeability soil. In order to represent such a heterogeneity, the permeability of a 2-D finite porous medium of width W and length L is considered everywhere constant ($f(\xi, \zeta) = 1$) except for a central segment where $f(\xi, \zeta) = 10$ (Fig.2a). The thickness of the porous medium along the z-axis is assumed equal to its width so that flow through a total cross-sectional area $A = W^2$ occurs. The lateral boundaries are impervious, and an aqueous solution of solute concentration $C^* = 1.0$ is injected at time $\tau = 0$ through a single source ($\xi = 0, \zeta_1 \leq \zeta \leq \zeta_2$) (Fig.2a). The aqueous solution outflows through an outlet port placed at the opposite side ($\xi = L/W, \zeta_1 \leq \zeta \leq \zeta_2$) of the porous medium (Fig.2a).

In order to investigate the effect of the functional form of the longitudinal dispersion coefficient (Fig.1a,b) on the pesticide transport pathways, Eqs.(8)-(10) were solved numerically with finite elements in the domain of the rectangular porous medium (Fig.2a) by using the commercial FlexPDE solver, and imposing flux type boundary conditions. The parameter values used in the simulations are given in Table 1. Two scenarios of heterogeneous porous media were examined: (a) Both the low (LPR) and high (HPR) permeability regions are soils with narrow grain size distribution (NGSD); (b) Both the LPR and HPR are soils with broad grain size distribution (BGSD). Depending on the dominant soil

type, Eqs.(2)-(4) were used to calculate D_L/D_m as a function of the local Pe , whereas it was assumed that $a_T = 0$.

TABLE 1. Parameter values used in simulations

Parameter	Value	Parameter	Value
Width, W (m)	1.0	Diffusion coefficient, D_m (m ² /s)	Glyphosate : 7.9×10^{-10} Phorate : 5.1×10^{-10} 2,4-D : 6.1×10^{-10}
Length, L (m)	1.2	Sorption coefficient, K_d (m ³ /kg)	Glyphosate : 61×10^{-3} Phorate : 18×10^{-3} 2,4-D : 5×10^{-3}
Permeability, k (D)	2.2	Half life time, $t_{1/2}$ (s)	Glyphosate : 4.06×10^6 Phorate : 5.2×10^6 2,4-D : 0.69×10^6
Porosity, ϕ	0.35		
Inlet / outlet port, ζ_1	0.45	Octanol/water partition coefficient, $\log K_{ow}$	Glyphosate : -3.5 Phorate : 3.33 2,4-D : 2.81 (pH=1) 0.75 (pH=7)
Inlet / outlet port, ζ_2	0.55		
Lower & left corner of HPR, (ξ_l, ζ_l)	(0.3,0.4)	Solubility, S (kg/m ³)	Glyphosate : 12.0 Phorate : 0.022 2,4-D : 0.62
Length of HPR, ξ_h	0.5	Flow rate, q (m ³ /s)	1×10^{-5}
Width of HPR, ζ_h	0.2	Grain density, ρ_g (Kg/m ³)	2700.0

4. RESULTS AND DISCUSSION

The macroscopic numerical simulator of contaminant transport in a heterogeneous porous medium was employed to determine the transient pattern of the spreading of several pesticides that are widely applied to agricultural cultivations of Western Greece: glyphosate, phorate, and 2,4-D. The physico-chemical properties of the pesticides (Table 1) were obtained from literature (Bascaran et al. 1996; Halfon et al., 1996; Yu and Zhou, 2005), whereas the diffusion coefficients at dilute aqueous solutions were calculated by using the Wilke-Chang correlation (Reid et al., 1977).

The solute dispersion front (SDF) is defined as the finite region within which the solute concentration changes appreciably. In both cases of NGSD and BGSD, the thickness of the SDF is relatively small in the LPR (Fig.3a-d) wherever the flow velocity is negligible and solute transport is controlled by diffusion (Fig.2b,c), or the flow velocity is finite (Fig.2b,c) but still so small ($D_L \propto Pe$) that solute transport is controlled by macrodispersion (Tsakiroglou et al., 2005).

However, the SDF widens over the HPR (Fig.3a-d) where the flow velocity and Pe increase sharply (Fig.2b,c). In the NGSD, at high flow velocities, solute transport is controlled by flow channelling (Taylor dispersion, $D_L \propto Pe^2$) which normally leads to a wide solute concentration profile (Tsakiroglou et al., 2005) so that the thickness of SDF increases significantly (Fig.3a,c). Regarding the NGSD, the SDF becomes wide not only over the HPR

but also over the LPR (Fig.3a,c), given that Pe increases at the vicinity of the outlet port (Fig.2b) as well. However, in the BGSD, macro-dispersion remains the dominant transport mechanism ($D_L \propto Pe$) even at high Pe values, with result that the thickness of the SDF (Fig.3b,d) is smaller than that observed in the NGSD (Fig.3a,c). These different pesticide spreading patterns in the two porous media (one with NGSD and one with BGSD) essentially arise from the different microscopic heterogeneity of the two media. In the NGSD porous medium, the spatial variation of the pore sizes is quite small and at increasing flow velocities, solute molecules follow the high velocity streamlines (flow channeling, Fig.1a). Instead, in the BGSD porous medium, the spatial variation of the pore sizes is very large and only interconnected clusters of large pores (critical paths) contribute substantially to both flow and dispersion (macro-dispersion, Fig.1b). The aforementioned phenomena become more evident for pesticide 2,4-D, where the retardation factor is small enough, and the “average pesticide velocity” ($\approx u_p/R_d$) is closer to the pore velocity (Fig.3c,d).

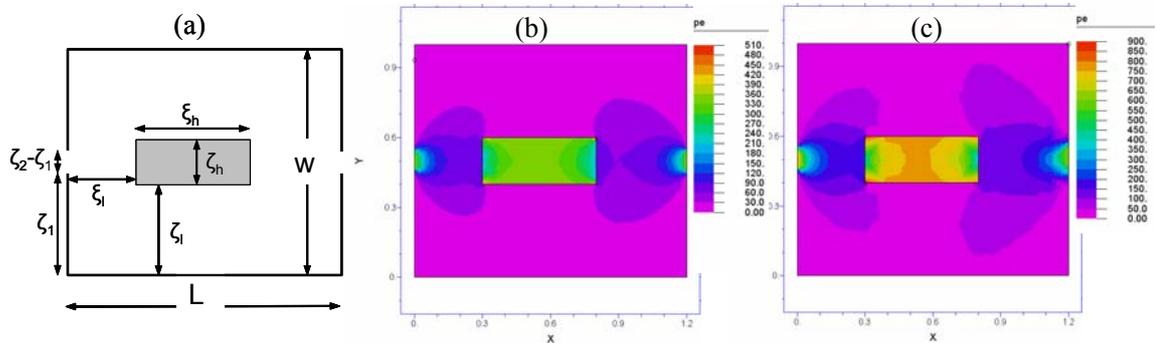


FIGURE 2. (a) Geometry of the 2-D porous medium. (b) Spatial distribution of the Peclet number over a porous medium having NGSD. (c) Spatial distribution of the Peclet number over a porous medium having BGSD.

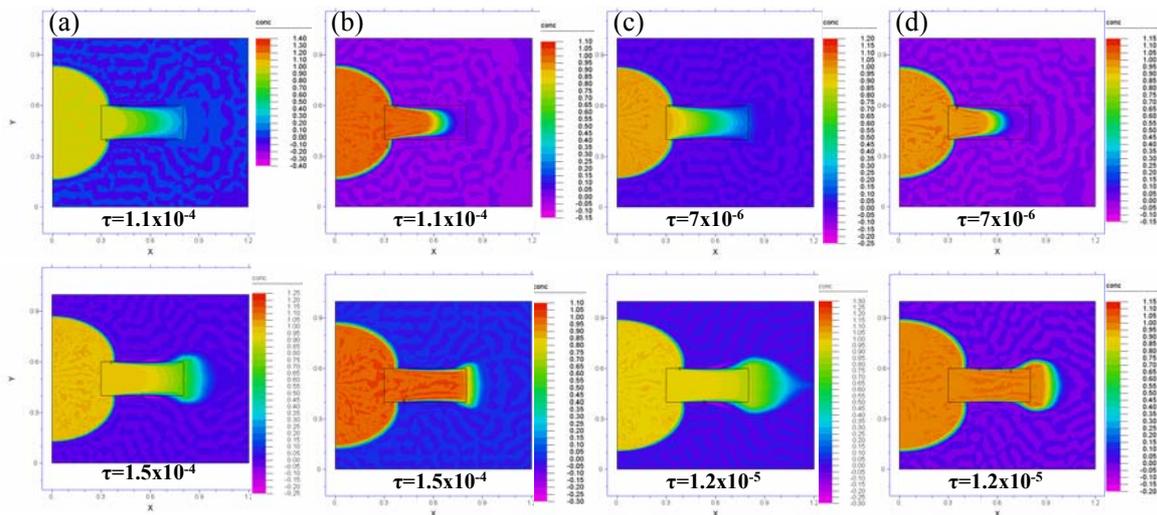


FIGURE 3. Simulated transient pesticide concentration profiles within the porous medium: Transient pattern of glyphosate spreading when both the LPR and HPR have (a) NGSD, and (b) BGSD. Transient pattern of 2,4-D spreading when both the LPR and HPR have (c) NGSD, and (d) BGSD.

The foregoing analysis revealed that the functional form of the dispersion coefficient, associated with microscopic heterogeneities and commonly overlooked in macroscopic simulations, is of key importance for predicting the pattern of pesticide spreading in aquifers.

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REFERENCES

1. Aden, K., and B. Diekkruger (2000), Modeling pesticide dynamics of four different sites using the model system SIMULAT, *Agricultural Water Management*, 44, 337-355.
2. Aggelopoulos, C. and C.D. Tsakiroglou (2005), Simultaneous determination of the two-phase flow and hydrodynamic dispersion coefficients of soils from transient immiscible and miscible displacement experiments, Paper SCA2005-58, *Proceed. of the 2005 International Symposium of the Society of Core Analysts*, August 21-25, 2005, Toronto, Canada.
3. Baskaran, S., N.S. Bolan, A. Rahman, and R.W. Tillman (1996), Pesticide sorption by allophanic and non-allophanic soils of New Zealand, *New Zealand J. of Agricult. Research*, 39, 297-310.
4. Bouchard, D.C., C.G. Enfield, and M.D. Piwoni (1989), Transport processes involving organic chemicals, In: *Reactions and Movement of Organic Chemicals in Soils*, B.L. Sawhney and K. Brown (eds), Soil Science Society of America, Madison, Wisconsin, USA.
5. Bruggeman, G.A., *Analytical Solutions of Geohydrological Problems*, Elsevier, Amsterdam, 1999.
6. Bruderer, C., and Y. Bernabe (2001), Network modelling of dispersion: transition from Taylor dispersion in homogeneous networks to mechanical dispersion in very heterogeneous ones, *Water Resour. Res.*, 37, 897-908.
7. Eweiss, J.B., S.J. Ergas, D.P.Y. Chang, and E.D. Schroeder (1998), *Bioremediation principles*, McGraw-Hill, NY, USA.
8. Halfon, E., S. Galassi, R. Bruggemann, and A. Provini (1996), Selection of priority properties to assess environmental hazard of pesticides, *Chemosphere*, 33, 1543-1562.
9. Harmon, T.C., W.P. Ball, and P.V. Roberts (1989), Nonequilibrium transport of organic contaminants in groundwater, In: *Reactions and Movement of Organic Chemicals in Soils*, B.L. Sawhney and K. Brown (eds), Soil Science Society of America, Madison, Wisconsin, USA.
10. Reid, R.C., J.M. Prausnitz, and T.K. Sherwood (1977), *The properties of gases and liquids*, McGraw-Hill, NY.
11. Sahimi M. (1995), *Flow and Transport in Porous Media and Fractured Rock: From Classical Methods to Modern Approaches*, VCH, Weinheim, Germany.
12. Stagnitti, F., L. Li, A. Barry, G. Allinson, J.-Y. Parlange, T. Steenhaus, and E. Lakshmanan (2001), Modeling solute transport in structured soils: performance evaluation of the ADR and TRM models, *Mathematical and Computer Modeling*, 34, 433-440.
13. Theodoropoulou, M., V. Karoutsos, C. Kaspiris, and C.D. Tsakiroglou (2003), A new visualization technique for the study of solute dispersion in model porous media, *J. Hydrology*, 274, 176-197.
14. Tsakiroglou, C.D., M.A. Theodoropoulou, V. Karoutsos, and D. Papanicolaou (2005), Determination of the effective transport coefficients of pore networks from transient immiscible displacement experiments, *Water Resour. Res.*, 41, W02014.
15. Weber, J.B., and C.T. Miller (1989), Organic chemical movement over and through soil, In: *Reactions and Movement of Organic Chemicals in Soils*, B.L. Sawhney and K. Brown (eds), Soil Science Society of America, Madison, Wisconsin, USA.
16. Yu, Y., and Q.X. Zhou (2005), Adsorption characteristics of pesticides methamidophos and glyphosate by two soils, *Chemosphere*, 58, 811-816.