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Mathematical and Computer Modelling 34 (2001) 433–440

MATHEMATICAL
AND
COMPUTER
MODELLING

www.elsevier.nl/locate/mcm

Modelling Solute Transport in Structured Soils: Performance Evaluation of the ADR and TRM Models

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(Received August 1999; revised and accepted April 2000)

Abstract—The movement of chemicals through the soil to the groundwater or discharged to surface waters represents a degradation of these resources. In many cases, serious human and stock health implications are associated with this form of pollution. The chemicals of interest include nutrients, pesticides, salts, and industrial wastes. Recent studies have shown that current models and methods do not adequately describe the leaching of nutrients through soil, often underestimating the risk of groundwater contamination by surface-applied chemicals, and overestimating the concentration of resident solutes. This inaccuracy results primarily from ignoring soil structure and nonequilibrium between soil constituents, water, and solutes. A multiple sample percolation system (MSPS), consisting of 25 individual collection wells, was constructed to study the effects of localized soil heterogeneities on the transport of nutrients (NO_3^-, Cl^-, PO_4^{3-}) in the vadose zone of an agricultural soil predominantly dominated by clay. Very significant variations in drainage patterns across a small spatial scale were observed (one-way ANOVA, $p < 0.001$) indicating considerable heterogeneity in water flow patterns and nutrient leaching. Using data collected from the multiple sample percolation experiments, this paper compares the performance of two mathematical models for predicting solute transport, the advective-dispersion model with a reaction term (ADR), and a two-region preferential flow model (TRM) suitable for modelling nonequilibrium transport. These results have implications

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The first author acknowledges funding support from the Australian Research Council's Large Grant Scheme (Grant Nos. A89701825 and A10014154); Department of Industry, Science and Tourism, International Collaboration (Grant #16), the Australia-India Council, and a travel fellowship from the Australian Academy of Science to the United Kingdom. The last author acknowledges funding support from the Indian Council of Scientific and Industrial Research.

PII: S0895-7177(01)00074-7

for modelling solute transport and predicting nutrient loading on a larger scale.

Keywords—Advective-dispersion equation, Preferential flow, Numerical methods, Solute transport, Nutrients, Nitrate, Chloride, Phosphate, Pollution..

1. INTRODUCTION

The movement of chemicals through the soil to the groundwater or discharged to surface waters represents a degradation of these resources. In many cases, serious human and stock health implications are associated with this form of pollution. The chemicals of interest include nutrients, pesticides, salts, and industrial wastes. In the case of nutrients, leaching losses also represent a decline in soil fertility with economic consequences, and in the case of nitrate leaching, reduction of productivity due to soil acidification [1,2]. In the case of pesticides and industrial wastes, small but highly toxic chemicals can be transported to groundwater and remain there for hundreds and even thousands of years [3–7].

Monitoring and modelling solute transport is complicated by nonrandom spatial and temporal variations of physical, chemical, and biological components of soils. Laboratory experiments based on repacked, sterile, homogenized soil cores bear little resemblance to physical reality and have often been shown to underestimate the solute loss and risk of contamination to groundwater reserves [8]. Hence, a better knowledge of the factors causing nonequilibrium and heterogeneous solute transport is required for sustainable ecological management of nutrients in agricultural soils [9]. Multiple sample percolation systems are an excellent means to obtain accurate values of the solute and water flux in vadose zone experiments and have been shown to effectively represent the impacts of soil heterogeneity on these fluxes [10]. Using this apparatus, an experiment was recently conducted to investigate the impacts of soil structure on nutrient transport in an agricultural soil typically found in Victoria, Australia [11]. The data from this experiment is used here to compare and contrast two approaches to modelling solute transport in the unsaturated zone. The models considered in this paper are the advective-dispersion equation with reaction (ADR) and a two-region preferential flow model (TRM).

2. MATERIALS AND METHODS

Free-draining, undisturbed soil columns offer the best means to study nutrient transport under field conditions because they preserve the natural structure of the soil. A large undisturbed soil core (42.5 cm × 42.5 cm wide × 40 cm deep) was extracted from a farm located in the Western District of Victoria, Australia. A multiple sample percolation system was constructed to sample moisture and chemicals leaching from the soil core. The multiple sample percolation system consists of a metal-alloy base-plate that is shaped into 25 equal sized collection wells (funnels) or mini-catchments. Leachate solutions were analysed for NO_3^-, Cl^-, and PO_4^{3-}. The daily leachate concentrations collected from each of the 25 individual collection wells were aggregated to calculate a total daily concentration for the entire soil core for each ion for each day of the duration of the experiment. The daily total concentrations were used to fit concentration breakthrough curves for the TRM and ADR models. The full experimental details are described in [8].

3. THEORY

3.1. Equilibrium Transport Model (ADR)

The most challenging problem confronting mathematical modelling of solute transport in field soils is how to effectively characterize and quantify the geometric, hydraulic, and chemical properties of porous media. Recently, Stagnitti *et al.* [10] and de Rooij and Stagnitti [12] proposed the use of the beta distribution to describe the statistical variation in solute and moisture patterns. However, this approach provides little insight into the complex physical and chemical processes that govern adsorption and transport in soils. The issue of how to deal with heterogeneity in the soil remains unresolved. To date, therefore, it is not surprising that very few attempts have specifically included soil structure in modelling solute transport [13]. To reduce the complexity involved in modelling solute transport, many models rely on the simplifying assumption of homogeneous soil structure and instantaneous sorption, sometimes referred to as the LEA (linear equilibrium adsorption) assumption. The general equation governing contaminant transport under saturated, steady flow conditions, and with chemical reaction, has the form of the classical advection-dispersion-reaction equation [14]

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - V\frac{\partial C}{\partial z} - \gamma C, \tag{1}$$

where R is the retardation factor (which is equal to $1 + \rho k/\theta$ and where ρ is the density of water, k is the distribution coefficient of absorption, and θ is the water content), γ is the reaction rate coefficient, D is the dispersion coefficient, and V is the pore water velocity. Analytical solutions to equation (1) for most practical circumstances have been compiled by Parker and van Genuchten [14], van Genuchten and Alves [15], and Barry and Sposito [16].

3.2. Nonequilibrium Transport Model—The Two Region Model (TRM)

The ADR has a simple form because it describes an ideal process, i.e., equilibrium transport. However, the LEA assumption is normally not valid in field studies. Nonideal transport (nonequilibrium transport) as observed in many experiments is more the norm than the exception. The causes of nonequilibrium transport in soils are soil heterogeneity and chemical nonequilibrium sorption [17]. Nonequilibrium transport is mainly due to physical and chemical phenomena reflecting the heterogeneous properties of soils. Also, biological forces are increasingly being recognized as a source of nonequilibrium [13]. In this paper, we examine the nonequilibrium transport caused by possible preferential flow through the soil column. Based on the bicontinuum conceptualization, Coats and Smith [18] developed the two-region model (TRM) to describe nonequilibrium solute transport in aggregated soils. The governing equations are

$$R\frac{\partial C_m}{\partial t} + \frac{1-\beta}{\beta}\frac{\partial C_{im}}{\partial t} = D\frac{\partial^2 C_m}{\partial z^2} - V_m\frac{\partial C_m}{\partial z}, \tag{2a}$$

$$\frac{1-\beta}{\beta}\frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im}), \tag{2b}$$

where the subscripts m and im denote regions in which mobile and immobile solute transport may occur, β is the ratio of the mobile region to the entire pore volume, i.e., $\beta = \theta_m/(\theta_m + \theta_{im})$, θ is water content, V_m is the flow velocity in the mobile region and the velocity in the immobile region is zero by definition (so the averaged flow velocity is $V_m\beta$), and ω is the rate coefficient (in the nondimensional form, $\alpha = \omega L/V_m$, and L is the column length).

The bicontinuum concept physically represents the soil structure in aggregated soils. The region within the aggregates is the immobile region where water and solutes are stagnant except for lateral diffusion. The region between the aggregates is the mobile region where water and solute move due to advection and dispersion. The lateral diffusion has been simplified by using the first-order equation (2b). Although this model was originally developed for solute transport in aggregated soils, it is often used to model other nonequilibrium transport processes. For example, Coats and Smith [18], Herr *et al.* [19], and Li *et al.* [20] have reported applications of this model to solute transport in stratified soils. Herein, we report the use of the TRM to investigate solute transport in an undisturbed soil column and compare it with the ADR.

4. RESULTS AND DISCUSSION

4.1. Effects of Spatial Variability in Leaching

Table 1 presents the daily average volume of leachate collected for each well of the multiple sample percolation system. The data has been ranked in order of magnitude of eluted leachate. Wells 1 to 5, 6, 10, 11, 15, 16, 20, and 21 to 25 were located on the edge of the percolation system, and these surrounded the inner wells numbered 7 to 9, 12 to 14, and 17 to 19. The table illustrates substantial heterogeneity in percolation rates from the core. The eluted volumes for each well were found to be statistically very highly variable (one-way ANOVA, $p < 0.001$).

Table 1. Average daily volume of soil moisture collected by each MSPS well. The data are the arithmetic mean and standard errors determined over an 18 day period.

Low Flow Wells			Medium Flow Wells			Rapid Flow Wells		
Well No.	Mean	St. Err.	Well No.	Mean	St. Err.	Well No.	Mean	St. Err.
8	11.9	5.38	14	84.8	7.49	21	133.0	36.52
3	26.5	5.39	18	87.0	6.71	7	135.0	9.06
1	31.4	3.23	12	106.7	7.08	24	142.7	25.32
2	55.5	8.94	13	117.9	8.57	22	197.2	37.77
6	57.5	11.75	16	120.6	10.69	23	199.2	35.41
11	60.0	6.19	10	123.1	19.92	5	204.3	33.25
4	66.8	9.85	19	127.7	13.86	25	241.4	44.49
17	84.3	16.93	9	131.3	12.49	20	307.1	43.61
						15	333.5	49.38

Figure 1 presents the results from one of the experiments conducted on the undisturbed, free-draining, field soil. The cumulative solute mass and volume of soil-moisture eluted from the core were monitored over an 18 day period. The irrigation rate applied to the surface of the core was uniform in time and areal coverage. Percolation of soil-water from the core was nearly uniform as indicated on the figure with a close correspondence to a one-to-one line. The relative mass of NO_3^- leaching from the core was very closely matched to the relative amount of Cl^-, indicating that Cl^- may be a suitable proxy for NO_3^- in solute transport studies. As much as 50% of the applied mass of Cl^- and NO_3^- leached from the core in 30% of the applied irrigation within five days after application, indicating very rapid transport. However, within the same time period, less than 15% of the applied PO_4^{3-} leached from the core, indicating strong adsorption.

4.2. Modelling Results

Solute breakthrough curves (BTC) are presented in Figures 2 to 4. The rate of evapotranspiration was determined from a water budget over the 18 days. The average rate was approximately 25%. Using this value, the initial solute concentrations in the irrigation were determined to be $C_{0\_\mathrm{Cl}} = 6186.10\,\mathrm{mg/L}$, $C_{0\_\mathrm{NO}_3} = 273.65\,\mathrm{mg/L}$, and $C_{0\_\mathrm{PO}_4} = 4724.10\,\mathrm{mg/L}$. The duration time for irrigation of the solutes was $T = 0.484$ days (input pulse). For each simulation, it was assumed that the initial (resident) concentrations of solutes in the soil were negligible; i.e., $C_i = 0\,\mathrm{mg/L}$. Using these values, the ADR and TRM were fitted to the Cl^- data, and BTCs are shown in Figures 2a and b. The fitting was achieved using simulated annealing [21]. Simulated annealing is a better technique for finding global optima than traditional gradient-type approaches such as nonlinear least squares methods [22]. Assuming that Cl^- behaves as a conservative element, then $\gamma = 0$ (i.e., no reaction) and $R = 1$ (i.e., no adsorption). The optimal values for the fitted parameters in the ADR were $V = 0.051\,\mathrm{m/d}$ and $D = 0.006\,\mathrm{m^2/d}$ (see Figure 2a). The model failed to match the data at the peak. The lack of agreement is due to the failure of the ADR to model the nonequilibrium effects caused by the observed heterogeneity in

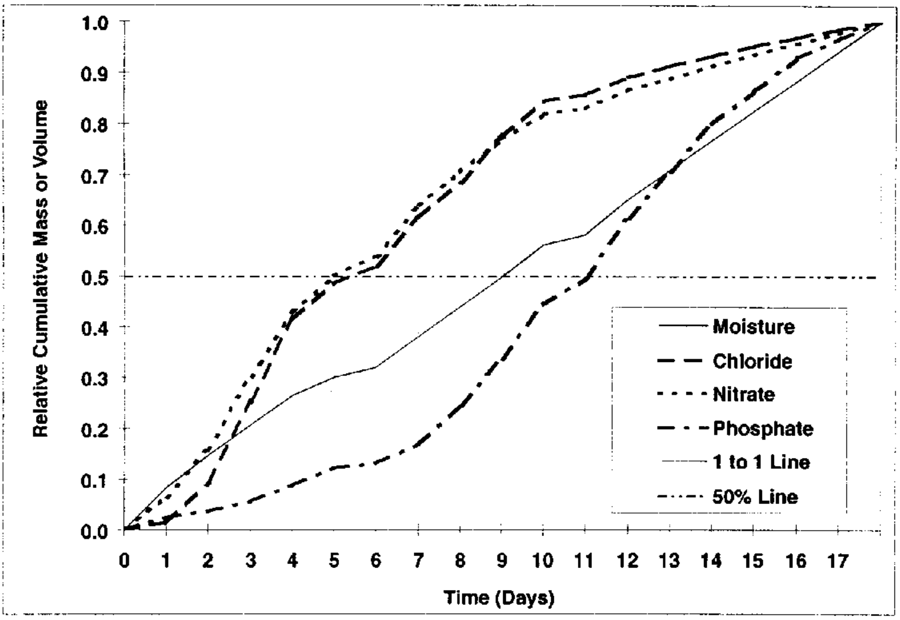

Figure 1. Relative cumulative mass of solutes and volume of eluted soil-water collected for all wells plotted as a function of time.

percolation rates. The fitted velocity and dispersion coefficients, however, are within the experimental constraints. The TRM was fitted to the data (see Figure 2b), and the optimal values for the model parameters were $V_m = 0.057\,\mathrm{m/d}$, $D = 0.001\,\mathrm{m^2/d}$, $\beta = 0.47$, and $\alpha = 1.72$. The predicted and actual BTCs are in excellent agreement, suggesting that nonequilibrium transport of Cl^- has occurred. The results also verify that little to no retardation of chloride in the core occurred. The fitted parameter values are also within experimental constraints and they have physical meaning. In particular, the averaged flow velocity, calculated according to $V_m\beta$, is in accordance with the experimental data. The fitted value for β is close to 0.5, which indicates that nearly 50% of the pore volume is actively responsible for Cl^- transport. This too is supported by experimental observations.

The predicted BTC for NO_3^- using the ADR is plotted with the actual BTC in Figure 3a. In this case, knowledge gained from fitting the BTCs for Cl^- is used to hold the values for V and D constant. The values for V and D determined from fitting the ADR to the Cl^- data set are used for the NO_3^- data set. However, in this case, the possibility of adsorption and reaction of NO_3^- is possible and therefore permitted; i.e., R and γ become "free" parameters and their values are determined by optimization. The optimal values for R and γ were found to be 1.06 and $0.035\,\mathrm{d}^{-1}$, respectively, indicating a small adsorption and significant reaction rate. These parameter values also make sense physically, e.g., resulting from mineralization and denitrification in the soil. The fit is surprisingly good even though the ADR does not explicitly include assumptions of variable flow domains. In a similar fashion, the values for the parameters V_m, D, β, and α in the TRM were fixed to be the same as those determined for the Cl^- BTC. In this case, however, the only free parameter is R. The optimal value for R was found to be 1.27, and the predicted BTC is presented in Figure 3b. The TRM overpredicted the concentration peak. This is not surprising, as the TRM in its present form does not contain a reaction term. The better performance of ADR in this case most likely results from the extra freedom of having two free parameters rather than one. Indeed, if the TRM included reaction, then the performance for nitrate prediction will undoubtedly improve. The phosphate experimental data showed strong adsorption and reaction (see Figure 1). For this reason, we did not fit the TRM to this data set. Figure 4 presents the predicted BTC using the ADR with V and D fixed to the same values as determined for the Cl^- BTC and R and γ fitted by optimization. The optimal values for R and γ were 8.117 and

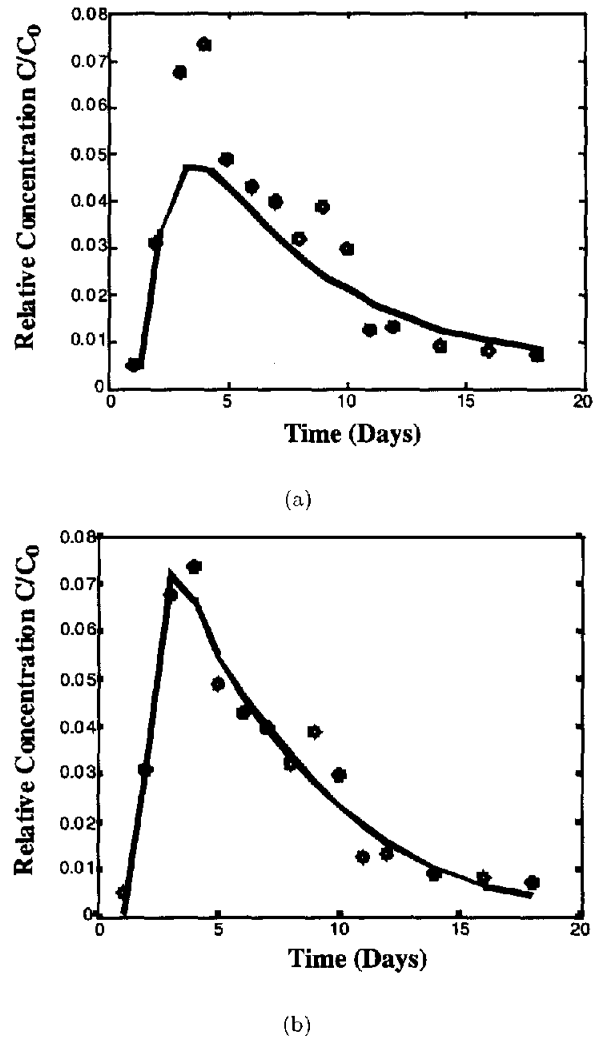

Figure 2. Comparison of breakthrough curves for chloride using (a) ADR and (b) TRM. Experimental data are circles, and model predictions are solid lines.

$\gamma = 1.781\,\mathrm{d}^{-1}$, respectively, indicating, as expected, very strong adsorption and quick reaction. The ADR predicted the data reasonably well. Again, the good performance of the ADR here does not necessarily imply that nonequilibrium transport is negligible; rather it may be due to the extra freedom in the fitting process. Also, the reaction rate appears to be too fast to be physically realistic.

5. CONCLUSIONS

Soil structure has an important role in distributing moisture and solutes. Considerable small-scale heterogeneity in the volume and solute concentrations in the percolate was observed. The performance of two models, the ADR and TRM, were contrasted and compared. The ADR model performed reasonably well even though the experimental data exhibited considerable heterogeneity in the percolation rate and solute concentrations. There are currently no analytical solutions for the TRM with a reaction term. Consequently, the TRM in its present form can only be expected to perform well for solutes that have negligible reaction times (e.g., conservative tracers). We are presently developing a numerical solution for the TRM that incorporates a reaction term. This solution will also be coupled to an annealing optimization algorithm. We anticipate that this model will significantly improve the predictions of nonequilibrium solute transport in field soils.

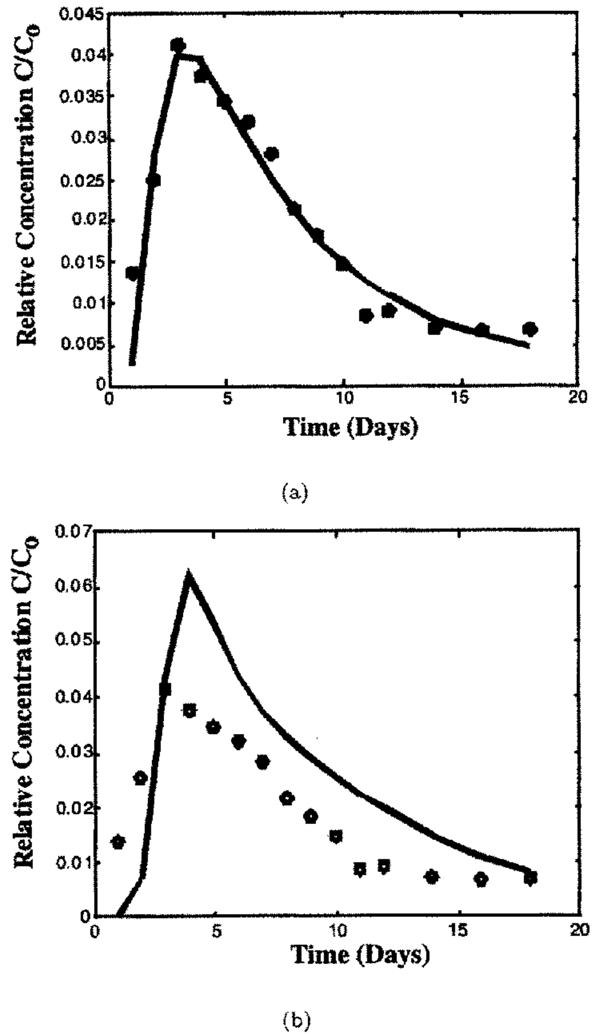

Figure 3. Comparison of breakthrough curves for nitrate using (a) ADR and (b) TRM. Experimental data are circles, and model predictions are solid lines.

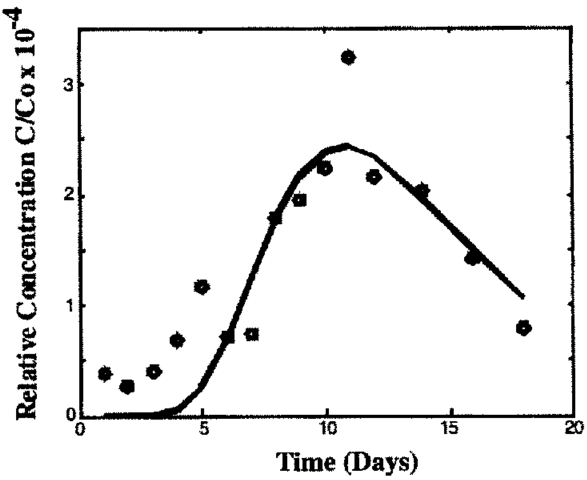

Figure 4. Breakthrough curve for phosphate predicted using TRM. Experimental data are circles, and model predictions are solid lines.

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