Modeling Chemical Transport in the Unsaturated Zone of the Subsurface

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1 INTRODUCTION

Because of the increasing emphasis in agriculture on monocultures and the intensive breeding of animals for food, the unsaturated zones of many unconfined aquifers are receiving greater quantities of nitrate fertilisers and a wide variety of pesticides and herbicides designed to control the growth of unwanted plants, insects, and other invertebrates (Vrba and Romijn, 1986). In addition, the unsaturated zone has been used for many years for the disposal of a wide variety of synthetic organic chemicals and for storage tanks containing liquid chemicals and fuel.

Because of continued overuse of agricultural chemicals and the leakage of chemicals from disposal sites and storage tanks, these chemicals have accumulated in the unsaturated zone. They have gradually migrated into underlying aquifers ultimately contaminating water resources used for drinking water, for irrigation of agricultural crops, and for many industrial uses (Pye, 1982). To prevent continued contamination of underlying groundwater resources and to develop more effective methods of cleaning up contaminated aquifers, it is necessary to have reliable mathematical models to describe chemical transport in the unsaturated zone of the subsurface. With these models, not only can concentrations of toxic chemicals in drinking water be predicted, but also a large number of possible modifications of present practices and possible reclamation strategies can be examined prior to actual field evaluation.

A possible mathematical description of transport in the unsaturated zone is given in Appendix A. From these equations presented in integral form, transport in the unsaturated zone is certainly complex. Transport in the unsaturated zone involves the transport of more than one phase through an unconsolidated porous medium. Accurately describing transport in the unsaturated zone must include the simultaneous solution of field equations for transport of moisture, heat, and chemicals.

The equations given in Appendix A represent a deterministic approach to describe these transport phenomena, and have been assembled from

reports and investigations by Philip and de Vries (1957), Bear (1972), Duguid and Reaves (1976), Milly (1982), and Lindstrom and Piver (1985). Model equations for transport in the unsaturated zone are derived from the integral forms of the equations in Appendix A by converting surface integrals to volume integrals with Gauss' theorem, multiplying both sides by $1/v$ and letting v approach $0+$. When adjoined with appropriate boundary conditions, the equations in Appendix A represent a complete phenomenological description of transport in the unsaturated zone of the subsurface.

For such complex deterministic models, numerical methods of solution are required. These equations are non-linear, and important transport variables and coefficients have spatial and moisture content variability. For the deterministic model presented in Appendix A, two common approaches for solution are finite difference and finite element approximations of the defining set of field equations. Even though these approximate methods make it possible to solve these equations, approximating the defining equations introduces artifacts that can produce calculation errors in the solution vector for chemical concentrations. For transport in the saturated zone of the subsurface, criteria have been established to minimise the influence of these approximation errors. These criteria will be described as background for recommendations to develop similar criteria for transport equations for the unsaturated zone.

Referring to the three field equations in Appendix A, the data requirements for transport variables and coefficients are very large. Several examples of empirical methods that have been developed to overcome this data deficiency are given in Appendix A. Presently available empirical and semi-empirical methods for several of the most important variables and coefficients will be described with recommendations for future activities. There is a wide variety of soil types that can be present in the subsurface, but the variables and coefficients that have been chosen are probably the most important for describing transport. In the development of better methods to estimate values for these chemical transport variables and coefficients, much more attention must be given to the chemical interactions between the chemical and the constituents of the porous media.

2   NUMERICAL DISPERSION AND OSCILLATORY BEHAVIOUR IN THE SOLUTION VECTOR FOR CHEMICAL TRANSPORT

With finite difference and finite element approximations for the defining set of transport equations, two particular problems produce errors in the calculation of chemical concentrations: numerical dispersion and oscillatory behaviour in the solution vector for chemical transport. The actual details for constructing finite difference and finite element approximations for these

equations are given by Finlayson (1975), Pinder and Gray (1977), Lapidus and Pinder (1982), and Wang and Anderson (1982).

Both problems are a function of nodal spacing, but their impacts on the solution are different. When nodal spacing is too great, numerical dispersion can give a greater value to the dispersion coefficient, thus giving the appearance that transport is more rapid than it really is. Oscillatory behaviour in the solution vector causes the concentration to change from a positive to a negative value. This occurs in the vicinity of steep concentration gradients, usually at the edge of a concentration plume. Both problems have been described by a number of investigators. Among the earliest were Peaceman and Rachford (1955, 1962) and Price et al. (1966). More recently, methods to reduce oscillatory behaviour have been proposed by a number of authors. Sun and Yeh (1983) and Heinrich et al. (1977) have proposed upstream weighting functions for multi-dimensional problems that use finite element methods of approximation. The weighting functions are designed to reduce oscillatory behaviour in the solution vector for concentration in the vicinity of steep gradients.

The problems of numerical dispersion and oscillatory behaviour in the solution vector can be illustrated with the one-dimensional, isothermal simplification of the chemical transport equation given in Appendix A. There is no vapour transport (saturated flow); the fluid velocity, dispersion coefficient and properties of the porous media are constant in time and space. The isothermal isotropic one-dimensional chemical transport equation in the saturated zone is given as

$$\frac{\partial}{\partial t}\left(1 + \rho_B K_d\right) C = D\,\frac{\partial^2 C}{\partial z^2} - V\,\frac{\partial C}{\partial z} - \Lambda C \tag{1}$$

where all transport properties have been previously defined except Λ which is the combined rate constant for chemical transformation by abiotic and biotic mechanisms in the liquid phase, h^{-1}.

The initial and boundary conditions are given as

$$C(z,0^+) = f(x);\, f \text{ integrable over the domain } [0,\infty] \tag{2}$$

$$C(0,t) = 0 \tag{3}$$

$$\lim_{z\to\infty} \frac{\partial C}{\partial z} = 0$$

Dividing by the retardation factor, $1 + \rho_B K_d$, gives the scaled variables and coefficients as

$$D^* = \frac{D}{1 + \rho_B K_d} \tag{5}$$

$$V^* = \frac{V}{1 + \rho_B K_d} \tag{6}$$

$$\Lambda^* = \frac{\Lambda}{1 + \rho_B K_d} \tag{7}$$

For both numerical methods, the subsurface is subdivided into a network of node points, $z_i = z_1, z_2 \ldots z_{n-1}, z_n$. Using a space-centered approximation scheme generates a set of linear equations that represent the transport equation at each node point. The coefficients of this set of equations for the finite difference method have the form

$$a_{FD} = -\left[D^* + \frac{V^* \Delta z}{2} \right] \frac{\Delta t}{\Delta z^2} \tag{8}$$

$$b_{FD} = 1 + \frac{2 D^* \Delta t}{\Delta z^2} + \Lambda^* \Delta t \tag{9}$$

$$c_{FD} = -\left[D^* - \frac{V^* \Delta z}{2} \right] \frac{\Delta t}{\Delta z^2} \tag{10}$$

where a_{FD}, b_{FD} and c_{FD} are the components of the coefficient matrix; FD stands for finite difference; Δz is the spacing between node points, cm; and Δt is the spacing between time steps, h.

For the Galerkin finite element method using Chapeau basis functions, the tridiagonal elements of the coefficient matrix are

$$a_{FE} = -6\left[D^* + \frac{V^* \Delta z}{2} \right] \frac{\Delta t}{\Delta z^2} + (1 + \Lambda^* \Delta t) \tag{11}$$

$$b_{FE} = 12 \frac{D^* \Delta t}{\Delta z^2} + 4(1 + \Lambda^* \Delta t) \tag{12}$$

$$c_{FE} = -6\left[D^* - \frac{V^* \Delta z}{2} \right] \frac{\Delta t}{\Delta z^2} + (1 + \Lambda^* \Delta t) \tag{13}$$

where the designation FE in the subscripts for the three elements of the tridiagonal matrix stand for finite element method.

In elements a_{FD}, c_{FD}, a_{FE} and c_{FE}, there are terms of the form $D^* \pm V^* \Delta z/2$. D^* is the true term for dispersion in the chemical transport equation and $V^* \Delta z/2$ is the true term for advection. It has been shown by Peaceman and Rachford (1955, 1962) and Richtmyer and Morton (1967)

that the nodal spacing criteria to minimise numerical dispersion in both the finite difference and finite element methods are given as

$$0 < \Delta z \le \frac{2D^*}{|V^*|} \le 2\alpha_L \tag{14}$$

where α_L is the longitudinal dispersivity of the porous media, cm.

For non-oscillatory behaviour with the finite difference method, Varga (1962) has established by analysis of the spectral distribution of the coefficient matrix that the same nodal spacing criteria required to minimise numerical dispersion are also the criteria to minimise oscillatory behaviour in the solution vector.

Using the analysis of the spectral distribution of the coefficient matrix generated with the finite element method, criteria for nodal spacing to minimise oscillatory behaviour in the finite element method are adapted from Price *et al.* (1966) and are given as

$$0 > \Delta z \le \frac{\dfrac{6D^*\Delta t}{1+\Lambda^*\Delta t}}{\sqrt{\left[\dfrac{6D^*\Delta t}{1+\Lambda^*\Delta t} + \dfrac{9|V^*|^2\Delta t^2}{4(1+\Lambda^*\Delta t)}\right]} + \dfrac{3|V^*|\Delta t}{2(1+\Lambda^*\Delta t)}} \tag{15}$$

Using nodal spacing crtieria from saturated transport to set nodal spacing criteria in unsaturated transport builds in a conservative estimate of nodal spacing criteria because all terms in these coefficients are functions of moisture content, and in the unsaturated zone moisture content is usually less than the saturated moisture content. When these criteria are used, numerical dispersion and oscillatory behaviour in the solution vector for chemical concentration in the unsaturated zone should be minimised.

3 DATA REQUIREMENTS FOR TRANSPORT MODELS

Whereas the equations given in Appendix A may represent the physics, chemistry, and biology of transport in the unsaturated zone, they also contain many variables and coefficients for which field data either are unavailable or are available only on a very limited basis. For transport through partially saturated porous media, the variables and coefficients needed to describe transport are functions of position, moisture content and temperature. For many contaminants in the subsurface, the most important transport processes appear to be hydrodynamic dispersion, convection, sorption, and chemical degradation/transformation (Kincaid *et al.*, 1984).

For hydrodynamic dispersion, empirical methods were first developed by Bear and Bachmat (1967) for longitudinal dispersivities. More recently,

Neuman *et al.* (1987) have described methods to determine longitudinal and transverse dispersivities. However, all these methods are for saturated flow, and need to be extended to transport in the unsaturated zone. In the equations for chemical transport given in Appendix A, it is assumed that the dispersion coefficient for the vapour phase is equal to the molecular diffusivity of the chemical in the vapour phase. This is a first approximation, and many more fundamental studies are required on hydrodynamic dispersion in both the saturated and unsaturated zones of the subsurface.

For hydraulic conductivity and moisture tension, Kool *et al.* (1985; 1987) and Lindstrom and Piver (1985) have developed empirical models that cover a wide range of soil conditions and moisture contents. Both methods are power law representations, and use data for hydraulic conductivity and moisture tension from a large number of soil types to develop empirical parameters used in these relationships.

Sorption studies and methods to calculate sorption coefficients have mainly been confined to sorption of organic chemicals to organic matter in soils. Most of these studies depended on correlations between the octanol/water partition coefficient and the water solubility of the chemical (Chiou *et al.*, 1982). The sorption coefficient to organic matter was directly proportional to the octanol/water partition coefficient and inversely proportional to water solubility. More recently, Sabljic (1987) developed a correlation that depends on the molecular properties of the chemical, and can be used to predict sorption coefficients for chemicals with diverse molecular structures. This is an important beginning, but much more fundamental information is required on the structure of humic substances and mechanisms of sorption (Wershaw, 1986).

Degradation and/or transformation of chemicals in the subsurface occurs by abiotic and biotic mechanisms (Armstrong and Konrad, 1974; Alexander, 1981). For chemicals such as chloroaromatics that are very persistent in soils, biotic mechanisms are probably the primary mechanisms of degradation (Alexander, 1981). These are very slow processes mediated by microorganisms that can be approximated by first-order reaction rate kinetics. For chemicals with very short persistence times in soils, such as some classes of triazines and organophosphates, degradation mechanisms are probably a combination of abiotic mechanisms such as hydrolysis and microbiologically mediated oxidative processes (NRCC, 1981). Even with complicated degradation mechanisms, because of the low water solubilities of many of these chemicals, degradation reactions can still be approximated very well with first-order reaction rate kinetics. Whereas most studies of chemicals in soils focus on degradation kinetics and mechanisms of biological decay, clay surfaces have been shown to be very effective in promoting the polymerisation or oligomerisation of benzene and benzene derivatives (Soma *et al.*, 1986; Laszlo, 1987). Both degradation and transformation mechanisms for chemicals present in the subsurface are very complex. Much more

fundamental work remains to be done on abiotic and biotic reaction mechanisms in porous media with variable compositions.

4 CONCLUSIONS AND RECOMMENDATIONS

The discussion of predictive models and data requirements for these models has described many important research needs, all of which are directed at developing reliable methods to predict chemical transport in the unsaturated zone. The models that have been described for transport in the unsaturated zone are deterministic. Indeed, because of the spatial variability of many of the important transport variables and coefficients needed to describe not only transport in the unsaturated zone but also in the saturated zone, stochastic models may be more appropriate. Several authors who have developed stochastic models for transport in the saturated zone are Gelhar (1976), Gelhar and Axness (1983), Gutjahr *et al*. (1978), and Neuman *et al*. (1987). Because both deterministic and stochastic approaches are valid for describing transport in the subsurface, continued development of both methods should proceed. In this development process, the two approaches should be applied to a wide range of problems of contamination of the unsaturated zone and their results compared. Strengths and weaknesses of each method for a variety of conditions should be clearly identified. Criteria should be identified that minimise the effects of mathematical artifacts on the ability of the model to predict changes in chemical concentration in space and time.

In the development of methods to estimate the many variables and coefficients needed in these models, much laboratory and field work is required to examine in more detail mechanisms of transport and transformation through porous media. Because dispersivities may be regarded as a mixing length for dispersion, a better understanding of dispersion may be available from theories and studies in turbulent heat and fluid flow. Water conductivity is a strong function of pore geometry, and methods to estimate water conductivities in the unsaturated zone must also include consideration of hysteresis. Sorption studies must include much more consideration of the interactions of the chemical and the substrate. Not only should consideration continue to be given to understanding sorption mechanisms for organic matter but also to clay minerals. The revelation that clay surfaces can promote the polymerisation of organic chemicals adds new incentive to developing techniques that examine the molecular interactions between chemicals and substrates. At the same time, studies are needed to examine abiotic and biotic mechanisms and the kinetics of degradation in the unsaturated zone of the subsurface for chemicals with a wide variety of molecular structures.

Finally, it has been tacitly assumed that these models for single chemicals

were appropriate for describing transport of many chemicals being transported simultaneously. For example, the leachate from a landfill usually contains a mixture of chemicals and not a single chemical. The assumption is that the water solubilities of those chemicals of public health concern are so low that, while mixtures of chemicals are being transported, the individual chemicals are acting as if the others are absent and that they would not interact with each other. In many instances, it may be true that single chemical models may be used as surrogates for the transport of chemical mixtures; but it is essential to know when this assumption is true and when it is not.

In some instances, such as an oil spill or the massive breakthrough of chemicals from a burial site, transport behaviour can be totally different from that predicted from single chemical models. If organic solvents are present in these situations, solubilities of very water insoluble chemicals will be greatly changed. Studies with multi-component sorption (Helfferich and Klein, 1970; Radke and Prausnitz, 1972; Rhee *et al.*, 1972; Hsieh *et al.*, 1977; and, Wang and Tien, 1982) have shown vastly different behaviours than with single chemical sorption. Multi-component modeling and multi-component studies on important soil processes are difficult but necessary, because this situation exists at many waste dumps and in the unsaturated zone because of agricultural chemicals (Abriola, 1984).

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APPENDIX A: FIELD EQUATIONS FOR SINGLE CHEMICAL TRANSPORT IN THE SUBSURFACE

A. MOISTURE CONTENT FIELD EQUATIONS

$$\int_v \frac{\partial}{\partial t}(\rho_w\theta + \rho_{wv}^{sat}(T)h(\epsilon - \theta))dV + \int_\Sigma \vec{q}_T \cdot \hat{n}\,ds = 0$$

The total moisture flux vector $\vec{q}_T$ is defined as

$$\vec{q}_T = \vec{q}_l + \vec{q}_v \text{ with } \vec{q}_l = \theta\rho_w \vec{V}_l \text{ and } \vec{q}_v = (\epsilon - \theta)\rho_{wv}\vec{V}_v$$

where ρ_w is the density of water, ML^{-3}; θ is moisture content, dimensionless; ϵ is soil porosity, dimensionless; $\rho_{wv}^{sat}(T)$ is the density of water vapour at saturation, ML^{-3}; $\vec{V}_l$ and $\vec{V}_v$ are the velocities of moisture in the liquid and

vapour phases, Lt^{-1}; h is relative humidity, decimal percent; and ρ_{wv} is the density of water vapour at temperature T, ML^{-3}

B. TEMPERATURE FIELD EQUATION

$$\int_v \frac{\partial}{\partial t} (((1-\epsilon)c_{solids}\rho_{solids} + c_{air}(\epsilon-\theta)\rho_{air} + c_w\theta\rho_w)T)dV - \int_\Sigma - \vec{H}_s \cdot \hat{n} \, ds$$

The total heat flux vector $\vec{H}_s$ is defined as

$$\vec{H}_s = (1 - \epsilon)\vec{H}_{ss} + \theta\vec{H}_{sl} + (\epsilon - \theta)\vec{H}_{sv}$$

with
$$\vec{H}_{ss} = \lambda_{solids}(x,y,z)\nabla T$$
$$= \text{heat conduction through the solid particles;}$$

$$\vec{H}_{sl} = -\lambda_w\nabla T + c_w\rho_w\vec{V}_l T$$
$$= \text{heat conduction and convection in the water phase}$$

and
$$\vec{H}_{sv} = -\zeta D_{atm}\alpha_{tort}\nabla\rho_{wv} - \lambda_{air}\nabla T$$
$$= \text{heat conduction in the vapour phase and the}$$
$$\text{transfer of latent heat;}$$

where λ_{solids} is the heat conductivity of solid particles, $MLt^{-3}T^{-1}$; c_{solids} is the heat capacity of solid particles, $L^2t^{-2}T^{-1}$; λ_{air} is the heat conductivity of air, $L^2t^{-2}T^{-1}$; ρ_{solids} is the density of solid particles, ML^{-3}; ζ is latent heat of vaporisation, L^2t^{-2}; D_{atm} is the diffusivity of air, L^2t^{-1}; α_{tort} is the tortuosity, $0.33 \leq \alpha_{tort} \leq 0.66$, dimensionless; and, c_w and c_{air} are heat capacities of water and air, $L^2t^{-1}T^{-1}$.

C. CHEMICAL FIELD EQUATION

$$\int_v \frac{\partial}{\partial t} \{\theta(1 + \rho_B K_{dl}) C_l + (e-\theta)(1+\rho_B K_{dv})C_v\}dV$$

$$= -\int_\Sigma (\theta\vec{q} \, c_l$$

$$+ (\epsilon-\theta)\vec{q} \, c_v \cdot \hat{n} \, ds + \int_v (\Lambda_l\theta \, C_l(\epsilon-\theta)\Lambda_v \, C_v)dV$$

The mass flux vectors, $\vec{q}_{C_l}$ and $\vec{q}_{C_v}$, are defined as

$$\vec{q}_{C_l} = -D_{C_l} \cdot \nabla C_l + V_l C_l \text{ and } \vec{q}_{C_v} = -D_{C_v} \cdot \nabla C_v + V_v C_v$$

where ρ_B is bulk density of the porous media, ML^{-3}; K_{dl} is liquid phase adsorption coefficient to solid surfaces, $L^3 M^{-1}$; K_{dv} is vapour phase adsorption coefficient from the vapour phase to solid surfaces, $L^3 M^{-1}$; C_l is liquid phase concentration ML^{-3}; C_v is vapour phase concentration ML^{-3}; D_{C_l} is the liquid phase dispersion coefficient, $L^2 t^{-1}$; D_{C_v} is vapour phase dispersion coefficient, $L^2 t^{-1}$; Λ_l and Λ_v describe chemical transformation by chemical and biological processes in the liquid and vapour phases, t^{-1}.