CONTAMINANT TRANSPORT MODELS FOR GROUNDWATER QUALITY SIMULATION

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ABSTRACT

Groundwater solute transport models are now capable of simulating the migration of contaminants in complex real-world systems when sufficient data are available. A variety of numerical methods have been applied successfully to solving the transport equation, and no single method is best for all problems. Over the past 10 to 15 years techniques have been developed to simulate chemical reactions that occur in the flowing groundwater as well as those that occur between the liquid and solid phases. Depending upon the type of chemical interactions, the model formulation can take various forms.

INTRODUCTION

Simulation models are now standard tools of the hydrologist. Virtually all modern hydrogeologists have some training in groundwater flow simulation and many are familiar with contaminant transport models. Although one might imagine that groundwater flow and transport simulation would be used primarily for prediction of impacts on drawdowns and contaminant migration, that has not been the case. For the most part models have been used to explore the behavior of particular aquifers. Models are used to test ideas about the controls over groundwater flow and contaminant transport. In essence, the primary function of models is that of a tool to enhance understanding of local and regional aquifer systems.

In this paper the basic ideas of contaminant transport simulation for reactive and nonreactive solutes for groundwater quality modelling are discussed. First, the flow and transport equations are presented. Second is an overview of solution methods. Third, methods of incorporating chemistry into models are briefly examined.

GOVERNING EQUATIONS

In order to build a contaminant transport simulation model one must begin with a good hydrogeologic field investigation. It is impossible to simulate solute transport without first simulating groundwater flow, for it is essentially the flow that controls both plume migration and spreading. Furthermore, it is equally impossible to accurately simulate groundwater flow without a good understanding of the aquifer system. The first problem is to define the system. Specifically, one must define the state of the aquifer system, determine the influence of boundaries, identify the locations (in time and space) and magnitudes of system stresses (pumping and recharge), quantify the hydraulic properties of the aquifer and map their distribution.
Although defining the system requires extensive field work and aquifer testing, the value of modelling at this early stage should not be overlooked. One can use a preliminary aquifer simulation model to test hypotheses regarding such things as the nature of the boundary conditions, the three-dimensionality of the flow system, the specification of areal recharge rates, and the importance of various physical and chemical processes. Models should be used from the outset to explore the worth of data. That is, a model can be used to determine the importance of certain data for developing a quantitative understanding of the functioning of the system and for enhancing predictive capabilities. Model development and data collection activities should grow together.

Frequently one is concerned with flow in the saturated zone. For a confined aquifer the governing equation for the heterogeneous, two-dimensional, anisotropic case is given by,

\[ \frac{\partial}{\partial x_i} \left( T_{ij} \frac{\partial h}{\partial x_j} \right) = S \frac{\partial h}{\partial t} + W \quad i,j = 1,2 \quad (1) \]

where
- \( T_{ij} \) is the transmissivity tensor, \( L^2/T \);
- \( h \) is the hydraulic head, \( L \);
- \( S \) is the storage coefficient, \( L^0 \);
- \( t \) is time, \( T \);
- \( W \) is the volume flux per unit area, \( L/T \); and
- \( x,y \) are cartesian coordinates.

The application of an analytic or numerical solution technique to solve the above equation is called a groundwater flow model. The flow model can predict the hydraulic heads over space and time when given proper specification of initial and boundary conditions, values of hydraulic properties of the media, and rates of recharge and depletion. Commonly numerical approximation techniques are used to solve the equation because they can handle a broad class of complicated problems for which analytic solutions are not available. A comparison of the numerical techniques is given in the next section. The initial task in modelling is to make sure that the model accurately describes the system. Because the model requires specification of more initial values, stress values, boundary values, and parameter values than are generally available, the hydrologist must calibrate the model by filling-in and adjusting parameters. Typically the calibration procedure is done by trial and error in which the model is run repeatedly under successive sets of parameter values until the simulated hydraulic heads match the measured heads. In the past several years automated parameter identification methods employing various types of multiple regression analysis have been successfully applied (see Neuman and Yakowitz, 1979; Cooley, 1982; or Yeh et al., 1983; ).

After the flow model has been calibrated to describe the flow system, a contaminant transport simulation model can be developed. As in aquifer simulation, one must define the initial and boundary conditions, chemical sources and sinks, and the important parameters affecting transport, mixing, and chemistry. Among the most common types of transport model is one based upon the physical processes of advection and dispersion. Advection is the movement of the solute
with the bulk fluid flow. The solute front would progress at the speed of the average linear groundwater velocity if it was controlled solely by the process of advection. Dispersion describes the mixing of the solute with the host fluid and represents processes that cause a solute to locally move faster or slower than the average groundwater velocity. These velocity variations may be due to such things as molecular diffusion, tortuosity, or aquifer heterogeneities. The result of the dispersion processes is a smearing of the solute concentration front or spreading of a solute plume.

To build an advective-dispersive model of miscible displacement, that involves a radioactively decaying but otherwise conservative tracer such as tritium, three parameters must be defined. They are the longitudinal dispersivity, the transverse dispersivity, and the effective porosity. The dispersivity parameters are commonly referred to as the "characteristic mixing length" values of the aquifer. They are related to the amount of solute mixing that occurs within the complex, heterogeneous aquifer materials. The third parameter is related to the speed of solute transport. The groundwater velocity is given by Darcy's law divided by the effective porosity. All three parameters can vary in space, but commonly data availability do not warrant use of more than single values for a given aquifer.

All too often we do not know the chemical behavior of the solutes of interest and therefore very crude assumptions are typically made. The most common and perhaps worst assumption is that the solute behaves conservatively; it does not interact with the solid media or other mobile phases, and does not decay. Only slightly less crude is the assumption that solute behavior is in keeping with a linear adsorption isotherm. That is, there is an equilibrium partitioning between solute associated with the mobile phase and solute associated with the solid phase and this partitioning is linearly proportional to the concentration in solution. To overcome the problem of overly simplistic chemical transport modelling, one must study the chemical interactions within the liquid phase and the interchange of chemicals between the liquid and solid aquifer media. This can be done by careful experimental work and recent efforts aimed at simulating chemically reactive transport have been quite successful (Valocchi et al., 1981). Incorporating chemistry into transport simulation will be discussed later.

Simulation of transport is generally based upon solution of the advective-dispersive equation. A schematic diagram of the procedure for modelling solute transport is presented in Figure 1. A recent review of groundwater contaminant modelling is given by Anderson (1979) and additional models are listed in the monograph by Bachmat et al. (1980). If we ignore multicomponent chemistry and consider a single dissolved species, the governing equation is,

$$\frac{\partial C}{\partial t} = LC - \frac{C'W}{nb} + \sum_{k=1}^{3} R_k$$

where

$$L = \frac{\partial}{\partial x_1} \left( D_{ij} \frac{\partial}{\partial x_j} \right) - \frac{\partial}{\partial x_1} \left( v_1 \right) \quad 1, j = 1, 2$$

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and where
\[ C \] is the concentration of the dissolved chemical species, \( M/L^3 \);
\[ \mathbf{D}_{ij} \] is the dispersion tensor, \( L^2/T \);
\[ \mathbf{v}_i \] is the seepage velocity in the direction of \( x_i \), \( L/T \);
\[ b \] is the saturated thickness of the aquifer, \( L \);
\[ n \] is the effective aquifer porosity, \( L^0 \);
\[ C' \] is the concentration of the dissolved chemical in a source or sink fluid, \( M/L \), and
\[ R_k \] is the rate of production of the chemical species in reaction \( k \) of \( s \) different reactions, \( M/L^3T \).

The term on the left is for the change in concentration over time. The first and second terms (in the differential operator, \( L \)) on the right describe spatial variation in chemical concentrations due to advective transport and those due to dispersion, respectively. The third term accounts for fluid and solute sources and sinks. The fourth term is a catch-all for kinetic-controlled chemical reactions. The dispersion coefficients are often assumed to be proportional to the groundwater velocity and to the dispersivity values and are defined by the identities given by Scheidegger (1961).

**METHODS OF SOLUTION**

Sometimes there are so few data that one can do nothing more than assume that the aquifer is homogeneous and isotropic, and that flow is unidirectional and steady. In this case analytic solutions to equation (2) are available. For instances in which very rough estimates of solute concentrations are required, analytic solutions may suffice (Hamilton et al., 1985). In general, the latter is not the case. Aquifers are formed by spatially variable processes over geologic time and are complex. They can have any geometry, are generally heterogeneous, and sometimes hydraulic conductivities may be considerably anisotropic. For this case, analytic solutions do not exist and approximate numerical solutions are used.

The three most common numerical methods used to solve the advective-dispersive equation are finite differences (FD), finite elements (FE), and the method-of-characteristics (MOC). Each have

![Fig. 1. Schematic diagram of procedures for modelling simple solute transport](image-url)
some advantages and some disadvantages and no single method is best for all cases. Diagrams showing discretization schemes for each of these methods appear in Figure 2. The simplest method is finite differences. This is the method most commonly used to solve the groundwater flow equation (1). Among the more commonly utilized finite difference computer codes are Trescott et al. (1976) and Prickett and Lonnquist (1971). In the finite difference method, the governing partial differential equation is replaced by its difference approximation. A finite difference grid is used to represent the aquifer in discrete form. An approximate concentration is given for each finite difference cell. Solutions are given over the spatial domain and then "marched through time", one time step after another. A particular finite difference approximation is selected (e.g., forward, backward, or central differences) and the resulting series of algebraic equations is solved using standard matrix algebra.

The strengths of the finite difference method are that it is fairly simple to understand and to program, has well known numerical properties, is economical, and is quite easy to get accustomed to for those who have used difference methods for solving groundwater flow problems. One disadvantage is that a very fine finite difference grid with many grid points must be used to accurately approximate the domain. If not, the exact geometry of the boundaries are not properly represented. Another perhaps more severe disadvantage is that sometimes the method doesn't work. When the dispersion term in equation (2) is small relative to the advective term, the equation behaves like a hyperbolic partial differential equation (the type used to describe the migration of a shock wave). This is problematic in that the finite difference method, as it is used to solve the flow equation, works well for parabolic equations (1 and 2), but for hyperbolic ones (equation (2) without the dispersion term) the solution may exhibit numerical oscillations as well as an artificial smearing of the concentration profile. This smearing is known as numerical dispersion and is an artifact that resembles the real dispersion process.

The finite element method was brought into the groundwater discipline because it can partially overcome the numerical and boundary geometry approximation problems associated with finite differences (see Huyakorn and Pinder, 1983). Various codes employing
finite elements are available (Voss, 1985 or Yen and Huff, 1983). In this method the domain is divided into regular or irregular elements and concentrations are computed for each of the nodes in the system. In finite elements, one does not attempt to approximate the governing equation, but rather the goal is to approximate the solution. The finite element method employs mathematical basis or shape functions. Linear combination of the basic functions are used to represent the concentration distribution at each time step. The most common finite element method for groundwater problems is the Galerkin method of weighted residuals. The residual is simply the difference between the true solution and that given by the discrete approximation of the solution. The Galerkin method minimizes the weighted sum of the residuals for each of the finite elements and in so doing attains the best approximate solution for the finite element mesh.

Even from the brief description above it is apparent that the finite element method is more complicated than finite differences and as a consequence it is more difficult to formulate mathematically, to program, and to modify. Solutions are typically more expensive than those using finite differences. The advantages revolve around the fact that good solutions can be attained for cases where the finite difference method fails.

The third method for solving the solute transport equation is the method-of-characteristics. This method has been applied to numerous field areas using the code of Konikow and Bredehoft (1978). It is quite different from the other methods in that the governing equation is solved in a Lagrangian rather than an Eulerian reference frame. That is, the solution is for a moving reference rather than a fixed one. The method is implemented by introducing a series of particles that have concentration values associated with them. The particles move with the flowing groundwater and their concentrations change due to dispersion. By tracking the particles one can get a good picture of concentration changes over space and time. This method has the advantage that it can handle problems with very small dispersion terms and in fact works best for problems where dispersion is neglected. The method is appealing in that it is quite intuitive, but it is extremely difficult to program. It has good numerical properties, but it is not rigorous. Although it is an expensive method it provides good solutions. Finally, it should be noted that there is some question as to how to handle multi-component chemistry using the method-of-characteristics.

MODELLING CHEMISTRY IN SOLUTE TRANSPORT

Modelling solute transport can be far more difficult than modelling groundwater flow not only because of the numerical problems mentioned previously, but because solutes react with each other and with the solid aquifer material. Simulation may involve more than one chemical species and consequently the solution of more than one partial differential equation for chemical transport. An excellent discussion of chemically reactive solute transport is given by Rubin (1983). The examples which follow are based closely on that significant work. In the limited space of this paper only a few of the points covered in Rubin (1983) will be touched upon here.

There are two categories of reactive transport that are of importance to formulating solute transport models (see Figure 3). First are those that are kinetically or rate controlled. There are two cases in which kinetics (chemical or physical) must be explicitly
modelled. One case is when reaction rates are slow in comparison to other processes that affect solute concentrations (i.e., advection and dispersion), then chemical kinetics must be modelled. The other case is when reactions proceed only in one direction (are irreversible). Second are reactions that are so rapid that one can assume local instantaneous chemical equilibrium. Equilibrium reactions must be reversible. The problem in dealing with kinetically controlled reactions is that we rarely know the rate constants and they are difficult to measure in the laboratory. On the other hand, when local equilibrium can be assumed, the equilibrium constants are available from thermodynamic properties measured in the lab. The type of solute transport equations that are used to represent kinetics versus equilibrium are quite different as shown in the forthcoming examples.

![Chemical equilibrium and Chemical kinetics](image)

**Fig. 3. Categories of Reactive Transport**

Another aspect of importance to chemically reactive solute transport is whether or not reactions occur solely in the liquid phase or also involve the solid phase(s). This is shown schematically in Figure 4. Reactions occurring in one phase are called homogeneous reactions. Those involving transfer between phases or phase transformations are called heterogeneous reactions. Heterogeneous reactions include processes such as precipitation and dissolution as well as the surface reactions of sorption and ion-exchange. The type of solute transport model that one develops will be heavily dependent upon which type of chemical processes are present. It is not within the scope of this brief paper to discuss the intricacies of chemical transport modelling. Rather, a few examples are given to show how the mathematical formulation of solute transport models differ when various types of chemistry are involved. In this paper only homogeneous reactions are considered. For a more complete treatment see the works of Rubin and James (1973), Jennings et al. (1982), and Rubin (1983).

It is straightforward to incorporate kinetics into transport models. Suppose there are two chemical participants \( P_1 \) and \( P_2 \) with concentrations \( C_1 \) and \( C_2 \) respectively. A certain proportion of collisions between these participants results in the formation of \( P_3 \) with concentration \( C_3 \). If the reaction is reversible, the kinetic reaction is represented by

\[
P_1 + P_2 \xleftrightarrow{K_f, K_b} P_3
\]
where \( K_f \) and \( K_b \) are the kinetic rate coefficients corresponding to the reaction proceeding to the right and left respectively.

The rate, \( R_1 \), of production of \( P_1 \) is given by,

\[
R_1 = (-K_f)(C1)(C2) + (K_b)(C3)
\]

This is equal to the rate production of \( P_2 \) or,

\[
R_1 = R_2
\]

The rate of production of \( P_3 \) is \((-R_1\) because \( P_3 \) is being produced at the same rate that \( P_1 \) is being consumed.

To model solute transport, one partial differential equation is needed for each chemical participant or

\[
\frac{\partial C_1}{\partial t} = LC_1 - K_f C_1 C_2 + K_b C_3
\]

\[
\frac{\partial C_2}{\partial t} = LC_2 - K_f C_1 C_2 + K_b C_2
\]

\[
\frac{\partial C_3}{\partial t} = LC_3 + K_f C_1 C_2 - K_b C_3
\]

The important point here is that one can incorporate chemical kinetics by simply writing solute transport equations for each participant and then including kinetic source and sink terms to account for production or removal of the participants. Here, the model involves three nonlinear equations (note multiplicative terms involving \( C_1 \) and \( C_2 \)). After discretizing the equations using finite differences or finite elements, solution is achieved using nonlinear matrix methods such as predictor-corrector or Gauss-Newton.

Fig. 4. Processes in Chemically Reactive Solute Transport
Homogeneous reactions that occur very rapidly may be treated using the local equilibrium assumption. Here we define the transport equations for chemical entities whose total mass is conserved in water. Next, we write the transport equations and also the chemical relation equations that define local chemical equilibrium. Finally the system of transport and chemical relation equations are solved.

Let us say that the chemical relation equations for an example system with six chemical participants are given by

\[ K_{12} P_{12} \leftrightarrow P_1 + P_2 \] (9)
\[ K_{13} P_{13} \leftrightarrow P_1 + P_3 \] (10)
\[ K_{23} P_{23} \leftrightarrow P_2 + P_3 \] (11)

and the equilibrium constants for a given temperature and pressure are

\[ K_{12} = \frac{(C_1)(C_2)}{(C_{12})} \] (12)
\[ K_{13} = \frac{(C_1)(C_3)}{(C_{13})} \] (13)
\[ K_{23} = \frac{(C_2)(C_3)}{(C_{23})} \] (14)

First we define the concentration of all chemical forms having \( P_1 \) as a new variable, \( u_1 \), the concentration of all chemical forms having \( P_2 \) as a new variable, \( u_2 \), and the concentration of all chemical forms having \( P_3 \) as a new variable, \( u_3 \), or

\[ u_1 = C_1 + C_{12} + C_{13} \] (15)
\[ u_2 = C_2 + C_{12} \] (16)
\[ u_3 = C_3 + C_{13} \] (17)

Because the total mass of each of \( u_1 \), \( u_2 \), and \( u_3 \) is conserved in water, we can write three solute transport (mass balance) equations, or

\[ \frac{\partial u_i}{\partial t} = Lu_i \quad i = 1, 2, 3 \] (18)

We have six unknown concentrations, so we need six equations. There are the three solute transport equations for \( u_1 \), \( u_2 \) and \( u_3 \) and the algebraic definitions for \( u_1 \), \( u_2 \), \( u_3 \). The three remaining equations are those defining chemical equilibrium. The procedure used to solve this system is to first solve the three partial differential equations (18) for \( u_1 \), \( u_2 \), and \( u_3 \) for a single time step. Given values for each \( u_i \) at every node (assuming the finite element method is being used), the remaining equations consisting of the definitions for \( u_1 \), \( u_2 \) and \( u_3 \) (linear algebraic equations, 15-17) and the
equations defining chemical equilibrium (nonlinear algebraic equations, 12-14) are solved simultaneously for each node. The six unknown concentrations are determined at each node. Once a solution is found for $C_1$, $C_2$, $C_3$, $C_{12}$, $C_{13}$, and $C_{23}$ the set of three partial differential equations is solved for the next time step. Then algebraic equations are solved for each node. The process is repeated for the problem time frame. The important point here is that the transport equations for the case of local equilibrium do not have chemical source or sink terms. Rather the chemical transport system is defined by two linked system of equations. First there is a series of mass balance equations written for chemical entities (here $u_1$, $u_2$, and $u_3$) whose total concentration is conserved in water. Second are chemical equations defining both chemical equilibrium and the conservative chemical entities.

DISCUSSION

The above examples show that chemical reactions for homogeneous kinetic or equilibrium systems may be combined with a model of advective-dispersive solute transport. The nature of the combination is dependent upon the phase or phases in which the reactions occur and upon the speed of the reactions in comparison to flow and dispersion. Sometimes simple chemistry can be modelled with a single partial differential equation which may be linear or nonlinear, as in the case of sorption reactions (see Freeze and Cherry, 1979). When more realistic chemistry is considered, the number of partial differential and algebraic equations that must be considered grows and they become nonlinear.

The modelling of chemical transport requires a good knowledge of aquifer hydraulic and transport parameters, knowledge of solute chemistry, chemical rate and/or equilibrium constants and data regarding the spatial distribution of concentrations. If such data cannot be obtain, one must seriously evaluate the utility of a model. Certainly a model based upon very sparse data will be next to useless in terms of prediction. It will be valuable as a tool to help the hydrologist understand the system and to target data needs. Under conditions where essentially no data are available the hydrologist must ask the following question,

"Should we guess the system parameters and use a model to speculate results, or should we simply guess the results based upon scientific and engineering judgement and avoid modelling altogether?"

REFERENCES


