

CHAPTER 31

MODELING GROUNDWATER FLOW AND QUALITY

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I. INTRODUCTION

In most areas, rocks in the subsurface are saturated with water at relatively shallow depths. The top of the saturated zone—the water table—typically occurs anywhere from just below land surface to hundreds of feet below the land surface. Groundwater generally fills all pore spaces below the water table and is part of a continuous dynamic flow system, in which the fluid is moving at velocities ranging from feet per millennia to feet per day (Figure 1). While the water is in close contact with the surfaces of various minerals in the rock material, geochemical interactions between the water and the rock can affect the chemical quality of the water, including pH, dissolved solids composition, and trace elements content. Thus, flowing groundwater is a major mecha-

nism for the transport of chemicals from buried rocks to the accessible environment, as well as a major pathway from rocks to human exposure and consumption. Because the mineral composition of rocks is highly variable, as is the solubility of various minerals, the human health effects of groundwater consumption will be highly variable.

Groundwater provides about 40% of the public water supply in the United States. Also, most of the rural population in the United States, more than 40 million people, supply their own drinking water from domestic wells (Alley et al., 1999). Consequently, groundwater is considered an important source of drinking water in every state (Figure 2). Groundwater also is the source of much of the water used for irrigation, especially in areas with arid to semi-arid climates. Nearly all surface-water features (streams, lakes, reservoirs, wetlands, and estuaries) interact with groundwater. Groundwater is the source of base flow to streams and rivers (see Figure 1) and often is the primary source of water that sustains a wetland habitat.

It is long recognized that the chemical content of drinking water can have an adverse or beneficial affect on human health (Keller, 1978). Although the potential side effects associated with some trace elements of natural origin (e.g., arsenic, selenium) or anthropogenic origin (e.g., hexavalent chromium, organic compounds) present in concentrations exceeding public health standards for human consumption of drinking water has

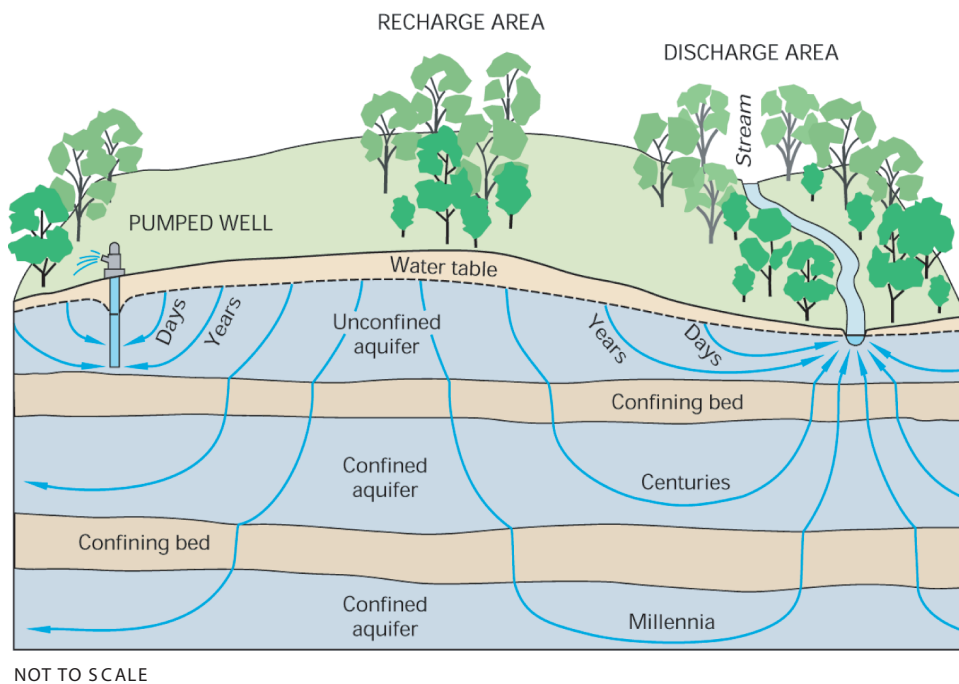
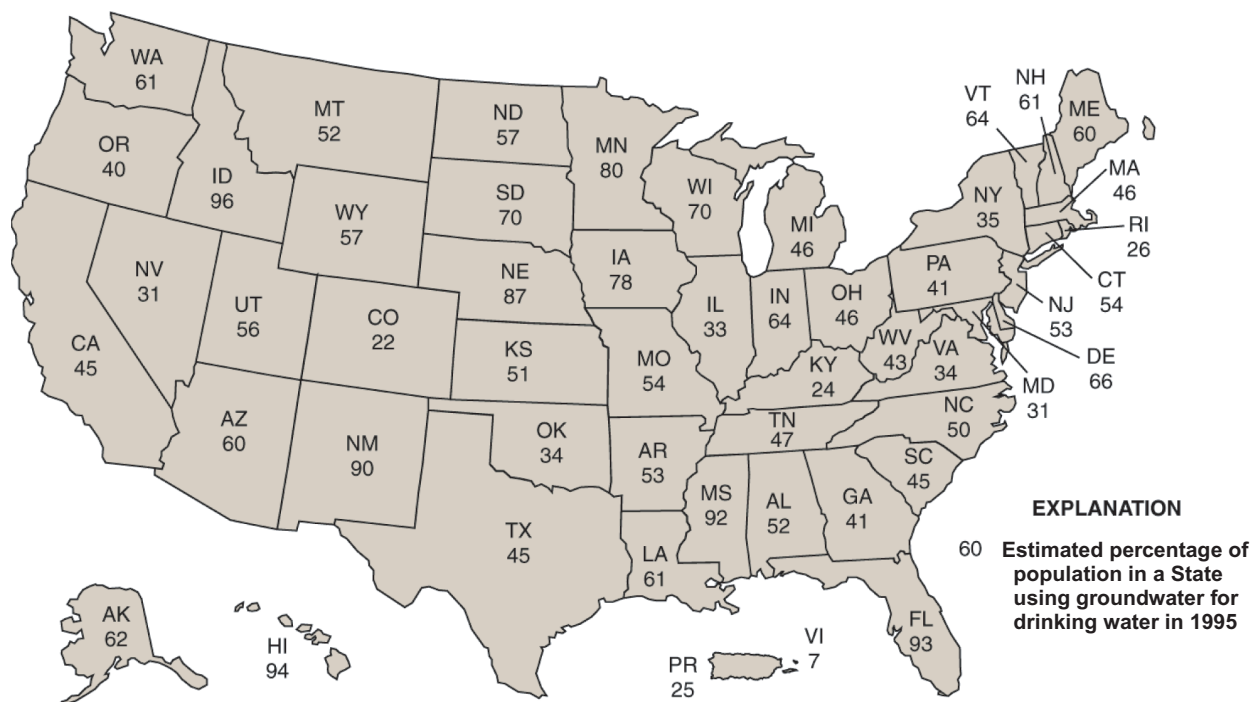


FIGURE 1 Groundwater flow paths vary greatly in length, depth, and travel time from points of recharge to points of discharge in the groundwater system. Flow lines typically are perpendicular to lines (or surfaces) of equal hydraulic head. (From Winter et al., 1998.)



received the most attention in recent years, it is important to realize that many trace elements are greatly beneficial to human health (Hopps & Feder, 1986).

It is clear that the chemical content of natural waters varies greatly from place to place. Geology has a stronger and more direct effect on the quality of groundwater than on surface water. Surface water sources include a much greater component of direct precipitation and represent the rapid integration of water derived from large and diverse source areas within a drainage basin than do groundwater sources. Surface water also includes a smaller component which reflects the geochemical environment of the watershed. Furthermore, public water supply systems based primarily on surface water sources typically include a large distribution network and centralized treatment and monitoring facilities. Conversely, groundwater has much greater direct contact with the geochemical environment (e.g., mineral surfaces) during its slow migration and long residence time through the void spaces of the rocks that compose an aquifer system. Therefore, prior to its collection and distribution into a water supply system, the chemical content of groundwater will have been strongly affected by the geochemical environment in the rocks along the flow paths feeding wells or springs to which groundwater discharges. Many groundwater supply systems are small domestic systems designed to supply individual homes; these systems often are monitored on a minimal basis for chemical constituents in the water, especially for trace elements.

Understanding the pathway of dissolved minerals from the source rock to the environment or to human consumption is critical for evaluating and remediating possible toxic hazards. Evaluation and remediation, in turn, requires an understanding of the processes and parameters that control rock-water interactions and groundwater flow and solute transport. Conceptual knowledge of these processes and parameters can be quantified and incorporated into generic deterministic models, which can be applied to site-specific problems and be used to predict the fate and transport of dissolved chemicals.

The purpose of this chapter is to review the state-of-the-art in deterministic numerical modeling of groundwater flow, solute transport, and geochemical reaction processes. This chapter is intended to describe the types of models that are available and how they may be applied to complex field problems. However, as this chapter is only a review, it cannot offer comprehensive and in-depth coverage of this complex topic: instead, it guides the reader to references that provide more details. Other chapters in this book covering elements

in groundwater are, for example, Chapters 10, 11, 12, and 13.

II. PHYSICAL PROCESSES

A. Groundwater Flow

It generally is assumed that the process of groundwater flow is governed by the relation expressed in Darcy's law, which was derived in 1856 on the basis of the results of laboratory experiments on the flow of water through a sand column. Darcy's law states that the groundwater flow rate (or specific discharge) is proportional to the hydraulic gradient (related to pressure and elevation differences) and to hydraulic conductivity, a property that depends on the characteristics of the porous media (such as grain size distribution or fractures) and the fluid (such as density and viscosity) (see Bear, 1979).

Darcy's law, however, has limits on its range of applicability. It was derived from experiments on the laminar flow of water through porous material. Flow probably is turbulent or in a transitional state from laminar to turbulent near the intakes of large-capacity wells. Turbulent flows also may occur in rocks as a result of the development of fractures, joints, or solution openings. What commonly is done in determining flow in such situations is to ignore local or small-scale turbulence and assume that flow behaves as if it were laminar flow through porous media on the regional scale, and, thus, that Darcy's law applies at that scale.

In some field situations, fluid properties such as density and viscosity may vary appreciably in space or time. This variation may occur where water temperature or dissolved-solids concentration changes greatly. When the water properties are heterogeneous and/or transient, the relations among water levels in monitoring wells, hydraulic heads, fluid pressures, and flow velocities are not straightforward. In such cases, the flow equation is written and solved in terms of fluid pressures, fluid densities, and the intrinsic permeability of the porous media.

B. Advective Transport

The migration and mixing of chemicals dissolved in groundwater obviously will be affected by the velocity of the flowing groundwater. That is, chemical con-

stituents dissolved in flowing water will tend to migrate with the water—the faster the water moves, the faster and further the solutes will migrate. This entrainment of dissolved chemicals is called advective transport.

The specific discharge calculated from Darcy's law represents a volumetric flux per unit cross-sectional area, but flow does not pass through the solid grains of the rock, only through the void spaces. Thus, to calculate the actual seepage velocity of groundwater, one must account for the actual cross-sectional area through which flow is occurring. The latter is done by dividing the specific discharge by the effective porosity of the porous medium. The effective porosity of fractured crystalline rocks can be less than 0.01, whereas for unconsolidated sands and gravels it can exceed 0.30.

C. Hydrodynamic Dispersion

Controlled laboratory and field experiments show that observed solute concentrations in a flow field cannot be predicted adequately just on the basis of seepage velocity, even for nonreactive constituents. Instead, it is observed that some solute will arrive at a given location sooner than predicted by the mean seepage velocity, whereas some solute arrives later than the mean velocity would indicate. That is, there is a spreading about the mean arrival time. Similarly, solute distribution will spread spatially with time and travel distance. This spreading and mixing phenomenon is called hydrodynamic dispersion. It results from molecular and ionic diffusion, and from mechanical dispersion arising from small-scale variations in the velocity of flow that cause the paths of solutes to diverge or spread from the average direction of groundwater flow (Bear, 1979). The outcome is a transient, irreversible, mixing (or dilution) process affecting the concentration distribution of a solute species in an aquifer.

The rate of solute flux caused by hydrodynamic dispersion is expressed in a form analogous to Fick's law of diffusion. This Fickian model assumes that the driving force is the concentration gradient and that the dispersive flux occurs in a direction from higher concentrations toward lower concentrations at a rate related to a constant of proportionality—the coefficient of hydrodynamic dispersion. However, this assumption is not always consistent with field observations and is the subject of much ongoing research and field study (see, for example, Gelhar et al., 1992). The coefficient of hydrodynamic dispersion is defined as the sum of mechanical dispersion and molecular diffusion (Bear,

1979). Mechanical dispersion is a function both of the intrinsic properties of the porous medium (expressed as a dispersivity coefficient, which is related to variability in hydraulic conductivity and porosity) and of the fluid flow (specifically, the fluid velocity). Molecular diffusion in a porous medium will differ from that in free water because of the effects of tortuous paths of fluid connectivity in porous media.

In most groundwater transport model applications, the dispersivity is defined in terms of just two unique constants: the longitudinal dispersivity and the transverse dispersivity of the medium. In practice, however, dispersivity values appear to be dependent on and proportional to the scale of the measurement. Field-scale dispersion (commonly called macrodispersion) results from large-scale spatial variations in hydraulic properties and seepage velocity. Consequently, the use of values of dispersivity determined for one scale of transport in a model designed to predict concentration changes over a different scale of travel probably is inappropriate. Overall, the more accurately and precisely a model can represent or simulate the true velocity distribution in space and time, then the uncertainty concerning representation of dispersion processes will be less of a problem.

D. Solute-Transport Equation

A generalized form of the solute-transport equation is presented by Bear (1979). The governing partial differential equation relates the change in concentration over time in a groundwater system to (1) hydrodynamic dispersion, (2) advective transport, (3) the effects of mixing with a source fluid that has a different concentration than the groundwater at the location of the recharge or injection, and (4) all of the physical, chemical, geochemical, and biological reactions that cause transfer of mass between the liquid and solid or air phases or conversion/decay of dissolved chemical species from one form to another. The chemical attenuation of inorganic chemicals can occur by sorption/desorption, precipitation/dissolution, or oxidation/reduction; organic chemicals can adsorb or degrade by microbiological processes and/or volatilization.

There has been considerable progress over the last 10–15 years in modeling reactive-transport processes; however, the complexity and computational requirements for solute-transport models and reaction models are intense and, therefore, applications of coupled multispecies reactive-transport models are rare. Although

some research tools are documented (e.g., see Lichtner et al., 1996; Ibaraki & Therrien, 2001), they still are at the leading edge of the state-of-the-art and usually require computational resources and input data that are beyond that available for most applications. Thus, for the analysis of field problems, it is much more common to apply only groundwater flow and solute-transport models or only multispecies geochemical reaction models, or to apply both sequentially.

In summary, the mathematical solute-transport model requires at least two partial differential equations. One is the equation of flow, from which groundwater flow velocities are obtained, and the second is the solute-transport equation, which describes the chemical concentration in groundwater. If the properties of the water are affected significantly by changes in solute concentration, as in a saltwater intrusion problem, then the flow and transport equations should be solved simultaneously (or at least iteratively). If the properties of the water remain constant and uniform, then the flow and transport equations can be decoupled and solved sequentially, which is simpler numerically.

III. GEOCHEMICAL PROCESSES

A. Basic Concepts

Thermodynamic models describing chemical reactions within an aqueous phase or between the aqueous phase and other phases (solid, gas, or surficial phases) use various common basic principles. Thermodynamic models assume that ion activities, which can be considered the “thermodynamically effective” concentrations determining the progress and direction of reactions, can be calculated from measured (or calculated) ion concentrations.

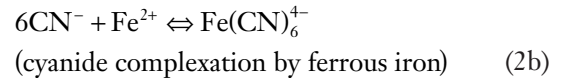
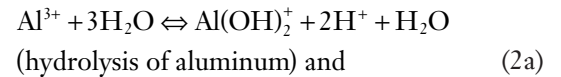
In addition to the calculation of ionic activities, thermodynamic models typically are based on the law of mass action. This law states that as the activity of the reactants is increased in a chemical reaction, the activity of the reaction products also will increase if equilibrium is maintained. For example, if the following chemical reaction is at equilibrium, $iA + jB \rightleftharpoons kC + lD$ where i , j , k , and l are stoichiometric coefficients, the law of mass action states that the following mathematical equation must hold:

$$K = \frac{a_C^k a_D^l}{a_A^i a_B^j} \quad (1)$$

where K is a constant (at a fixed temperature and pressure) and a_A , a_B , a_C , and a_D represent the activities of A , B , C , and D at thermodynamic equilibrium. The law of mass action applies to any kind of chemical reaction at thermodynamic equilibrium, not just to aqueous reactions.

B. Aqueous Speciation, Hydrolysis, and Oxidation/Reduction Reactions

The calculation of solution ionic strength, ionic activity coefficients, and ionic activities must be conducted iteratively with the solution of the mass-action equations that determine the speciation of the aqueous solution. Aqueous speciation is the partitioning of chemical constituents present in a solution (whose total concentrations are typically measured) into various aqueous species that represent the different molecular forms assumed by the constituents in the aqueous solution. Aqueous speciation reactions are homogeneous reactions; all reactants and products are aqueous species. Two examples of speciation reactions are



Simple mass-action equations describing the relative aqueous activities of products and reactants can be written for any of the above reactions. Aqueous speciation reactions control the concentrations of individual aqueous species, and, thereby, may appreciably affect the toxicity of a solution. Some aqueous species can be much less toxic than others. For example, cyanide present in the complexed $\text{Fe}(\text{CN})_6^{4-}$ form is much less toxic than cyanide in the CN^- or HCN^0 forms. Aqueous speciation reactions also affect the total concentration of constituents in solution through their control of general solution characteristics such as ionic strength, acidic nature (pH), and redox potential (pe) of the solution, and through their control of individual aqueous species involved in mass-transfer reactions (e.g., mineral precipitation/dissolution, surface sorption/desorption, ingassing/exsolution reactions).

The pH and pe of an aqueous solution are sometimes described as the *master variables*, which control the speciation of aqueous solutions. The pH of a solution simply relates to the acidic nature of a solution, and more specifically to the activity of protons (H^+) or

equivalently of hydronium ions (H_3O^+ or H_9O_4^+) in the solution, as $\text{pH} = -\log a_{\text{H}^+}$. The pe of a solution is related to the ratio of the activity of an aqueous species present in oxidized form to that present in reduced form. Mathematically, the definition of the pe of a solution is analogous to that of the pH variable, except that it is defined in terms of the activity of free electrons in the solution, as $\text{pe} = -\log a_e$. For all practical purposes, however, any electrons produced by an oxidation reaction always must be consumed by a reduction reaction. Nevertheless, the redox potential of a solution does have practical relevance in describing the degree to which aqueous species are in oxidized or reduced form.

The Eh of a solution is the redox potential measured in the field. It is directly related to pe by the relation:

$$\text{pe} = \text{Eh} \frac{F}{2.303RT} \quad (3)$$

where F is the Faraday constant, R is the gas constant, and T is the temperature in Kelvin. At 25°C , the relation is $\text{pe} = 16.904 \text{ Eh}$, where Eh is expressed in volts.

Field measurements of Eh are problematic. First, the redox-active species present in a water often are not in redox equilibrium and, therefore, the measurement may be meaningless; that is, more than one redox potential may be present for the solution depending on which redox couple (e.g., $\text{Fe}^{3+}/\text{Fe}^{2+}$) is chosen, and the measurement may at best represent some sort of “mixed” potential. Second, the only redox-active species to which platinum electrodes (typically used for Eh measurements) have been demonstrated to respond quickly, and, therefore, reflect their electrochemical equilibrium, are Fe^{2+} , Fe^{3+} , and S^{2-} , and only when these species are present at concentrations of 10^{-5} mol/L or greater (Nordstrom & Munoz, 1994). In general, redox equilibria and disequilibria in groundwater are best assessed through the measurement of individual redox couples, rather than through measurements of Eh.

Oxidation/reduction reactions can occur either in the aqueous phase only (homogeneous reactions) or between the aqueous phase and other phases (heterogeneous reactions). In most groundwaters, the presence of organic carbon commonly drives a sequence of redox reactions as water migrates from the unsaturated zone and water table to greater depths. Typically, organic carbon reduces dissolved oxygen in the water then reduces nitrate to nitrogen gas (and sometimes to ammonia). Dissolved organic carbon also may react with manganese oxide minerals producing Mn^{2+} in the water; at slightly lower oxidation potentials the organic carbon will react with ferric-iron minerals (typically

oxides) and generate dissolved ferrous iron in the water. At greater depths, water becomes sulfidic as the carbon starts to reduce dissolved sulfate to sulfide. Finally, when no further electron acceptors (such as SO_4 , O_2 , and NO_3) are present, water typically becomes methanic, i.e., any remaining organic matter decomposes through a process of fermentation to methane and carbon dioxide. In this process, hydrogen generally is produced as an intermediate product. Despite strong thermodynamic potentials for their occurrence, rates of redox reactions are often slow unless microbially catalyzed. Most redox reactions in natural and contaminated environments are catalyzed microbially.

Redox reactions are important in medical geology, whether for natural or contaminated environments, because they affect the relative toxicity of various dissolved constituents in water. For example, Cr(IV) is a suspected carcinogen, whereas Cr(III) is an essential trace element for humans. Redox reactions also affect the solubility of various compounds (e.g., metal sulfides present in the rock materials).

C. Geochemical Mass-Transfer Processes

Mineral dissolution and precipitation processes are important in controlling the chemical evolution of groundwater. These processes strongly affect the overall chemical characteristics of the water through their effect on pH and pe conditions, ionic strength, and complexant concentrations (dissolved carbonate, sulfate, chloride, etc.). For example, the pH of natural waters often is buffered by the dissolution of calcite and described as $\text{CaCO}_{3,s} + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$.

Mineral precipitation processes also commonly limit the concentrations of many constituents in water. For example, barium and aluminum concentrations in water often are limited by the precipitation of barite and aluminum hydroxide:



Although the above reactions are written for pure minerals, mineral phases invariably contain foreign ions and impurities, which were entrained as occlusion pockets during the formation of the minerals or are substituting as an integral part of the mineral lattice. In either case, minerals can take up and/or release these impurities through recrystallization processes. The thermodynamic theory describing the uptake and release of substitutional impurities in minerals (also

known as solid solutions) is fairly complex and remains an area of active research (Glynn, 2000), but it is increasingly implemented in geochemical modeling codes. Examples of solid-solutions reactions that may control trace element concentrations include (1) the uptake of copper, nickel, cobalt, and zinc by precipitating manganese oxides; (2) the uptake of chromate by barite recrystallization in contaminated waters; and (3) the control of fluoride concentrations through dissolution and recrystallization uptake of apatites. Biogenic apatites, such as found in fossil bones and teeth, commonly are initially rich in hydroxylapatite and slowly recrystallize upon contact with groundwater to fluorapatite. In certain groundwater systems, however, the reverse process also has been demonstrated to occur. For example, Zack (1980) has shown that the exchange of hydroxide ions for fluoride present in fossil shark teeth is responsible for anomalously high fluoride concentrations in the Atlantic Coastal Plain aquifers of South Carolina (this is discussed in more detail below).

Sorption reactions often are important in controlling the concentrations of constituents in groundwater and often may even affect the observed pH. A typical porous medium aquifer (with a porosity of 0.2 and a cation exchange capacity of 5 mEq/100 g) has about 500 mEq of cation exchange capacity per liter of water (Drever, 1997). This value is more than two orders of magnitude greater than the concentration of dissolved ions in dilute groundwater, and consequently can be expected to have a large effect on the chemistry of the water.

Sorption reactions generally are described either through an ion-exchange model (primarily affecting cations) or through a surface-complexation model. Ion-exchange models typically apply to mineral surfaces and interlayers with constant surface charge (e.g., clays and zeolites), and they usually only consider cation exchange reactions such as $[\text{Na} - \text{clay} + \text{K}^+ \rightleftharpoons \text{Na}^+ + \text{K} - \text{clay}]$.

Surface-complexation models commonly are used to describe the sorption of aqueous species on surfaces with variable charge (e.g., iron and manganese oxides, silica, organic matter, and clay edges). These surfaces become more negatively charged with increasing pH, and, therefore, their cation sorption capacity increases and their anionic sorption capacity decreases. At any pH, the surfaces are considered to contain a mix of positively charged, negatively charged, and neutral sites. This mix and the ensuing chemical reactions among the various sites and aqueous ions and complexes are fully described by a speciation of the surface in a manner analogous to that for an aqueous solution. This speciation describes the surface as a series of various surface-complexes and bare-surface sites of different charges.

Gas dissolution/exsolution/volatilization reactions can affect the concentrations of organic (aromatic and light aliphatic compounds) and inorganic (O_2 , CO_2 , N_2 , noble gases) constituents in groundwater near the water table. These reactions can strongly affect the general chemistry of water through their effect on pH, redox potentials, and ionic strength; in some cases (e.g., volatilization of HCN and light organic compounds), the reactions also can directly affect the concentrations of contaminants in water.

D. Biodegradation/Biotransformation

Microorganisms are important in the chemical evolution of waters, and, for all practical purposes, can be considered present in almost every groundwater environment, even under extreme conditions. Microorganisms have been found underground at depths of more than a kilometer (Pedersen, 1993), at temperatures as high as 110°C (Stetter, 1998), and in waters with up to 30% salinity (Grant et al., 1998). Most microorganisms are heterotrophic and use organic carbon as a primary energy source. However, chemolithotrophic organisms can use reduced inorganic substrates, such as NH_4 , H_2 , H_2S , and CH_4 to derive energy in both aerobic and anaerobic environments.

Microbes also are essential in the degradation of organic molecules, generally of complex molecules to simpler ones, ultimately to inorganic compounds and forms of C, N, H, S, Cl and other elements. Complete transformation to inorganic compounds (mineralization) involves multiple, successive, biologically mediated reactions, which may proceed at different rates. Although the initial degradation rate of an organic molecule may be fast, degradation of some of its metabolites may be slow, which can be a problem if the metabolite is associated with a health risk. Although microbial "remediation" is an important issue considered in investigations of anthropogenic groundwater contaminants (such as pesticides, herbicides, and petroleum products), microbes also are likely to affect the "natural contamination" of groundwater through their catalysis of coal-water interactions and their consequent mobilization of soluble polar aromatic and polynuclear aromatic hydrocarbons. These compounds are thought to be an important factor in the observed incidences of Balkan endemic nephropathy (Feder et al., 1991).

Microbes also are known to catalyze many inorganic reduction reactions by generally using organic carbon as a reducing agent. Examples from naturally occurring

subsurface constituents, which when modified by microorganisms may become more mobile, include: solid Fe(III)-oxyhydroxides to dissolved Fe(II), nitrate to N_2 (denitrification) or further to ammonia, sulfate to sulfide, As(V) to As(III) (Dowdle et al., 1996), Se(VI) to Se(IV) and Se(0) (Switzer Blum et al., 2001), and U(VI) to U(IV) (Lovley et al., 1991). Microbes also are known to catalyze many of the reverse oxidation reactions in the list above. Redox reactions usually are associated with large changes in free energy, and therefore provide microbes with an energy source.

Although the occurrence of these redox reactions can be predicted from thermodynamic considerations, in practice the kinetics of the reactions would be orders of magnitude slower if they were not mediated by microbes. Numerical modeling of biodegradation/bio-transformation reactions reduces the complexity of the multiple chemical, enzymatic, biological, and ecological processes that are mediating the transformation of a constituent of interest to a simple mathematical description of the overall transformation kinetics. The mathematical model chosen often considers not just the degradation or transformation of a particular compound, but also keeps track of the effect of the transformation on the size and productivity of the microbial community responsible for the catalysis of the transformation. Monod and Michaelis-Menten kinetic models are used to describe microbial utilization of chemical substrates and microbial growth kinetics (Schwarzenbach et al., 1993). The computer codes BIOMOC (Essaid & Bekins, 1997) and RT3D (Clement, 1997) are examples of groundwater flow and transport codes that allow the simulation of biodegradation and transformation reactions using a variety of kinetic model formulations.

IV. MODELS

A. Overview

The word *model* has many definitions. A model perhaps is most simply defined as a representation of a real system or process. A *conceptual model* is a hypothesis for how a system or process operates. This hypothesis can be expressed quantitatively as a mathematical model. *Mathematical models* are abstractions that represent processes as equations, physical properties as constants or coefficients in the equations, and measures of state or potential in the system as variables.

Most groundwater models in use are deterministic mathematical models. *Deterministic models* are based on conservation of mass, momentum, and energy and describe cause-and-effect relations. The underlying assumption is that, given a high degree of understanding of the processes by which stresses on a system produce subsequent responses in that system, the system's response to any set of stresses can be predetermined, even if the magnitude of the new stresses falls outside of the range of historically observed stresses.

Deterministic groundwater models generally require the solution of partial differential equations. Exact solutions often can be obtained analytically, but *analytical models* require that the parameters and boundaries be highly idealized. Some deterministic models treat the properties of porous media as lumped parameters (essentially, as a black box), but this precludes the representation of heterogeneous hydraulic properties in the model. Heterogeneity, or variability in aquifer properties, is characteristic of all geologic systems and now is recognized as critical in affecting groundwater flow and solute transport. Thus, it often is preferable to apply distributed-parameter models, which allow the representation of more realistic distributions of system properties. Numerical methods yield approximate solutions to the governing equation (or equations) through the *discretization* of space and time. Within the discretized problem domain, the variable internal properties, boundaries, and stresses of the system are approximated. Deterministic, distributed-parameter, *numerical models* can relax the rigid idealized conditions of analytical models or lumped-parameter models, and, therefore, they can be more realistic and flexible for simulating field conditions (if applied properly).

The number and types of equations to be solved are determined by the concepts of the dominant governing processes. The coefficients of the equations are the parameters that are measures of the properties, boundaries, and stresses of the system; the dependent variables of the equations are the measures of the state of the system and are determined mathematically by the solution of the equations. When a numerical algorithm is implemented in a computer code to solve one or more partial differential equations, the resulting computer code can be considered a *generic model*. When the grid dimensions, boundary conditions, and other parameters (such as hydraulic conductivity and storativity), are specified in an application of a generic model to represent a particular geographical area, the resulting computer program is a *site-specific model*. The capability of generic models to solve the governing equations accurately typically is demonstrated by example applications

to simplified problems. This does not guarantee a similar level of accuracy when the model is applied to a complex field problem.

B. Numerical Methods

The partial differential equations describing groundwater flow and transport can be solved mathematically by using either analytical solutions or numerical solutions. In general, obtaining the exact analytical solution to the partial differential equation requires that the properties and boundaries of the flow system be highly and perhaps unrealistically idealized. Many of the limitations of applying analytical methods to complex field problems can be overcome by using analytical element methods, which apply analytical methods to subareas of the problem domain (see Haitjema, 1995).

Alternatively, for problems where the simplified analytical models no longer describe the physics of the situation, the partial differential equations can be approximated numerically. In numerical approaches, the continuous variables are replaced with discrete variables that are defined at grid blocks or nodes. Thus, the continuous differential equation, which defines hydraulic head or solute concentration everywhere in the system, is replaced by a finite number of algebraic equations that defines the hydraulic head or concentration at specific points. This system of algebraic equations generally is solved using matrix techniques. This approach constitutes a numerical model.

Two major classes of numerical methods have come to be well accepted for solving the groundwater flow equation. These are finite-difference methods and finite-element methods. Each of these two major classes of numerical methods includes a variety of subclasses and implementation alternatives. An overview of the application of these numerical methods to groundwater problems is presented by Wang and Anderson (1982). Both of these numerical approaches require that the area of interest be subdivided by a grid into a number of smaller subareas (cells or elements) that are associated with nodal points (either at the centers or peripheries of the subareas).

Finite-difference methods approximate the first derivatives in the partial differential equations as difference quotients (the differences between values of the independent variable at adjacent nodes with respect to the distance between the nodes, and at two successive time levels with respect to the duration of the time-step increment). Finite-element methods use assumed func-

tions of the dependent variable and parameters to evaluate equivalent integral formulations of the partial differential equations. Huyakorn and Pinder (1983) present a comprehensive analysis of the application of finite-element methods to groundwater problems. In both numerical approaches, the discretization of the space and time dimensions allows the continuous boundary-value problem for the solution of the partial differential equation to be reduced to the simultaneous solution of a set of algebraic equations. These equations then can be solved using either iterative or direct matrix methods.

Each approach has advantages and disadvantages, but there are few groundwater problems for which one approach clearly is superior. In general, the finite-difference methods are simpler conceptually and mathematically, and are easier to program. They typically are keyed to a relatively simple, rectangular grid, which also eases data entry. Finite-element methods generally require the use of more sophisticated mathematics but, for some problems, may be more accurate numerically than standard finite-difference methods. A major advantage of the finite-element methods is the flexibility of the finite-element grid, which allows a close spatial approximation of irregular boundaries of the aquifer and/or of parameter zones within the aquifer when they are considered. However, the construction and specification of an input data set are much more difficult for an irregular finite-element grid than for a regular rectangular finite-difference grid. Thus, the use of a graphical model preprocessor that includes a mesh generator should be considered. A hypothetical aquifer system with impermeable boundaries and a well field (Figure 3A) has been discretized using finite-difference (Figure 3B) and finite-element (Figure 3C) grids. Grids can be adjusted to use a finer mesh spacing in selected areas of interest. The rectangular finite-difference grid approximates the aquifer boundaries in a step-wise manner, which results in some nodes or cells outside of the aquifer, whereas sides of the triangular elements of the finite-element grid can closely follow the outer boundary using a minimal number of nodes.

C. Groundwater Flow Models

A major revolution in the quantitative analysis of groundwater flow systems came in the early 1970s with the introduction and documentation of two-dimensional, deterministic, distributed-parameter, digital computer simulation models. These models rep-

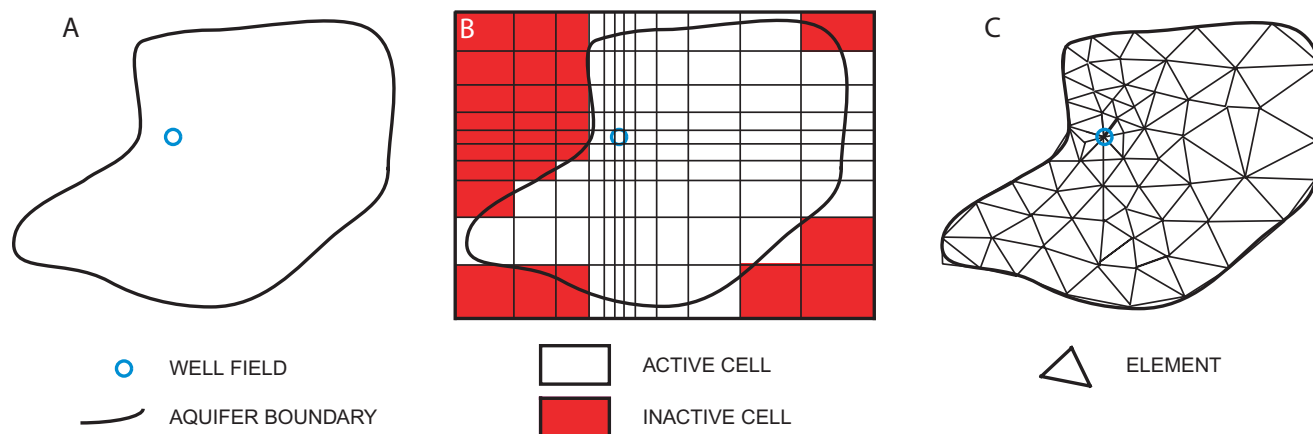


FIGURE 3 Application of a numerical model to simple hypothetical problem, showing (A) an irregularly bounded aquifer discretized using (B) a finite-difference grid and (C) a finite-element grid. (From Konikow & Reilly, 1998.)

resented a major improvement over analytical methods because they allowed the representation of heterogeneous properties, complex boundary conditions, and time-varying stresses. As improved numerical methods were developed and more powerful computers became widely available, three-dimensional modeling became standard practice by the early 1990s. Practical aspects of applying groundwater models are reviewed by Anderson and Woessner (1992).

Groundwater flow models solve a governing partial differential equation. The solution defines the hydraulic-head distribution at every point within the boundaries of the problem domain. When this is accomplished using numerical methods, the solution inherently also provides the fluid fluxes throughout the discretization grid. Solving the flow equation requires the specification of the properties of the groundwater system (and their spatial variability), the boundary conditions, and, for transient problems, the initial conditions.

The knowledge of the heads (or water levels or fluid pressures) and the direction and rate of flow provides much insight into the nature of the groundwater flow system, and allows inferences to be made about (1) potential source areas for toxic substances detected in groundwater and (2) potential discharge areas or receptors for flow and transport of dissolved toxic constituents away from known sources of soluble toxic substances. When problems are detected and analyzed using a simulation model, the model can be used as a management tool to help evaluate alternative decisions for reducing risks to public health or the environment.

The major difficulty in groundwater modeling is accurately defining the properties of the system and the

boundary conditions for the problem domain. The subsurface environment is a complex, heterogeneous, three-dimensional framework. To determine the unique parameter distribution for a field problem, so much expensive field testing would be required that it is seldom feasible either economically or technically. Therefore, the model typically represents an attempt, in effect, to solve a large set of simultaneous equations with more unknowns than equations. It inherently is impossible to obtain a unique solution to such a problem. Therefore, limited sampling and understanding of the geological heterogeneity causes uncertainty in the model input data (aquifer properties, sources and sinks, and boundary and initial conditions). This uncertainty leads to non-uniqueness in the model solution.

Uncertainty in parameters logically leads to a lack of confidence in the interpretations and predictions that are based on a model analysis, unless the model can be demonstrated to be a reasonably accurate representation of the real system. To demonstrate that a deterministic groundwater simulation model is realistic, usually field observations of aquifer responses (such as changes in water levels for flow problems or changes in concentration for transport problems) are compared to corresponding model-calculated values. The objective of this calibration procedure is to minimize differences between the observed data and calculated values. The minimization is accomplished by adjusting parameter values within their ranges of uncertainty until a best fit is achieved between the calculated values of dependent variables and the corresponding observations. Thus, model calibration often is considered a parameter-estimation procedure. Usually, the model is considered

calibrated when it reproduces historical data within some acceptable level of accuracy. The level of acceptability is, of course, determined subjectively. Although a poor match provides evidence of model errors, a good match does not necessarily prove the validity or adequacy of the model (Konikow & Bredehoeft, 1992).

The calibration of a deterministic groundwater model often is accomplished through a trial-and-error adjustment of the model input data to modify model output. Because a large number of interrelated factors affect the output, trial-and-error adjustment may be a highly subjective and inefficient procedure. Advances in automatic parameter-estimation procedures help to eliminate some of the subjectivity inherent in model calibration. The newer procedures generally treat model calibration as a statistical procedure using multiple regression approaches. Parameter-estimation procedures allow simultaneous model construction, application, and calibration using uncertain data, so that the uncertainties in model parameters and in predictions and assessments can be quantified.

Automated parameter-estimation techniques improve the efficiency of model calibration and have two general components: one that calculates the best fit (sometimes called automatic history matching) and a second that evaluates the statistical properties of the fit. These techniques also are called *inverse models*, as they treat the system parameters as unknowns. The minimization procedure uses sensitivity coefficients that are based on the change in calculated value divided by the change in the parameter (for example, the change in head with changing transmissivity). The sensitivity coefficients may be useful in the consideration of additional data collection. Hill (1998) provides an overview of methods and guidelines for effective model calibration using inverse modeling.

One of the most popular and comprehensive deterministic groundwater models available today is the U.S. Geological Survey's (USGS) MODFLOW code (McDonald & Harbaugh, 1988; Harbaugh et al., 2000). This model actually is an integrated family of compatible codes that centers on an implicit finite-difference solution to the three-dimensional flow equation. The basic model uses a block-centered, finite-difference grid that allows variable spacing of the grid in three dimensions. Flow can be steady or transient. Aquifer properties can vary spatially and hydraulic conductivity (or transmissivity) can be anisotropic. Flow associated with external stresses, such as wells, distributed recharge in areas, evapotranspiration, drains, lakes, and streams, can also be simulated through the use of specified head, specified flux, or head-dependent flux boundary condi-

tions. The implicit finite-difference equations can be solved using any one of several solution algorithms. Although the input and output systems of the program were designed to permit maximum flexibility, usability and ease of interpretation of model results can be enhanced by using one of several commercially available preprocessing and post-processing packages; some of these operate independently of MODFLOW, whereas others are directly integrated into reprogrammed and/or recompiled versions of the MODFLOW code.

A variety of other MODFLOW accessory codes, packages, and features are available. Most of these were developed by the USGS; examples include coupled surface water and groundwater flow, aquifer compaction, transient leakage from confining units, rewetting of dry cells, horizontal flow barriers, alternative interblock transmissivity conceptualizations, cylindrical flow to a well, a statistical processor, a data-input program, and a program that calculates water budgets. Other packages have been developed by non-USGS sources to work with MODFLOW; one example is the advective-dispersive solute-transport model MT3D (Zheng & Wang, 1999). The latest version of MODFLOW (MODFLOW-2000) has an inverse modeling capability built in to the code, which allows the user to do parameter estimation and sensitivity analyses directly (Hill et al., 2000).

The utility of groundwater flow modeling is illustrated by its application to a selenium problem in California, where more than 2 million acres of agricultural land is irrigated in the western San Joaquin Valley (see Chapter 15). Since 1967, imported surface water has been the primary source for irrigation; hence, groundwater pumping simultaneously declined (Belitz & Phillips, 1992). This combination caused increased recharge to the underlying aquifers and subsequent water-table rises. By the early 1990s, the water table was high (within 10 feet of the land surface) over more than half of the area. Because such areas are prone to soil salinization and other problems, subsurface tile drains have been used to keep the water table deep enough to minimize these problems. However, the agricultural drainage water was high in selenium and eventually flowed into the Kesterson Wildlife Refuge, which led to deaths and deformities of waterfowl and aquatic biota (Deverel et al., 1984; Presser & Barnes, 1985). These problems led to the closure of drains contributing selenium, which left considerable concern about how to manage the groundwater flow system in a manner that maintained agricultural productivity yet precluded selenium transport.

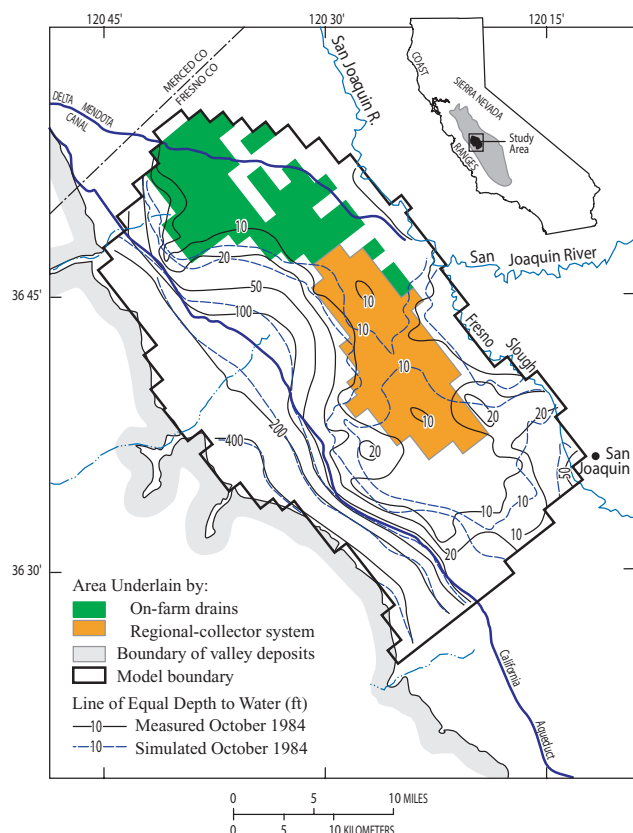


FIGURE 4 Measured and simulated depths to water in the central part of the western San Joaquin Valley, California, October 1984. (Modified from Belitz et al., 1993.)

According to Presser et al. (1990), the source of the selenium is from weathering of pyritic marine shales in the Coast Ranges just west of the San Joaquin Valley. They believe that selenium is mobilized by oxidative weathering in an acidic environment, which concentrates the soluble selenate form of selenium. Selenate is transported readily in flowing groundwater and surface runoff.

A transient, three-dimensional, finite-difference model of the regional groundwater flow system was developed to assess water-table responses to alternative management that would affect groundwater recharge and discharge (Belitz et al., 1993). The model was calibrated using hydrologic data collected from 1972 to 1988. The model results indicate good agreement between measured and simulated depths to water (Figure 4).

The calibrated model was used to evaluate the possible effects of various management practices on the depth of the water table (see Figure 5 for representative

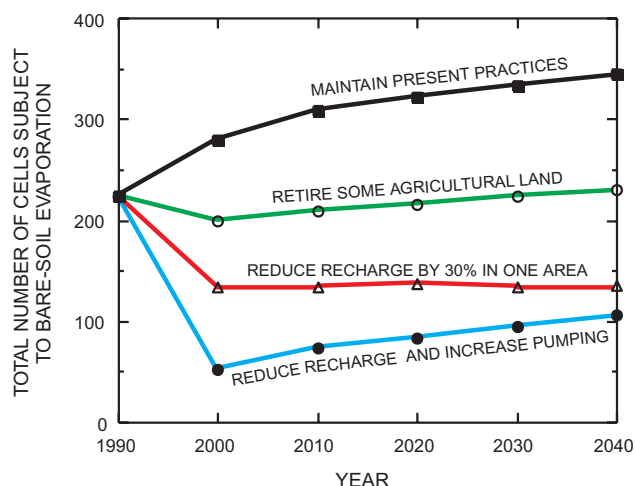


FIGURE 5 Predicted effects of selected water management alternatives on area of high water table. (Modified from Belitz & Phillips, 1992.)

results). The number of cells (each having an area of one square mile) subject to bare-soil evaporation is an indicator of the depth to water because only cells in which the water table is less than 7 feet deep will fall into this category. Higher water-table elevations also yield greater discharge to drains. If present practices are maintained, the area underlain by a high water table will continue to increase, as will discharge to drains. Reducing recharge (by increasing irrigation efficiency), increasing pumping, and removing land from agricultural production all will help to mitigate the problem. Thus, the groundwater flow model provides a powerful tool to help water managers mitigate the selenium problem while considering cost-benefit ratios.

D. Groundwater Pathline Models

Pathline models simulate the process of advective transport. They use calculated velocities to compute where and how fast water and nonreactive dissolved chemicals migrate. This requires the specification of an additional physical parameter—the porosity of the groundwater system (and its spatial variability). Also, the hydraulic-head gradients must be known, typically from the output of a groundwater flow model. It is useful for estimating where fluid and dissolved solutes are moving, how fast they are moving, and their source. They also can be useful for cross-checking age dates estimated from isotopic analyses. Pathline models, however, cannot calculate solute concentrations because dilution

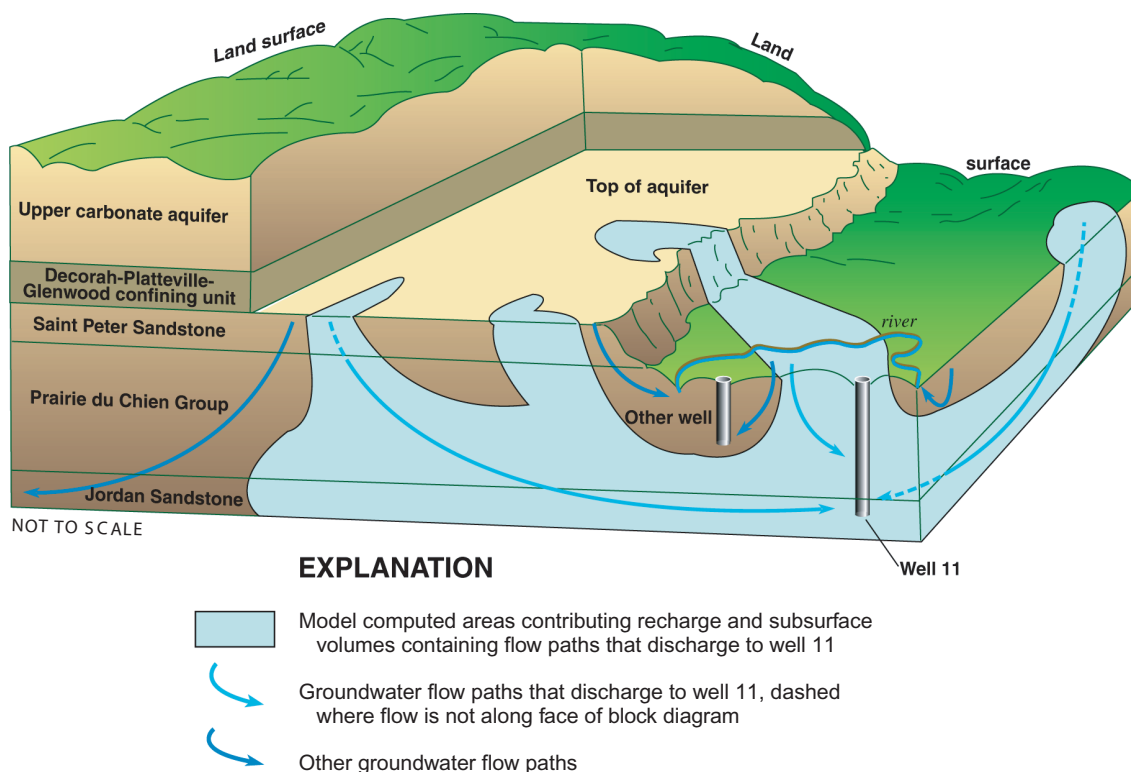


FIGURE 6 Long-term (steady-state) contributing recharge areas for well 11 near Rochester, Minnesota, calculated using pathline model. Complex three-dimensional patterns of groundwater flow yield irregularly shaped volumes in the subsurface containing the many flow paths that originate at the water table and discharge at well 11. (From Franke et al., 1998.)

or reaction mechanisms are not included in these models. Pathline models usually are much more efficient to run than transport models.

A widely used pathline program is MODPATH (Pollock, 1989), which uses MODFLOW model output and determines paths and travel times of water movement under steady-state and transient conditions. The semi-analytical, particle-tracking method assumes that each directional velocity component varies linearly within a grid cell in its own coordinate direction. For example, MODPATH was used to delineate source areas contributing recharge to a well in Minnesota (Figure 6). The results depict the complicated and discontinuous spatial patterns of contributing recharge areas to wells in highly developed aquifer systems and would be extremely difficult to derive without the aid of such a model. If toxic constituents are detected in a particular well (such as well 11 in Figure 6), the pathline model would help delineate the volume of rock material with which groundwater was in contact at earlier times. This is an invaluable aid in a search for the source of the toxic constituents.

E. Advection-Dispersion Models

The purpose of a model that simulates solute transport in groundwater is to compute the concentration of a dissolved chemical species in an aquifer at any specified time and place. The theoretical basis for the equation describing solute transport has been well documented in the literature (e.g., Bear, 1979). Zheng and Bennett (2002) provide a conceptual framework for analyzing and modeling solute-transport processes in groundwater as well as guidelines and examples for applications to field problems.

The mathematical solute-transport model requires at least two partial differential equations. One is the equation of flow, from which groundwater flow velocities are obtained, and the second is the solute-transport equation, whose solution gives the chemical concentration in groundwater. If the properties of the water are affected significantly by changes in solute concentration, as in a saltwater-intrusion problem, then the flow and transport equations should be solved simultaneously (or at least iteratively). If the properties of the

water remain constant, then the flow and transport equations can be decoupled and solved sequentially, which is simpler numerically.

The solute-transport equation is more difficult to solve numerically than the groundwater flow equation, largely because the mathematical properties of the transport equation vary depending upon which terms in the equation are dominant in a particular situation. When solute transport is dominated by advection, as is common in many field problems, then the governing equation approximates a hyperbolic type of equation (similar to equations describing the propagation of a wave or of a shock front). But if transport is dominated by dispersive fluxes, such as might occur where fluid velocities are low and/or hydrodynamic dispersion is relatively high, then the governing equation becomes more parabolic in nature (similar to the transient groundwater flow equation).

The numerical methods that work best for parabolic partial differential equations are not best for solving hyperbolic equations and vice versa. Thus, no one numerical method or simulation model will be ideal for the entire spectrum of groundwater transport problems likely to be encountered in the field. Further compounding this difficulty is that the seepage velocity of groundwater in the field is highly variable, even if aquifer properties are homogeneous, because of the effects of complex boundary conditions. Thus, in low permeability zones or near stagnation points, the velocity may be close to zero and the transport processes will be dominated by dispersion processes; in high permeability zones or near stress points (such as pumping wells), the velocity may be up to several meters per day and the transport processes will be advection dominated. In other words, the governing equation may be more hyperbolic in one area (or at one time) and more parabolic in another area (or at another time). Therefore, regardless of which numerical method is chosen as the basis for a simulation model, it will not be accurate or optimal over the entire domain of the problem. The transport modeling effort must recognize this inherent difficulty and strive to minimize and control the numerical errors.

Additional complications arise when the solutes of interest are reactive. Simple reaction terms do not necessarily represent the true complexities of many reactions (see, for example, Glynn, 2003). Also, particularly difficult numerical problems arise when reaction terms are highly nonlinear, or if the concentration of the solute of interest is strongly dependent on the concentration of other chemical constituents. For field problems where reactions appreciably affect solute

concentrations, simulation accuracy is less limited by mathematical constraints than by data constraints. That is, the types and rates of reactions for the specific solutes and minerals in the particular groundwater system of interest rarely are known and require an extensive amount of data to assess accurately.

Finite-difference and finite-element methods also can be applied to solve the transport equation, particularly when dispersive transport is large compared to advective transport. However, numerical errors, such as numerical dispersion and oscillations, may be large for some problems. The numerical errors generally can be reduced by using a finer discretization (either shorter time steps or finer spatial grid), but this discretization will increase the computational work load. An example of a documented three-dimensional, transient, finite-difference model that simultaneously solves the fluid pressure, energy-transport, and solute-transport equations for non-homogeneous miscible fluids is HST3D (Kipp, 1997). An example of a finite-element transport model is SUTRA (Voss, 1984).

Although finite-difference and finite-element models commonly are applied to transport problems, none of the standard numerical methods is ideal for a wide range of transport problems and conditions. Thus, there currently is much research on developing better mixed or adaptive methods that aim to minimize numerical errors and combine the best features of alternative standard numerical approaches. Examples of other types of numerical methods that also have been applied to transport problems include method of characteristics, random walk, Eulerian-Lagrangian methods, and adaptive grid methods. All these numerical methods have the capability to track sharp fronts accurately with a minimum of numerical dispersion. Documented models based on variants of these approaches include Konikow et al. (1996) and Zheng and Wang (1999).

As an example, the public domain MOC3D model (Konikow et al., 1996) is integrated fully with the MODFLOW-2000 code. The model computes changes in concentration over time caused by the processes of advective transport; hydrodynamic dispersion; mixing or dilution from fluid sources; matrix diffusion; a first-order irreversible-rate reaction, such as radioactive decay; and reversible equilibrium-controlled sorption with a linear isotherm. The model couples the groundwater flow equation with the solute-transport equation. MOC3D uses the method of characteristics to solve the solute-transport equation, by which a particle-tracking procedure represents advective transport and a finite-difference procedure calculates concentration changes caused by hydrodynamic dispersion.

There are many examples in the literature illustrating the application of solute-transport models to problems involving contaminant plumes emanating from point sources of contamination, but few dealing with natural sources. One of the few involves the application of MODFLOW and MT3D to the arsenic problem in Bangladesh, wherein the sustainability of groundwater development is evaluated on the basis of constraining increases in arsenic concentrations in supply wells calculated by the coupled models (Cuthbert et al., 2002).

F. Aqueous Speciation Modeling

Geochemical speciation models, such as WATEQF (Plummer et al., 1976) and WATEQ4F (Ball & Nordstrom, 1991), calculate the distribution of chemical elements among different aqueous species (bare ions, complexes, and ion pairs) at a given temperature and pressure, determine whether the aqueous solution is supersaturated or undersaturated with respect to various solid mineral phases, and calculate the partial pressure of gases that would be in equilibrium with the calculated solution composition. Speciation models also calculate the total dissolved inorganic concentration (TDIC) of a solution given its measured alkalinity, or conversely calculate its alkalinity given a measured TDIC concentration.

Speciation codes solve a set of algebraic equations that are basically of two types: mass-balance and mass-action. Mass-balance equations relate the total dissolved concentration (a user-provided measured quantity) of given elements or components to the sum of the concentrations of their aqueous species multiplied by the stoichiometric coefficient of the element/component in each species. Mass-action equations provide thermodynamic relations describing the dependence of the activity (i.e., the thermodynamically effective concentration) of a given aqueous species on the activities of other aqueous species, pH, and redox potential.

To solve the equations described above, speciation codes require that the user provide a complete chemical analysis of the water, including not only the total dissolved concentrations of major and minor elements, but also the pH of the solution and some indication of its redox potential. The redox potential either can be indicated by an Eh or pe value, or alternatively by one or more redox couples. If only one redox couple (e.g., the Fe(II)/Fe(III) couple) is entered, it typically will be used to define the redox potential for all redox-active elements in the solution. More advanced codes, such as PHREEQC (Parkhurst, 1995; Parkhurst & Appelo,

1999), allow the specification of more than one redox couple and allow the user to apply each couple to control the redox distribution of specific redox-active elements.

In addition to the solution-specific data that must be entered by the user, speciation codes also require a thermodynamic database that provides equilibrium constants, as a function of temperature and pressure, for the various aqueous-speciation and complexation reactions considered, and for potential mineral and gas dissolution and precipitation/exsolution reactions. The quality of a speciation code's output will, in large part, be determined both by the quality of the user-entered data and by the quality of the thermodynamic database associated with the code. Ideally, thermodynamic databases should be internally consistent, should consider all major aqueous species, and should be based on accurate measurements. Thermodynamic consistency has many meanings (Nordstrom & Munoz, 1994) such as (1) the data are consistent with basic thermodynamic relations; (2) common scales are used for temperature, energy, atomic mass, and fundamental physical constants; (3) the same mathematical and chemical models were used to fit different data sets; (4) conflicts among measurements were resolved; and (5) appropriate choices of standard states were made and used for all similar substances. In practice, there is considerable uncertainty in thermodynamic data and judging the extent of the uncertainty for different elements, conditions, and calculated results requires geochemical expertise and experience in using the database.

Thermodynamic databases typically consider few organic species, even though organic species are important constituents in both natural and contaminated waters. Most codes and associated thermodynamic databases also are limited to modeling the speciation of relatively dilute waters, with ionic strengths (or salinity) lower than seawater. The few codes that are available to model the speciation of saline waters and brines usually have little or no data available to model the speciation of minor elements, metals, or radionuclides or redox states. Finally, most speciation codes assume that the aqueous species present are at equilibrium with each other. Although most "homogeneous" aqueous-speciation reactions are fast, this is not always the case for reactions involving redox-active species and elements, and/or strong aqueous complexes and polymerized species. The kinetics of formation/dissociation of those species can be slow and the kinetics of redox reactions often depend on microbial catalysis.

Speciation models help in understanding the speciation of an aqueous solution and its thermodynamic

state, particularly with respect to the potential dissolution/precipitation/exsolution of various minerals and gases, and to the potential for the exchange or sorption of ions and aqueous species on mineral surfaces. Also, the results of speciation codes can provide valuable insight into the potential toxicity of a natural or contaminated water. For example, dissolved Cr species are more toxic in the +6 oxidation state than in the +3 oxidation state, and strongly complexed cyanide species such as ferro- and ferricyanides also are less harmful than CN^- and HCN^0 species. The speciation of a water immediately reveals the predominant forms of potentially toxic elements in a water (assuming that proper thermodynamic data are available) in addition to total concentrations. Finally, aqueous speciation codes often form the core of other geochemical modeling codes, such as “inverse” geochemical modeling codes, sometimes also confusingly referred to as mass-balance models, and also “forward” modeling codes (mass-transfer codes and mass-transport codes).

G. Inverse Geochemical Modeling

Inverse geochemical modeling uses available chemical and isotopic analyses, which are assumed to be representative of the chemical and isotopic evolution of groundwater along a given flow path, and attempts both to identify and quantify the heterogeneous reactions that may have been responsible for that chemical and isotopic evolution. A speciation code typically is run, as part of the inverse modeling process, to help the user determine the set of reactions that is thermodynamically feasible, to convert alkalinity measurements into TDIC concentrations, and to calculate the redox state (not the redox potential) of the waters considered. Establishing the redox state of the waters is a convention-based process and simply allows the user to ensure that an electron mass balance is maintained, and that no free electrons are created or destroyed as a result of the reactions considered. Nevertheless, apart from the above considerations, the inverse modeling approach does not require that reactions proceed to thermodynamic equilibrium and indeed some of the early inverse modeling codes did not contain a speciation code or a thermodynamic database.

Inverse modeling codes essentially solve a set of algebraic mass-balance equations describing the changes in chemistry and isotopic composition between two waters (or more in the case of “mixtures”) and relate those changes to lists of potential reaction sets and reaction

amounts. “Initial” waters represent source waters prior to mixing and reactions considered by the model. “Final” water represents measured composition after mixing and reaction processes. Typically, the user specifies a list of plausible reactions (sometimes called “phases”) and also provides a list of components (chemical or isotopic) that will be used to set up and solve the set of mass-balance equations. The inverse modeling code calculates one or more possible “models” (i.e., reaction sets and amounts) that obey the specified mass balances. Glynn and Brown (1996) provide a detailed description of inverse geochemical modeling, its requirements and limitations, and the relative capabilities of the two most commonly used codes, NETPATH (Plummer et al., 1994) and PHREEQC (Parkhurst & Appelo, 1999).

The PHREEQC code has an advantage over NETPATH in that it accounts for the uncertainties in the analyses provided and, therefore, avoids consideration of reactions with small mass transfers that instead could be explained by uncertainties in the basic data. To do this analysis, PHREEQC assumes that the charge balance error on each given aqueous solution is caused by errors in the analytical data provided, and attempts to “adjust” the analytical data to correct for the charge balance error without exceeding uncertainty limits provided by the user for each analytical datum (total concentrations of each element, pH, isotopic data). PHREEQC also does a more complete accounting of redox balances than NETPATH, and allows redox balances to be maintained not only among the overall redox states of the different waters and reactions, but also among specified redox states for individual elements. Finally, PHREEQC also solves a water-balance equation, an alkalinity balance equation, and a mass balance on inorganic carbon.

NETPATH has some capabilities that are not matched by the inverse modeling capabilities of PHREEQC. Foremost, NETPATH incorporates ^{14}C dating capabilities using various literature-based models, or alternatively and preferably, using reaction-based inverse models. Additionally, NETPATH incorporates isotopic fractionation factors to calculate the ^{13}C , ^{34}S , and ^{15}N compositions of the final water. In its isotopic calculations, NETPATH also solves differential equations, which account for the progressive isotopic evolution of a water as various phases dissolve into it and various phases precipitate or exsolve from it with differing and evolving isotopic compositions. In contrast to NETPATH, PHREEQC inverse modeling only considers isotopic mass-balance constraints, as posed by the user. The PHREEQC user is required to provide

the measured isotopic compositions and their uncertainties for the initial and final waters, for dissolving phases, and for precipitating/exsolving phases.

Inverse geochemical modeling is used to *explain* and help understand the observed chemical and isotopic evolution of natural (or contaminated) waters, rather than to *predict* future compositions (as is done by forward geochemical modeling). A minimum amount of data is required to use an inverse geochemical modeling code, namely the compositions of at least one “initial” water and a final water. Inverse geochemical modeling is best used early in the data-acquisition process because it forces the user to think and evaluate the nature and extent of knowledge gaps and uncertainties. Therefore, inverse geochemical modeling can be used to guide the field-data acquisition process. As should be the case for most hydrological and geochemical modeling, inverse geochemical modeling should be used as part of a continuous iterative cycle between data acquisition and data interpretation and modeling until some desired level of detail is obtained in understanding the system investigated.

Although inverse geochemical codes at a minimum require two chemical analyses, one for each water, the modeling process requires appreciable knowledge and expertise. The user has to postulate a list of possible reactions that may be responsible for the observed evolution, and, therefore, needs to have a mineralogical knowledge of the system to be able to make reasonable guesses as to what minerals and gases might be dissolving, precipitating, or exsolving. The user also needs to consult the speciation results to determine which reactions are thermodynamically feasible. For example, if both the initial and final waters are undersaturated with respect to a given mineral, it is unlikely that a reaction model that requires precipitation of the mineral would be valid.

The user needs to have some understanding of the relative kinetics of various reaction processes to be able to judge whether a given reaction process is likely to occur to the extent calculated for a given reaction model, given the estimated travel and evolution time of the water. Establishing a plausible hydrologic relation between the initial and the final waters and estimating a likely travel time between sampling points requires hydrological knowledge of the system and may involve application of a groundwater flow model. Conversely, the inverse geochemical modeling process may result in an improved, or sometimes radically modified, hydrologic understanding of the groundwater system. For example, if all available models predict that a chloride-containing phase needs to precipitate, a thermodynam-

ically unrealistic conclusion in most cases, it is likely instead that either (1) the initial and the final waters are not hydrologically related or (2) the inverse geochemical modeling process perhaps should consider the diluting effect of an additional initial water to explain the lower chloride concentration of the final water.

Inverse geochemical models can account for the possibility of having more than one initial water responsible for the evolution to a final water composition. Inverse geochemical codes do not consider the various possible mechanisms responsible for the “mixing” of the various initial waters: hydrodynamic dispersion, solute diffusion, mixing of various waters as a result of the sampling process (long screens, temporal variations in water chemistry), and other possibilities. It is the responsibility of the model user to assess the hydrological situation and consider the likelihood of the various processes that might cause this “mixing.”

A primary value of inverse geochemical modeling is to force the model user to put all available hydrological, chemical, isotopic, and mineralogical data within a conceptual framework. This action should (1) result in an improved understanding of the chemical and isotopic reactions that may be responsible for the observed evolution of the waters, (2) help refine and improve the user’s hydrological understanding of the system, and, most importantly, (3) help assess the nature of some of the remaining uncertainties in the constructed conceptual framework.

H. Forward Geochemical Modeling: Overview

Forward geochemical modeling differs conceptually from inverse geochemical modeling. Inverse modeling uses available aqueous-solution data and calculates the mass-transfer amounts of various reactions suspected of accounting for the evolution of an initial water to a final water. Inverse modeling is most useful when abundant chemical, isotopic, mineralogical, and hydrologic data are available, and when the user’s objective is to explain the past chemical evolution of a groundwater system.

In contrast, forward modeling attempts to predict the future chemical composition of an aqueous solution given an initial solution and given certain postulated reactions, some of which usually are considered to go to thermodynamic equilibrium. Forward modeling is most useful when the amount of chemical and isotopic data available for a given groundwater system is limited and when the modeler’s objective is to predict the future evolution of the system.

I. Forward Modeling: Mass-Transfer Codes

Mass-transfer geochemical codes are used to predict the possible evolution of a water as it contacts, forms, and/or reacts with other phases such as minerals, gases, surface phases, organic matter, and non-aqueous-phase liquids (NAPLs). Most currently available geochemical codes consider only interactions with minerals, gases, and surfaces. A mass-transfer code essentially is an extension of a speciation code. The main difference is that a mass-transfer code uses thermodynamic (and sometimes kinetic) information to calculate not only the speciation of the aqueous solution (i.e., the aqueous-phase reactions), but also to calculate the effect of heterogeneous reactions (reactions between the aqueous phase and other phases) on the composition and speciation of the aqueous phase and on the composition of contacting phases. Many possible reactions and processes can be simulated, including mineral dissolution and precipitation, gas dissolution and exsolution, gas bubble formation, ion exchange on fixed-charge surfaces, ion sorption on variable charge surfaces, evaporation, dilution and mixing of aqueous solutions, precipitation and dissolution of solid-solution phases, boiling, temperature and pressure changes, radioactive decay, and biodegradation reactions. Most commonly, the user makes the assumption that the processes go to full (or partial) thermodynamic equilibrium, but the most recent codes, such as PHREEQC (Parkhurst & Appelo, 1999) and EQ3/6 (Wolery, 1992) also can consider reaction kinetics (given appropriate rate law and kinetic constant information from the user) and can calculate changes in composition as a function of time.

Similar to a speciation code, a mass-transfer numerical model solves a set of algebraic mass-balance and mass-action equations. The mass-balance equations impose conservation of mass for the various components of the system across all phases. The mass-action equations provide for specification of thermodynamic equilibrium for both homogeneous (aqueous-only) and heterogeneous (mass-transfer) reactions. If reaction kinetics are simulated, a set of one or more ordinary differential equations also is solved. Mass-transfer codes have all the limitations of speciation codes (uncertainties, errors, and gaps in thermodynamic and analytical data). In addition, numerical convergence problems tend to occur more frequently in mass-transfer codes than in speciation codes. These problems usually are caused by the extreme changes in the concentrations of individual species that can result from even minor heterogeneous-reaction-driven changes in the pH or pe conditions.

Mass-transfer geochemical codes are useful tools in understanding and predicting the effects of reaction processes in groundwater systems. They can be used to predict the minimum and maximum concentrations that may be expected, as a function of varying physicochemical conditions, for various chemical elements and constituents that may be either toxic or essential to human health. The accuracy of the predictions will be much greater for major constituents (Ca, Na, Mg, K, Cl, SO_4 , C, SiO_2) than for minor and trace elements, which often are of concern in water-quality studies. Multiple competing processes often control the concentrations of minor and trace elements; these elements usually are associated and heterogeneously distributed across many different mineral phases and surfaces. Considerable uncertainties and gaps exist in the available thermodynamic data for minor and trace element processes. Finally, many of the processes are kinetically controlled and are not adequately described by the assumption of thermodynamic equilibrium.

Despite the above uncertainties, geochemical mass-transfer codes have the potential to improve the understanding of minor and trace element geochemistry. These codes are essential in determining and predicting the effects of the major reaction processes that are responsible for the evolution of pH, pe, and major element and complexant concentrations. Understanding and predicting the dominant chemical characteristics of the groundwater system is key to understanding and predicting the effects of reaction processes that control the concentrations of minor and trace elements.

Inverse and forward geochemical modeling codes can be complementary, as illustrated by an example describing a fluoride water-quality problem. Groundwater from the Black Creek aquifer in the coastal region of South Carolina has elevated concentrations of fluoride. The general geochemistry of the groundwater, the occurrence and causes of elevated fluoride concentrations, and the public-health aspects of the fluoride problem have been discussed by Zack (1980) and Zack and Roberts (1988). Fluoride concentrations in groundwater in this region generally range from 0.5 mg/L in shallow upgradient (younger) waters to 5.5 mg/L in downgradient (older) waters (compared to a recommended limit of 2.0 mg/L). Dentists in the area have noted a high occurrence of dental fluorosis (mottling of dental enamel) among people who have lived since childhood in the area. The problem seems to be mainly cosmetic; epidemiological studies have indicated no significant long-term health risk for fluoride concentrations of 10 mg/L or less.

TABLE I. Water Chemical Compositions Used in Inverse and Forward Geochemical Modeling of Groundwaters From the Black Creek Aquifer in South Carolina.

	Geo-113	Geo-117	Seawater
Temp	20	20	25
pH	8.5	8.5	8.22
HCO ₃	390	626	142
Ca	2	3.4	410
Mg	1.8	1.4	1350
Na	170	320	10500
K	7	0.9	390
Fe	0.02	0.3	0.003
Cl	51	83	19000
SO ₄	9.2	4.2	2700
F	0.5	4.6	1.3
SiO ₂	13	19	6.4
PO ₄	0.09	0.15	0.28

Units in mg/L.
Seawater composition from Hem, 1992.

Zack (1980) and Zack and Roberts (1988) gave a thorough and reasonable explanation of the sources and factors affecting fluoride concentrations and the general geochemistry of the groundwater in the region. Our numerical modeling analysis supports their conclusions and provides further insight, which may allow a better understanding of fluoride geochemistry in groundwaters of the Atlantic Coastal Plain and elsewhere.

Geochemical speciation of a typical high-fluoride water (Table I; Well Geo-117) indicates that the water is undersaturated with respect to fluorite (CaF₂), a mineral with fast reaction kinetics. If fluorite were the source of the dissolved fluoride, speciation of the high-fluoride groundwater likely would be close to thermodynamic equilibrium with respect to fluorite. Although some phosphate nodules found in the Black Creek aquifer also contain fluoride, tests have shown that water drawn from phosphatic deposits in eastern North Carolina contain relatively little fluoride (0.4 mg/L), and, consequently, are not thought to be a source of fluoride in the Black Creek aquifer. Instead, Zack (1980) and Zack and Roberts (1988) suggest that fossil shark teeth found in the most hydraulically conductive layers of the aquifer are the source of fluoride. Shark teeth consist of almost pure cryptocrystalline fluoroapatite.

The Black Creek Formation consists of fine to very fine sands interbedded with laminated clays. The shark

teeth were deposited during the Upper Cretaceous in a marine environment and now are abundant in thin, relatively continuous layers of calcite-cemented quartz sands. These layers are present in the most transmissive upper third of the aquifer. Zack (1980; 2002, personal communication) notes that there is a strong linear correlation between dissolved fluoride concentration and alkalinity (mainly dissolved bicarbonate).

Zack suggests that the geochemical evolution of the groundwater is controlled primarily by the reaction of dilute low-pH, CO₂-rich recharge waters that, while flowing, dissolve calcite cement and exchange Ca for Na present in the initially Na-rich marine clays. The cation exchange reaction causes more dissolution of calcite than otherwise would occur. In turn, dissolution of calcite cement exposes surfaces of shark teeth. The high pH environment found at the calcite-dissolution interface causes substitutional exchange of hydroxide for fluoride in the apatite of the shark teeth, which results in high dissolved fluoride concentrations. Zack argues convincingly that substitutional exchange rather than fluoroapatite dissolution is the cause of the high fluoride concentrations.

Inverse geochemical simulations were used to identify and quantify reactions that could explain the geochemical evolution of a recharge water into a more saline high-fluoride water. The simulations were conducted first with the NETPATH code, and, subsequently, with the PHREEQC code. PHREEQC has the advantage because it accounts for data uncertainties and keeps a mass balance on H, O, charge, and alkalinity. NETPATH, which gave similar results to PHREEQC, is easier to use in the initial exploration of possible reaction models. The simulation results (Table II) largely confirm Zack's conceptual model, although it was found that proton exchange reactions occurring on disseminated organic materials could offer an additional control on the pH values of the groundwater without invoking a source of dissolved CO₂. Among reactions that were not considered in our preliminary modeling, silicate mineral weathering reactions could provide a sink for protons, whereas pyrite and marcasite oxidation could provide a source of protons. Additional information, such as isotopic data, would be required for further determination of the most likely reactions controlling the evolution of the groundwater.

Mass-transfer modeling (Figure 7) with PHREEQC indicates that thermodynamic consideration of reactions with a fluoroapatite-hydroxyapatite solid-solution series is essential in explaining the fluoride concentrations, pH values, and other geochemical characteristics observed in the groundwater. Reacting the

TABLE II. Three Inverse Models Determined with PHREEQC for the Evolution of a Low-Fluoride Water (Well Geo-113) to a High-Fluoride Water (Well Geo-117)

	CO_2 Diss.	H^+ release	H^+ Uptake
Geo-113 fraction	0.9984	0.9984	0.9984
Seawater fraction	0.0016	0.0016	0.0016
CO_2	1.904		4.134
Calcite	2.23	4.135	
HX		3.808	-4.461
CaX_2	-2.214	-4.118	0.0168
KX	-0.173	-0.173	-0.173
MgX_2	-0.110	-0.110	-0.110
NaX	4.819	4.819	4.819
CH_2O	0.223	0.223	0.223
Goethite	0.104	0.104	0.104
FeS(ppt)	-0.099	-0.099	-0.099
SiO ₂	0.100	0.100	0.100
Fluoroapatite	0.216	0.216	0.216
Hydroxyapatite	-0.216	-0.216	-0.216

Note: Minor mixing of seawater is included. Mass transfers in millimoles per kilogram of H_2O . Positive numbers indicate mass transfer into the aqueous phase.

low-fluoride water (well Geo-113) with calcite and a 99.9% fluoroapatite solid solution resulted in a fluoride concentration slightly above the maximum observed in the Black Creek aquifer, although the pH was lower than observed by about half a pH unit. Adding a proton buffering surface (previously equilibrated with seawater) increased the pH to the observed field value of 8.5, but also resulted in an increase in the fluoride concentration to 17 mg/L, three times the maximum observed in the field. Modifications of the number of surface-complexation sites and of the zero-point-of-charge of the surface proton buffer could be attempted to obtain a better fit of the field data. Further modeling analyses (incorporating other reactions) should be conducted to provide a better understanding of the factors controlling fluoride concentrations in the Black Creek aquifer.

J. Forward Modeling: Mass-Transport Codes

Geochemical mass-transport codes are used to simulate (1) the movement of groundwater, (2) the transport of

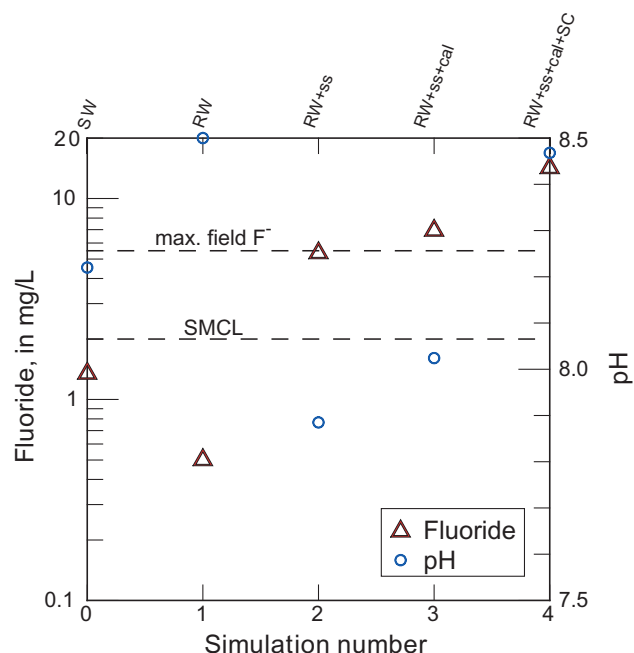


FIGURE 7 Simulated pH values and fluoride concentrations resulting from reactions between a low-fluoride recharge water (RW) sampled from well Geo-113 in the Black Creek aquifer, and combinations of the following: a fluoroapatite solid-solution (ss), calcite (cal), and a proton buffering surface (SC) modeled using a goethite surface-complexation model. Seawater (SW), pH, and fluoride values also are provided for reference, as are fluoride values corresponding to the U.S. Environmental Protection Agency's Secondary Maximum Contaminant Level (SMCL) and the maximum observed in the aquifer (dashed lines).

dissolved constituents, and (3) their reactions both within the water phase and with other phases. In addition to solving sets of algebraic mass-balance and mass-action equations, mass-transport codes also solve sets of partial differential equations describing, as a function of space and time, the distribution of groundwater potentials and velocities, and the advective and dispersive movement of solutes.

Geochemical mass-transport codes incorporate all the limitations and uncertainties associated with the use of geochemical mass-transfer codes and nonreactive solute-transport codes. Geochemical mass-transport codes commonly have convergence problems and other numerical problems (e.g., numerical oscillations, numerical dispersion) associated with the numerical solution of partial differential equations. Also, the description and simulation of physicochemical processes in geochemical transport codes suffers from a dichotomy of scale. Physical transport processes are

described at a much larger scale than the molecular level based scale applicable to chemical reactions. This dichotomy generates conceptual and numerical errors and uncertainties in the application and use of geochemical mass-transport codes.

Additionally, running geochemical transport codes can require large computer time and memory, even on today's computers. Increases in computer processing speeds have been matched by the increasing sophistication and simulation capabilities of geochemical transport codes. Possible increases in the "realism" offered by more sophisticated and complex codes, however, are counterbalanced by increased data requirements and associated increases in the uncertainties relating both to the data entered and to the mathematical representation of the simulated processes. Sensitivity analyses, where simulations are run multiple times to test the effects of the data and process uncertainties, are crucial in any intelligent use of geochemical transport codes, but commonly are hampered by computer time requirements.

Geochemical mass-transport codes can be used to predict "best case" and "worst case" scenarios of contaminant transport, but in most cases they are not exact predictive tools. Both geochemical mass-transfer and mass-transport codes are useful tools that can be used to improve conceptual understanding and to gain an appreciation of the relative quantitative importance of processes controlling the chemical evolution (and transport) of natural or contaminated waters.

The use of geochemical transport modeling is illustrated by an application to an arsenic problem in Oklahoma. The Central Oklahoma aquifer underlies about 8000 km² of central Oklahoma and is a major source of drinking water for the region. The aquifer is composed mostly of fine-grained sandstones interbedded with siltstone and mudstone. Schlottmann et al. (1998) describe its mineralogy and geochemistry, and they also recognize the occurrence of arsenic as a problem. Recharge to the aquifer occurs mainly in its unconfined eastern area and most streams are gaining (see Figure 8). To the west, the aquifer is confined by low-permeability rocks.

Concentrations of dissolved arsenic in the Central Oklahoma aquifer exceed the 1986 federal drinking water limit of 50 µg/L in about 7% of 477 analyses and even more frequently exceed the more recent standard of 10 µg/L. The highest dissolved arsenic concentrations are found primarily in the western confined part of the aquifer (Figure 8).

Mineralogical and sequential extraction analyses have shown that iron oxides (goethite and hematite) in the sandstones are the primary mineral sources of arsenic.

Arsenic sorbs strongly to iron oxides, particularly at pH values below 8. Discrete arsenic mineral phases were not found, although some evidence was found of high arsenic concentrations in pyrite grains. Pyrite only is found in isolated, poorly conductive, low redox zones. Indeed, waters in the Central Oklahoma aquifer generally are oxidic, with dissolved oxygen concentrations above 1 mg/L, and there is little organic matter or iron sulfides present. Iron oxide minerals predominate instead.

Extensive geochemical modeling of the Central Oklahoma aquifer has succeeded in elucidating the factors controlling dissolved arsenic concentrations and the general geochemical evolution of the waters (Parkhurst et al., 1993; Parkhurst, written communication, 2002). Both inverse and forward geochemical modeling was conducted, including a three-dimensional geochemical transport model using the USGS code PHAST (based on coupling HST3D with PHREEQC). Parkhurst's geochemical model assumes that the aquifer initially is filled with sodium chloride brine equilibrated with calcite and dolomite minerals, a cation-exchanger (clays), and a hydrous iron oxide surface with complexed arsenic.

In Parkhurst's model, fresh recharge water, equilibrated with calcite, dolomite, and with carbon dioxide at a partial pressure close to 100 times atmospheric (typical soil CO₂ partial pressure) enters the unconfined part of the aquifer in the east. The recharge water reacts with the initially Na-rich exchanger clays and with the As-rich and proton-depleted hydrous ferric oxide surfaces. As the groundwater flows through the porous media, ion exchange gradually changes the calcium-magnesium bicarbonate recharge water into a sodium bicarbonate water. The initial dissolution of soil carbon dioxide keeps the pH of the recharge water relatively low (between 7.0 and 7.5). After loss of contact with the soil CO₂ reservoir, however, the pH of the recharging water gradually increases from the further dissolution of calcite and dolomite (because of uptake of calcium and magnesium on exchange sites) and also from the protonation of the initially proton-depleted hydrous ferric oxide surface. The calculated pH of the resulting sodium bicarbonate water ranges from 8.5 to 9.2, which is close to the observed values. Under these higher pH conditions, sorption sites on the hydrous ferric oxide surface become predominantly negatively charged and, consequently, desorption of arsenic occurs, resulting in higher dissolved As concentrations.

In addition to simulating geochemical reactions, the PHAST code applied by Parkhurst to the Central Oklahoma aquifer also simulates groundwater flow and

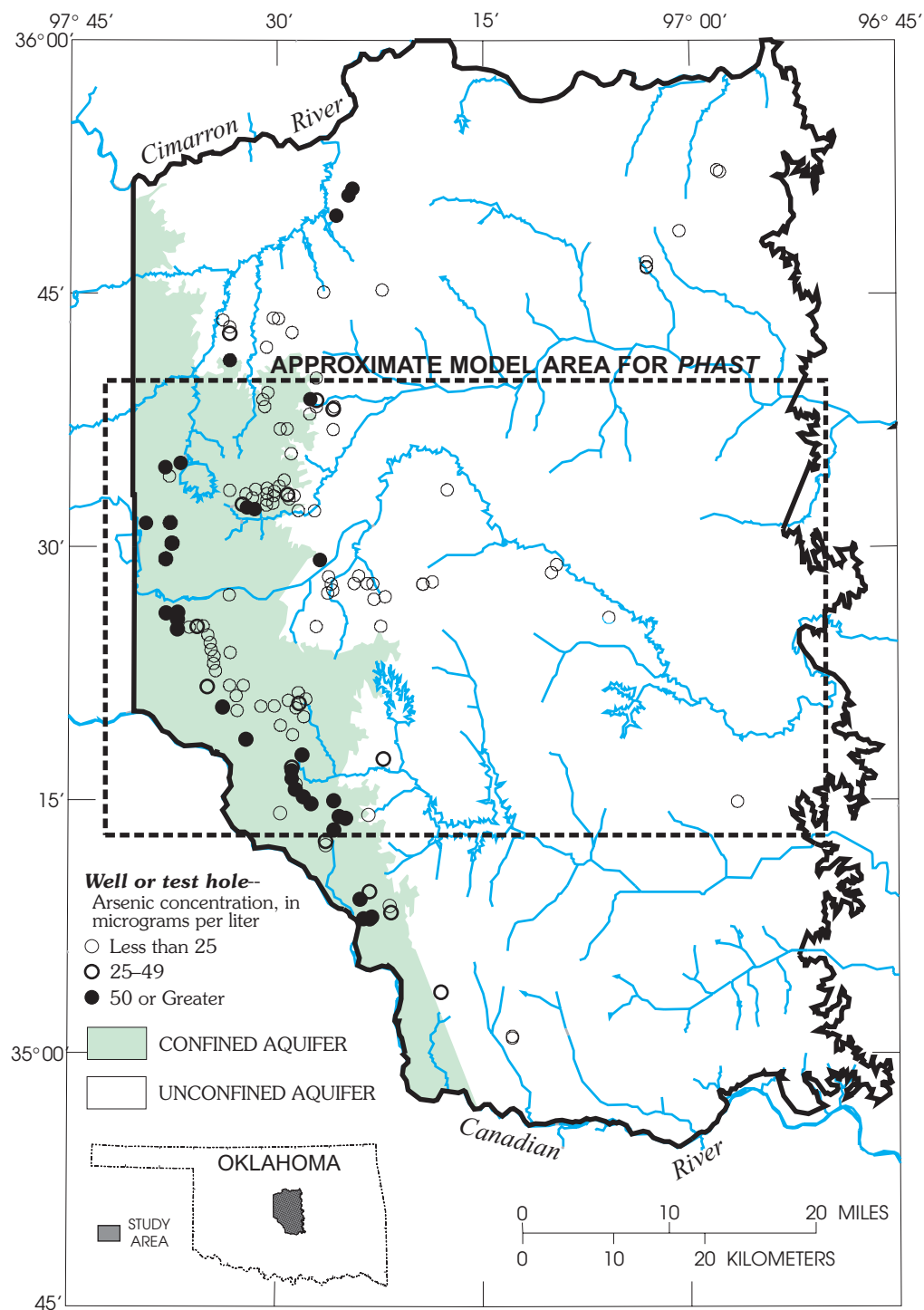


FIGURE 8 Areal distribution of arsenic in water from deep (>100m) wells and test holes from the Central Oklahoma aquifer, showing the area where the PHAST model was applied. (Modified from Schlottmann et al., 1998, and D. Parkhurst, written communication, 2002.)

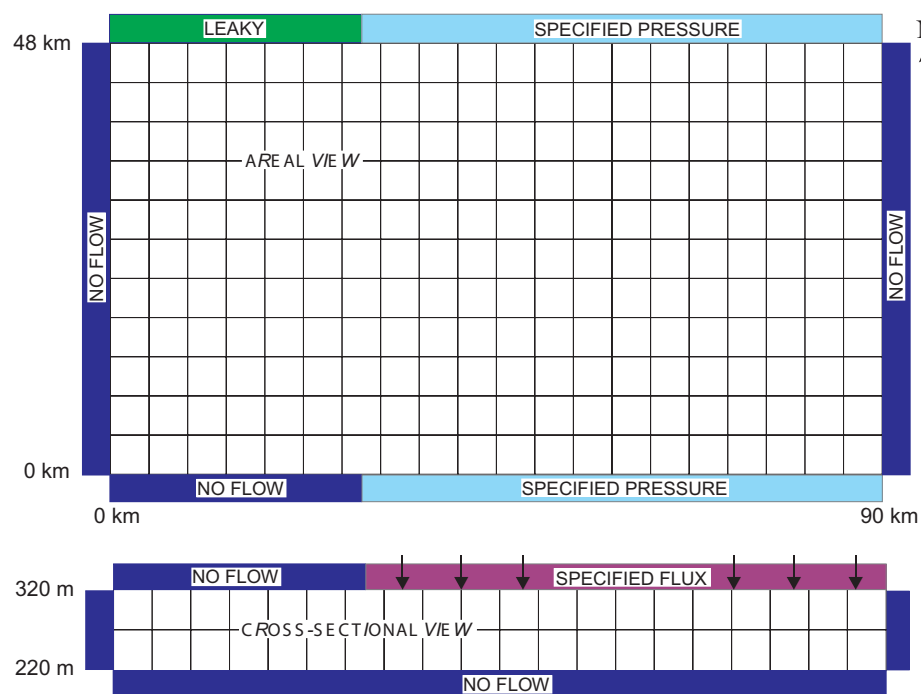


FIGURE 9 Schematic representation of grid and boundary conditions for application of *PHAST* model to Central Oklahoma aquifer. (From D. Parkhurst, written communication, 2002.)

solute-transport processes. Boundary conditions for the simulation domain (Figure 9) included specified pressures along the eastern part of the northern and southern boundaries to represent the hydrologic effects of adjacent rivers, which are the primary sinks for water discharge from the aquifer. A specified-flux boundary condition also was placed over the unconfined eastern part of the aquifer to simulate recharge.

The use of the *PHAST* model enabled Parkhurst and his coworkers to analyze the magnitude and sensitivity of various factors affecting groundwater flow, solute transport, and geochemical evolution observed in the Central Oklahoma aquifer. Their integrated model was successful in matching general hydrological and geochemical observations and in explaining the occurrence of high arsenic concentrations in the western part of the aquifer.

V. MODEL DESIGN AND APPLICATION

A. Overview

The first step in model design and application is to define the nature of the problem and the purpose of the

model (Figure 10). This step is linked closely with the formulation of a conceptual model, which is required prior to development of a mathematical model. In formulating a conceptual model, one must evaluate which processes are important for the particular problem at hand. Some processes may be important to consider at one scale of study, but negligible or irrelevant at another scale. Good judgment is required to evaluate and balance the trade-offs between accuracy and cost, with respect to model development, model use, and data requirements. The key to efficiency and accuracy in modeling a system probably is more affected by the formulation of a proper and appropriate conceptual model than by the choice of a particular numerical method or code.

Once a decision to develop a model has been made, a code (or generic model) must be selected (or modified or constructed) that is appropriate for the given problem. Next, the generic code must be adapted to the specific site or simulated region. Development of a numerical deterministic, distributed-parameter, simulation model involves selecting or designing spatial grids and time increments that will yield an accurate solution for the given system and problem. The analyst must then specify the properties of the system (and their distributions), boundary conditions, initial conditions (for

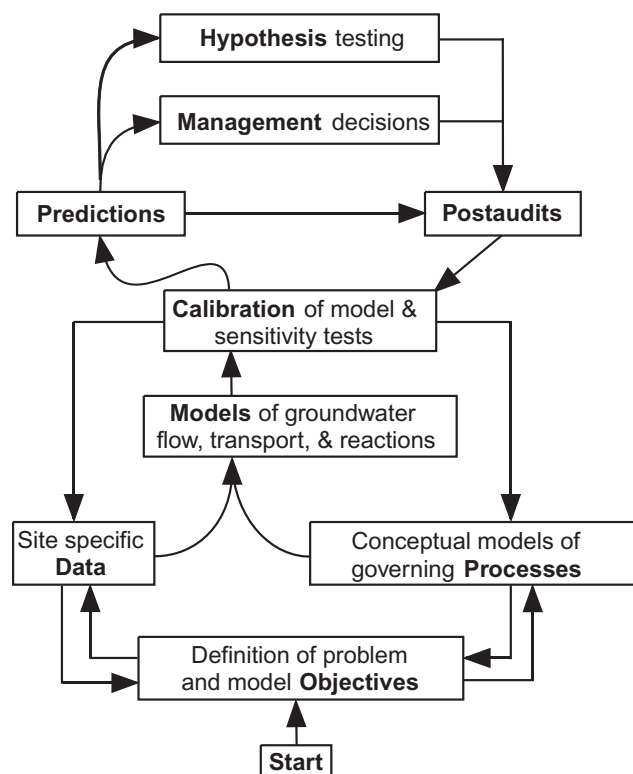


FIGURE 10 The use of models in the analysis of groundwater systems. (Modified from Konikow & Reilly, 1998.)

transient problems), and geochemical processes/reactions. All of the parameter specifications and boundary conditions really are part of the overall conceptual model of the system.

Any model is a simplified approximation of a very complex reality, but the model should capture the essential features and processes relative to the problem at hand. The selection of the appropriate model and appropriate level of model complexity remains subjective and dependent on the judgment and experience of the analysts, the objectives of the study, the level of prior information available for the system of interest, and the complexity of the modeled system. The trade-off between model accuracy and model cost always will be difficult to resolve, but always will have to be made and may affect model reliability.

Because the groundwater seepage velocity is determined from the head distribution and because both advective transport and hydrodynamic dispersion are functions of the seepage velocity, a model of groundwater flow typically is calibrated before a pathline, solute-transport, or geochemical reaction model is

developed. In a field environment, perhaps the single most important key to understanding a transport or reaction problem is the development of an accurate definition (or model) of flow. In highly heterogeneous systems, the head distribution and flow directions often can be simulated fairly accurately, whereas the calculated velocity field still may be greatly in error, which results in considerable errors in simulations of transport.

B. Grid Design

The dimensionality of a flow or transport model (i.e., one, two, or three dimensions) should be selected during the formulation of the conceptual model. If a one- or two-dimensional model is selected, then it is important that the grid be aligned with the flow system so that there is no unaccounted flux into or out of the line or plane of the grid. For example, if a two-dimensional areal model is applied, then there should be no major vertical components of flow and any vertical leakage or flux must be accounted for by boundary conditions. If a two-dimensional profile model is applied, then the line of the cross section should be aligned with an areal streamline, and there should not be any major lateral flow into or out of the plane of the cross section.

To minimize a variety of sources of numerical errors, the model grid should be designed using the finest mesh spacing and time steps that are possible, given limitations on computer memory and computational time. The boundaries of the grid also should be aligned, to the extent possible, with natural hydrologic and geologic boundaries of the aquifer. Where it is impractical to extend the grid to a natural boundary, then an appropriate boundary condition should be imposed at the grid edge to represent the net effects of the continuation of the aquifer beyond the grid. These boundaries also should be placed as far away as possible from the area of interest and areas of stresses on the system to minimize any effect of conceptual errors associated with these artificial boundary conditions.

In specifying boundary conditions for a particular problem and grid design, care must be taken not to overconstrain the solution. That is, if dependent values are fixed at too many boundary nodes, at either internal or external nodes of a grid, the model may have too little freedom to calculate a meaningful solution (Franke & Reilly, 1987).

To optimize computational resources in a model, it sometimes is advisable to use an irregular (or variably-

spaced) mesh in which the grid is finest in areas of point stresses, where gradients are steepest, where data are most dense, where the problem is most critical, and/or where greatest numerical accuracy is desired. Similarly, time steps often can be increased geometrically during a transient simulation.

C. Model Calibration and Refinement

Model calibration may be viewed as an evolutionary process in which successive adjustments and modifications to the model are based on the results of previous simulations. Overviews on the philosophy of applying and testing groundwater flow and geochemical models are presented by Konikow and Bredehoeft (1992) and Nordstrom (1994). In general, it is best to start with a simple model and add complexity or refine the grid in small increments as needed and justified.

In applying and evaluating a model, one must decide when sufficient adjustments have been made to the representation of parameters and processes and at some time accept the model as adequately calibrated (or perhaps reject the model as inadequate and seek alternative approaches). This decision often is based on a mix of subjective and objective criteria. The achievement of a best fit between values of observed and computed variables is a regression procedure and can be evaluated as such. That is, the residual errors should have a mean that approaches zero and the deviations should be minimized. There are various statistical measures that can be used to assess the reliability and “goodness of fit” of groundwater models. The accuracy tests should be applied to as many dependent variables as possible.

The use of deterministic models in the analysis of groundwater problems is illustrated, in a general sense, in Figure 10. Perhaps the greatest value of the modeling approach is its capability to integrate site-specific data with equations describing the relevant processes as a quantitative basis for predicting changes or responses in a groundwater system. One objective of model calibration should be to improve the conceptual model of the system. The improvement in understanding of a system derived from a model application and calibration exercise for hypothesis testing often is of greater value than the predictive value for management purposes. Another objective should be to define inadequacies in the database and help set priorities for the collection of additional data.

D. Model Error

Discrepancies between observed and calculated responses of a groundwater system are the manifestation of errors in the conceptual or mathematical model. In applying groundwater models to field problems, there are three sources of error, and it may not be possible to distinguish among them (Konikow & Bredehoeft, 1992). One source is conceptual errors, that is, misconceptions about the basic processes that are incorporated in the model. Conceptual errors include both neglecting relevant processes as well as inappropriate representation of processes. Examples of conceptual errors include the use of a two-dimensional model where significant flow or transport occurs in the third dimension, or the application of a model based upon Darcy's law to media or environments where Darcy's law is inappropriate. A second source of error involves numerical errors arising in the equation-solving algorithm, such as truncation errors, round-off errors, and numerical dispersion. A third source of error arises from measurement errors and from uncertainties and inadequacies in the input data that reflect our inability to describe comprehensively and uniquely the properties, stresses, and boundaries of the groundwater system. In most model applications, conceptualization problems and data uncertainty are the most common sources of error.

In solving advection-dominated transport problems in which a sharp front (or steep concentration gradient) is moving through a groundwater system, it is difficult numerically to preserve the sharpness of the front. Obviously, if the width of the front is narrower than the node spacing, then it is inherently impossible to calculate the correct values of concentration in the vicinity of the sharp front. Even in situations where a front is less sharp, the numerical solution technique can calculate a greater dispersive flux than would occur by physical dispersion alone or would be indicated by an exact solution of the governing equation. That part of the calculated dispersion (or spreading of solute about the center of mass) introduced solely by the numerical solution algorithm is called numerical dispersion. Numerical dispersion can be controlled most easily by reducing the grid spacing, although that will increase computational costs proportionately.

One measure of numerical accuracy is how well the model conserves mass. This can be measured by comparing the net fluxes calculated or specified in the model (e.g., inflow and sources minus outflow and sinks) with changes in storage (accumulation or depletion). Mass-balance calculations always should be performed and

checked during the calibration procedure to help assess the numerical accuracy of the solution.

As part of the mass-balance calculations, the hydraulic and chemical fluxes contributed by each distinct hydrologic component of the flow and transport model should be itemized separately to form hydrologic and chemical budgets for the modeled system. The budgets are valuable assessment tools because they provide a measure of the relative importance of each component to the total budget.

E. Geochemical Model Design

The guidelines for the design and application of geochemical models are similar to those outlined above, especially concerning geochemical transport modeling, which depends on the establishment of flow and solute-transport models. Other types of geochemical models do not depend on the establishment of a spatial grid and on the attendant issues of grid spacing and boundary conditions. The accuracy of a geochemical mass-transfer model may depend on time step size if reaction kinetics are simulated. Other types of geochemical calculations (equilibrium mass-transfer calculations, speciation calculations, inverse geochemical modeling) do not depend on the numerical value of any time-step increments, but can, in some cases, depend on the specification of an initial system state and also on the order in which different isolated geochemical processes or sets of processes are applied/simulated in the system. In all cases of geochemical modeling, the quality of results obtained strongly depend on the quality of the input chemical data and on the quality of any thermodynamic data used by the model.

Inverse geochemical modeling can be used as a first step in helping to construct a geochemical transport model (e.g., Glynn & Brown, 1996). The idea is to use inverse geochemical modeling to determine all the possible sets of reaction processes that potentially could explain the observed chemical and isotopic evolution of one groundwater into another. Consequently, different sets of reaction processes, and different geochemical characteristics, can be considered in a suite of transport simulations, thereby allowing the modeler to assess: (1) the dependence of the movement of a particular contaminant front or concentration on the reaction processes considered and (2) the need for additional specific field data that potentially could eliminate some of the uncertainties regarding the applicable geochemical processes. As stated by Glynn and Brown (1996):

“Identifying knowledge gaps and critical data needs, preventing us from more accurately determining the identity and importance of the reactions . . . was one of the most important results of the inverse and reactive transport modeling simulations conducted.”

VI. OBTAINING MODEL CODES

A large number of generic deterministic groundwater models, based on a variety of numerical methods and a variety of conceptual models, are available. In selecting a model that is appropriate for a particular application, it is most important to choose one that incorporates the proper conceptual model; one must avoid force-fitting an inappropriate model to a field situation solely because of model convenience, availability, or familiarity to the user. Usability also is enhanced by the availability of graphical preprocessing and post-processing programs or features, and by the availability of comprehensive yet understandable model documentation.

A large number of public and private organizations distribute public domain and/or proprietary software for groundwater modeling. Some Internet sites allow computer codes to be downloaded at no cost whereas other sites provide catalog information, demonstrations, and pricing information. The International Groundwater Modeling Center in Golden, Colorado (www.mines.edu/research/igwmc/software/), maintains a clearinghouse and distribution center for groundwater simulation models. Many of the U. S. Geological Survey public domain codes are available from links on their Web sites at water.usgs.gov/nrp/models.html and water.usgs.gov/software/. The U. S. Environmental Protection Agency's Center for Subsurface Modeling Support (www.epa.gov/ada/csmos.html) also provides public domain groundwater modeling software.

SEE ALSO THE FOLLOWING CHAPTERS

Chapter 11 (Arsenic in Groundwater and the Environment) · Chapter 12 (Fluoride in Natural Waters) · Chapter 15 (Selenium Deficiency and Toxicity in the Environment)

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