Modeling Contaminant Transport in Subsurface: Theory and Computer Programs

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3.1 INTRODUCTION

The purpose of this chapter is to discuss the theory of chemical transport in soil, as well as available computer codes for implementing that theory. Chemical transport in the subsurface flow is generally a complex process. Mathematical models that describe contaminant transport can involve substantial contributions from the basic disciplines of mathematics, biology, physics, and chemistry. The interdisciplinary nature of contaminant transport modeling requires that it be a synthesis of disciplinary components. Accurate predictions of chemical transport phenomena are required in many different domains, spanning hydrology, environmental engineering, soil science, and agriculture. The circumstances in which a model may be needed vary widely as well. At the local scale, one might model a leachate plume moving from a landfill into a groundwater system, while at a much larger scale one might consider regional salinization leading to degradation of both water supplies and soil. The unifying theme is that a basic theoretical structure can be applied in each case. That is, besides modeling contaminant transport per se, the same basic theoretical approach applies to a wide range of processes that include both geochemistry and transport, e.g., weathering, diagenesis, hydrothermal ore deposition, geothermal energy production, and oil recovery (Lichtner, 1985). Of course, all these applications require different manifestations of the basic theory.

In this chapter we review the theory underlying the transport models that are used. The contaminant transport subdiscipline of hydrology and the geochemistry

subdiscipline of hydrogeology seem to be separated by a gulf of both time and spatial scales in the processes that they consider. This gulf is most highlighted when the crustal flow problem is considered. Torgensen (1991), reporting on the scientific approaches taken to this problem, suggests that the hydrologic view is that large-scale fluid flow in the crust is essentially a continuum process in sedimentary basins. These processes are driven by topography and additional gradients in fluid density caused by temperature and solute concentration. Chemical reactions in such systems are rare, and can be ignored. The geological viewpoint, which Torgensen (1991) calls the structural/metamorphic view, is that fluid flow in the crust is highly episodic and controlled by rock structural features such as fractures. Chemical reactions are thought to be poorly understood but very important. The difference between these approaches is mainly one of temporal and spatial scales and emphasis. The hydrologic viewpoint is appropriate for assessing anthropogenic concerns at the regional scale or below. The structural/metamorphic view applies to much larger scales, both in time and space. An appropriate spatial scale might be, for example, a continental or subcontinental scale. Australia's Great Artesian Basin, which underlies a large portion of the eastern half of the continent, represents the scale appropriate to the structural/metamorphic view. On the other hand, the hydrologists' view is the one adopted to determine a yearly water balance on a single catchment. We adopt the perspective of the hydrologist, but consider that both physical and chemical processes need be included in developing models of solute transport in soil. To adopt the rather humorous phrasing of Torgensen (1991), the soil is not a "Teflon box" in which chemical reactions can be ignored. For that reason some emphasis is placed on elucidating the underlying chemical and physical models that are the basis of flow and transport computer codes. Consequently, to have some appreciation of the chemical reaction and speciation modeling that is used, relevant chemistry concepts and theory are discussed as well. The modeling approaches are discussed in the text, while basic chemistry concepts are presented in the appendix (Section 3.10). Mathematical formulations of speciation and transport models are presented with the aim of indicating the diverse approaches one can take in formulating and solving a governing model. Computer modeling efforts have been divided into three categories:

1. Geochemical models
2. Multicomponent transport models
3. Semianalytical transport models

Models in category 1 consider the chemical reactions but ignore flow and transport. Those in category 2 incorporate category 1 models into a flow and transport model to produce a comprehensive ("hydrologic") description of solute movement and reactions in soil. Category 3 models are mostly single-species transport models that include approximations for reactions, ion exchange, and/or solute sorption. We begin by a brief discussion of the problem of determining equilibrium speciation in aqueous solutions. Many of the existing models are based on decoupling of water flow and solute transport, particularly for single-species transport. The codes devoted to flow

only are not included here. Mangold and Tsang (1991) provide a valuable overview of these and other available programs.

3.2 REACTIONS IN AQUEOUS SOLUTIONS: DETERMINATION OF SPECIATION AT EQUILIBRIUM

Chemicals in aqueous solution may or may not react with each other. In natural soil environments there may be many chemical species in solution at any one time. Speciation models have been developed to determine the composition of the solution at equilibrium in terms of the constituent species. The total set of species can be defined by a set of equations involving components. Components are chemical entities that are indivisible for the purpose of the speciation calculations. Thus, components can be ions or complexes, for example. Coves and Sposito (1986, §1.1) point out — to use the language of functional analysis — that the components form a basis for the linear (species) space (Brown and Page 1970, §3.1). Before any speciation calculations can begin, a component equation for each chemical species must be written. Each species is written as the result of a chemical reaction involving only the components. The relationship between the species and components is quantified using the law of mass action (see the appendix). If there are N species, N equations of the following form can be derived (Coves and Sposito, 1986, §1):

$$\{c_i\} = K_{e,i} \prod_{j=1}^{M} \{X_j\}^{a_{i,j}}, \quad i = 1,...,N \tag{1}$$

The activities in Equation (1) may be replaced by molar concentrations for dilute solutions. If there are no sources or sinks of species in the system then the total mass of each component must be fixed, i.e.,

$$X_{T,j} = \sum_{i=1}^{N} a_{i,j} c_i, \quad j = 1,...,M \tag{2}$$

The aim is to compute the equilibrium concentrations, c_i, of the N species in solution. Because each species is written in terms of components, the problem is equivalent to computing the concentration of each component. The total concentration of each component, $X_{T,j}$, $j = 1, ..., M$, is known, so Equation (2) gives M equations to find the M unknown component concentrations. Of course, the species concentrations in the summation of Equation (2) are unknown, but they are given in terms of the individual components by Equation (1), because the equilibrium coefficients are assumed known. Thus, Equations (1) and (2) define a nonlinear system of equations from which the component concentrations can be found numerically. Most computer codes use Newton's method (e.g., Bajpai et al., 1977, Ch. 4) for this purpose. Finally, the concentration of each species in the system — the object of the exercise — is calculated from the component concentrations.

Mineral precipitation or dissolution can be handled with a minor variation to this process. The equilibrium constant is replaced by the solubility product, K_{sp}. From Equation (A7) we obtain:

$$K_{sp} \geq \left\{R_1\right\}^{r_1} \times \cdots \times \left\{R_N\right\}^{r_N} \tag{3}$$

where the denominator in Equation (A7) has been replaced by unity, which is the activity of a precipitate. If Equation (3) holds, then the precipitate will be formed and the reaction needs to be accounted for. Conversely, it can be ignored when Equation (3) does not hold. Morel and Morgan (1972), Reed (1982), Walsh et al. (1984), Wigley (1977), and Kirkner and Reeves (1990) all present computational algorithms for including such reactions.

The procedure outlined here to calculate the equilibrium speciation of a closed system is but one method to achieve this goal. Other methods can be derived and, incidentally, traced to Brinkley (1946, 1947), but they contain the same essential elements as those mentioned above (Sposito, 1984a, §2). The key factors are the development of the chemical equations for the system and knowledge of the equilibrium constants for the various reactions. The former must characterize the major reactions in the system while the algebraic accuracy of solution depends, in part, on the latter.

3.3 SOLUTE ADSORPTION AND EXCHANGE

Solute adsorption in soil occurs when solute is removed from the transporting water and is collected at sites within the solid porous medium at the interface of the solid and liquid phases (Tan, 1982, §4.1). For a particular soil sample that is mixed with a given mass of fluid of known initial concentration, it is clear that the concentration of solute in the fluid may increase or decrease depending on the chemical status of the soil. For example, Sposito (1989, §8.1) considers an experiment in which 1 kg of dry soil is combined with M_{Tw} kg of water containing a solute at a specified molality. The excess, q, of the chemical species is defined as

$$q = \Delta m M_{Tw} \tag{4}$$

where Δm is the change in molality, relative to the original composition of the solution, of the soil due to adsorption. Thus, if the soil initially has no net charge and solute is adsorbed onto the soil then $q < 0$ and vice versa. For experiments carried out at constant temperature, it is permissible to measure concentration of the solute in terms of molarity (Sposito, 1981, §2.2), c, instead of molality. Experiments are usually carried out under isothermal conditions. In such experiments, one measures the quantity of solute adsorbed per unit mass of dry soil, s, for various predetermined concentrations of the pore fluid. The experimental results consist of data pairs (s_i, c_i) that, when plotted, define an adsorption isotherm. If, for example, the c_i data are measured in units of moles per cubic meter of soil solution (i.e., pore fluid), while

the s_i data are measured in units of moles per kilogram of dry soil, then $w_i = s_i\rho_b/\theta$ gives the adsorbed concentration in moles per cubic meter of soil to solution. In this review we focus only on rapid sorption, i.e., the isotherms do not have an explicit time dependence. A readable discussion of the latter topic is provided by Barrow (1989).

3.3.1 Adsorption Isotherms

The two most common isotherms used in practice to describe data from adsorption experiments are the Langmuir and Freundlich isotherms, given by Equations (5) and (6) in Table 3.1, respectively. Numerous derivations of the Langmuir isotherm are available (Young and Crowell, 1962, Ch. 4), including one based on statistical mechanics (Sposito, 1979). It is possible also to derive the Freundlich isotherm (Sposito, 1980) mechanistically, although Jaycock and Parfitt (1981, §5.3) state that it is "essentially empirical, and perhaps only useful for fitting data." Indeed, referring

Table 3.1   Adsorption Equations

Isotherm	Name	Ref.	Equation No.
$w = \dfrac{k_1 c}{1 + k_2 c}$	Langmuir	Langmuir (1918)	(5)
$w = k_3 c^{k_1}$	Freundlich	Freundlich (1909, 1926, p. 172)	(6)
$w = \dfrac{k_1 c}{1 + k_2 c} + \dfrac{k_4 c}{1 + k_5 c}$	Double Langmuir	Shapiro and Fried (1959)	(7)
$w = \dfrac{k_1 c}{1 + k_2 c + k_6 \sqrt{c}}$	Gunary	Gunary (1970)	(8)
$w = k_3 c^{k_4} - k_7$	Fitter-Sutton	Fitter and Sutton (1975)	(9)
$w = \dfrac{k_8 c^{1-k_1}}{1 + k_9 c^{1-k_1}}$	Extended Langmuir	Sibbesen (1981)	(10)
$w = k_{10} c^{c^{k_1/k_8}}$	Extended Freundlich	Sibbesen (1981)	(11)
$w = k_7 \left\{ 1 - \left[1 + (k_2 c)^{k_1} \right]^{k_4} \right\}$	Langmuir-Freundlich interpolation	This work	(12)

to phosphate adsorption, Sibbesen (1981) suggests that all isotherms be treated as being empirical due to the observation that "soils are complex with surfaces of mostly unknown heterogeneity."

As already stated, adsorption in soils refers to the chemical species accumulating at the surface of the solid matrix. On the other hand, absorption occurs when the species accumulates within the matrix. These two processes are not readily distinguishable in soils, so one refers instead to sorption, which includes both cases. In Table 3.1 various adsorption equations have been listed (cf. van Genuchten and Cleary, 1982, Table 10.1). Note that these isotherms do not account for time dependence of adsorption, i.e., adsorption kinetics; they account only for systems in equilibrium. Table 3.1 does not exhaust the possible adsorption isotherms that may be employed. The efficacy of various isotherms in fitting data has been compared for a variety of isotherms by Kinniburgh et al. (1983) and Kinniburgh (1986). Kinniburgh (1986) and Barry (1990a) point out that some common graphical techniques of fitting isotherms to data will lead to erroneous parameter estimates. Graphic methods involve transforming the experimental data such that straight line fits can be employed. This method is prone to error, as accurate parameter estimates will result only when the transformed data are weighted appropriately.

Sposito (1982) demonstrates that the double Langmuir isotherm can be used to describe any adsorption isotherm for which the distribution coefficient is smooth, concave, and tends asymptotically to a finite limit. As mentioned above, most isotherms are empirical, but some are based on foundational theories. Such theories provide a sufficient, but not a necessary, condition for the adsorption mechanism. One cannot reach any conclusions concerning the adsorption mechanism just from the ability of a particular isotherm to describe the experimental data; other, ancillary information is needed. Many of the equations in Table 3.1 have been compared by Ratkowsky (1986) using data collected by Holford (1982). The Freundlich isotherm and its extension, Equation (11), were found to be the best statistical descriptions of the data. Therefore, if an adsorption isotherm is used merely as a convenient description of data, one can choose the most accurate mathematical description available from Table 3.1 or elsewhere. It must be recognized that the adsorption predicted by the Freundlich-type isotherms is not bounded as concentration increases, and so extrapolation based on a fitted isotherm may describe poorly the case being modeled.

Sposito (1989, Figure 8.1) identifies four types of adsorption isotherm, namely the S-, L-, H-, and C-curve, and discusses possible mechanisms underlying each one. Qualitative depictions of these types have been included in Figure 3.1. The designations of the curves come from their behavior at relatively low concentrations (Sposito, 1981, §5.2). If one considers only the two most common isotherms, the Langmuir and Freundlich isotherms, then it can be shown that either or both isotherms have the form of the latter three curves. However, neither isotherm can reproduce the S-curve. Equation (12) in Table 3.1 is a proposed new empirical isotherm. It is suggested because it reduces to an interpolation between the Langmuir and Freundlich isotherms. Additionally, it can reproduce S-curves without difficulty. First, consider Equation (12) with $k_1 = -k_4 = 1$:
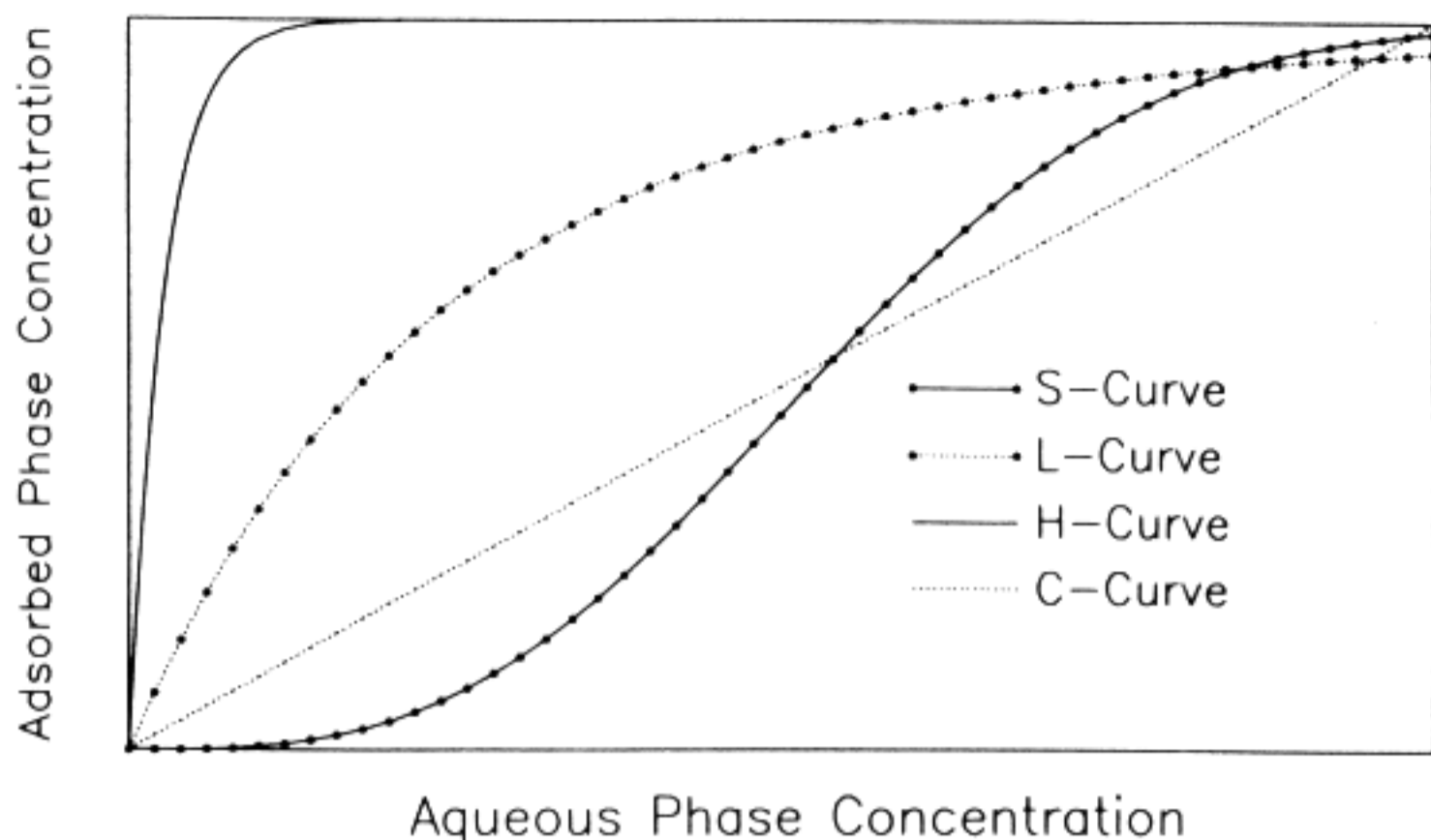
FIGURE 3.1. General classes of adsorption or exchange isotherms. S-curve (●—●): relatively low affinity of the exchangeable ion for the exchanger; L-curve (●··●): relatively high affinity of the exchangeable ion for the exchanger; H-curve (—): extremely high affinity of the exchangeable ion for the exchanger; C-curve (···): linear exchange isotherm. Equation (12) can produce each class of isotherm.

$$w = k_7 \left(1 - \frac{1}{1 + k_2 c} \right) = \frac{k_7 k_2 c}{1 + k_2 c} \qquad (13)$$

If we take $k_7 = k_1/k_2$ then Equation (13) reduces to Equation (5). If, instead, we set $k_4 = 1$ then Equation (12) reduces to

$$w = k_7 \left(1 - 1 + k_2^{k_1} c^{k_1} \right) = k_7 k_2^{k_1} c^{k_1} \qquad (14)$$

Equation (14) is equivalent to Equation (6) if $k_7 k_2^{k_1} = k_3$. That Equation (12) produces S-curves can be confirmed by comparison with the characteristic S-shaped water content-pressure head function proposed by van Genuchten (1979, [3]). Equation (12) can be seen to be a variation of van Genuchten's function. To demonstrate the utility of Equation (12), we fit it to some experimental data extracted from Figure 4.1 of Sposito (1984c), as shown in Figure 3.2. The data show copper adsorption by the Altamont clay loam. This figure shows that w, as predicted by Equation (12), is constrained to lie between 0 and k_7. However, the experimental data shown in Figure 3.2 suggest a nonzero value of w near $c = 0$. The isotherm in Equation (12) could easily be scaled to pass through this nonzero datum, and so improve the fit to these data.

3.3.2   Ion Exchange

Thus far, no mention has been made of the ions displaced during the sorption process. If different ions are being displaced then ion exchange must be considered. For example, a generic cation exchange reaction is
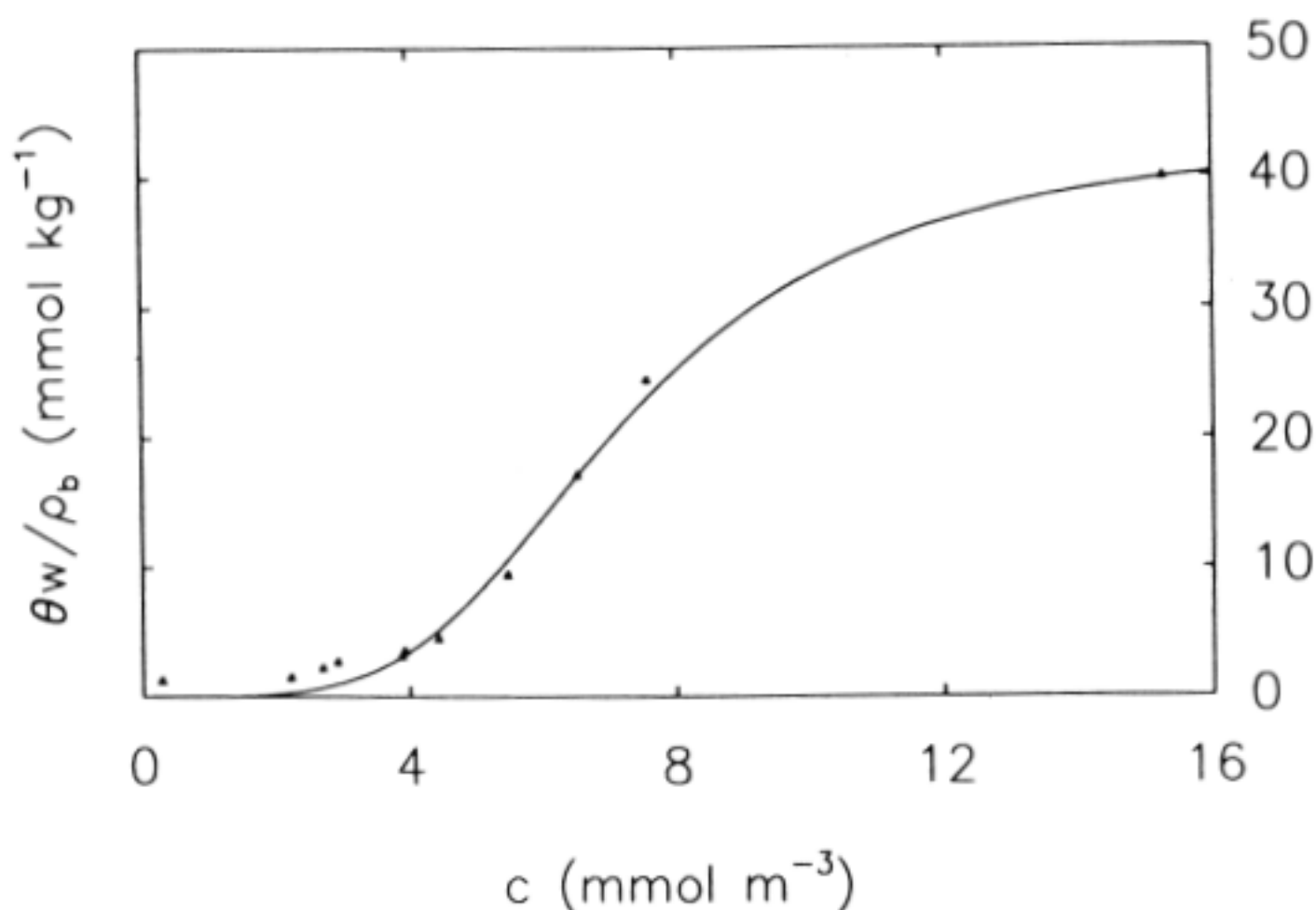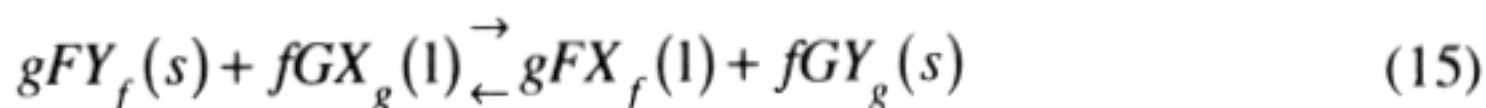
FIGURE 3.2. Plot of the adsorption isotherm [Equation (12)] and experimental data (Sposito, 1984c, Figure 4.1) showing copper adsorption onto the Altamont clay loam. Symbols: ▲, experimental data; —, Equation (12) with the parameter values k_1 = 4.411 and k_2 = 0.161 mmol^{-1} m^3, k_4 = –0.627 and k_7 = 43.474 mmol m^{-3}.

$$gFY_f(s) + fGX_g(1) \underset{\leftarrow}{\overset{\rightarrow}{}} gFX_f(1) + fGY_g(s) \tag{15}$$

where s is the solid phase and l is the liquid phase, F and G are cations with valence f and g, respectively, and X and Y are anions, or anion complexes, with valence -1. The equilibrium constant for this reaction is defined by analogy with Equation (A7). Then, the resulting expression can be written in terms of equivalent fractions of F and G in the solid and liquid phases. Let E_F be the equivalent fraction of F in the solid phase, and $\tilde{E}_F$ be the equivalent fraction of F in the liquid phase, with similar quantities defined for cation G. The equilibrium constant for Equation (15) can then be written in terms of these equivalent fractions (Barrer and Klinowski, 1974; Sposito, 1981, §5.2). To simplify matters, let F have valence 2 and G have valence 1, and consider a reaction where the equilibrium constant has unit value, i.e., the exchanger has no preference for either cation. An equation relating the equivalent fractions in the adsorbed and liquid phases for the univalent ion G is given by (Sposito, 1981, §5.2):

$$\frac{E_G^2}{1 - E_G^2} \propto TN \frac{\tilde{E}_G^2}{1 - \tilde{E}_G} \tag{16}$$

where TN is the total normality of the liquid phase. We note that the proportionality factor in Equation (16) varies with TN. We note that the simple algebraic form of Equation (16) is due to the valences chosen for each species. Equation (16) serves, however, to illustrate two points: first, that the amount of a single species in the solid and liquid phases can be related by a single expression and, therefore, can be used

to compute isotherms because equivalent fractions can be converted easily to concentration units. In many cases, the adsorption isotherms presented above are general enough to reproduce these curves empirically. Second, these isotherms can change as the chemical conditions of the system change. In Equation (16) the relationship between E_G and $\tilde{E}_G$ varies from nearly linear to strongly nonlinear depending on the value of TN. So far, the solid phase on which the exchange is occurring has been assumed to be homogeneous. Soil can contain many different classes of exchange sites, and theory accounting for exchange reactions in such situations has been developed (Barrer and Klinowski, 1979).

3.4 CONTINUUM MODEL OF MULTICOMPONENT, AQUEOUS-PHASE SOLUTE TRANSPORT

Until this point only basic aqueous-phase chemical reactions have been discussed. Each chemical component in the porous medium is also advected and dispersed by the flowing fluid. The starting point for predicting solute concentration in the subsurface is the construction of a model describing both the physical processes induced by the fluid flow field as well as the chemical reactions that are occurring. Only with such a model can the effects of combined physical and chemical processes be quantified. Such a model is presented here, although a more detailed presentation is available elsewhere (Kirkner and Reeves, 1988). We point out that the mathematical basis for the model presented is that the porous medium and the fluid constituents can be replaced by a continuum or, rather, a set of continua that interact over the spatial domain of interest. Foundational theories leading to continuum models (e.g., Hassanizadeh and Gray, 1979a,b; Marle, 1982) are based on the concept of a representative elementary volume, denoting a local averaging scale for the porous medium. It is assumed here that a continuum modeling approach is valid.

The basic equations governing the flow of N_c chemical components in a flowing system are (Bear, 1972; Bryant et al., 1986)

$$\frac{\partial\left(\theta c_i^T\right)}{\partial t} + \mathbf{L}\left(u_i\right) = 0, \quad i = 1,\ldots,N_c \tag{17}$$

where c_i^T is the *total* concentration of the ith component in any form whatsoever in the system and u_i is the concentration of the same component in the *flowing* (aqueous) solution. The right side of Equation (17) is nonzero if production terms need be included, or if irreversible dissolution or precipitation occurs. The operator $\mathbf{L}$ is defined by (Kirkner and Reeves, 1988)

$$\mathbf{L}\left(u_i\right) = div\left(u_i\mathbf{q} - \theta\mathbf{D}\ grad u_i\right) \tag{18}$$

Now, the total concentration of the ith component in the system is, by definition,

$$c_i^T = c_i + s_i + \sum_{j=1}^{N_x} A_{ij} x_j \qquad (19)$$

Total	Component	Sorbed	Complexed
concentration	concentration	concentration	concentration

In Equation (19) it has been assumed that there is no precipitation or dissolution taking place. For conditions where precipitation can occur, an additional precipitation term must be included on the right side of Equation (19). In terms of equilibrium chemical processes, the inclusion of such a term does not present any difficulties. For solute transport within a permeable medium, the inclusion of such a term is a complicating factor, because porosity will vary as precipitation or dissolution occurs. On the other hand, if the quantity of precipitation is such that porosity changes are not significant then the usual approach is to model precipitation as a kind of aqueous complexation. Indeed, the only change is that instead of an equilibrium constant applying to the reaction, one considers the solubility product for the particular precipitate. If the solubility product is exceeded then precipitation takes place, else dissolution occurs.

There have been models developed that explicitly account for porosity changes accompanying precipitation (Helgeson et al., 1984; Lasaga, 1984; Lichtner, 1987). The impact of precipitation is often more important under geologic time scales. Typical contaminant transport operates at much shorter time scales with relatively dilute chemical concentrations, so precipitation effects are not considered further here. We recognize, however, that such phenomena need be included in general models.

The latter two terms on the right side of Equation (19) are now discussed. In the case of soluble complexation, the appropriate chemical reactions are of the generic form (Kirkner and Reeves, 1988):

$$\sum_{j=1}^{N_x} A_{ij} \hat{c}_j \underset{\leftarrow}{\rightarrow} \hat{x}_i; K_i, \quad i=1,\ldots,N_x \qquad (20)$$
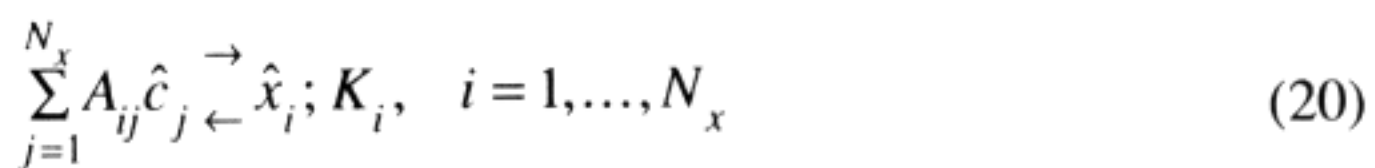
where K_i is the equilibrium constant for the reaction and the circumflex indicates a chemical formula, not a concentration. Upon using the law of mass action (see the appendix), one obtains from Equation (20):

$$x_i = K_i \prod_{j=1}^{N_c} c_j^{A_{ij}}, \quad i=1,\ldots,N_x \qquad (21)$$

If the concentrations in Equation (20) are not dilute, then each concentration variable must be replaced by the activity of each species. The total soluble concentration of the ith component, u_i, is defined by

$$u_i = c_i + \sum_{j=1}^{N_x} A_{ij} K_j \prod_{k=1}^{N_c} c_k^{A_{jk}}, \quad i=1,\ldots,N_c \qquad (22)$$

Equation (22) shows that the soluble concentration can be specified as a nonlinear function of the component concentration variables alone. For later use, we observe that Equation (22) defines N_c unknowns, u_i, in terms of N_c (presumed) known variables, c_i. In principle then, Equation (22) can be inverted to give each c_i as a function of the set of N_c u_i variables, i.e. (Kirkner and Reeves, 1988):

$$c_i = f_i^{cu}\left(u_1,\ldots, u_{N_c}\right), \quad i - 1,\ldots, N_c \tag{23}$$

Previously, adsorption isotherms were discussed in some detail. The main point to note here is that it is always possible to write the adsorbed concentration, s_i, in terms of the fluid phase solute concentration, i.e.,

$$s_i = f_i^{sc}\left(c_1,\ldots, c_{N_c}, x_1,\ldots, x_{N_x}\right) \tag{24}$$

Equation (24) becomes a function of the component concentrations, c_i, if the complexed concentrations are eliminated using Equation (21). The form of the function in Equation (21) is more general than the isotherms presented in Table 3.1. In Table 3.1, adsorption was considered for a single species only, whereas in Equation (24) the adsorption of any component depends on the concentration of all species in solution. The isotherms in Table 3.1 can be extended to account for different species in solution. For example, Kirkner and Reeves (1988) provide a simple derivation of the multicomponent Langmuir isotherm (Butt, 1980):

$$s_i = \frac{c_i K_{s_i} x_T}{1 + \displaystyle\sum_{j=1}^{N_c} c_j K_{s_j}} \tag{25}$$

The governing Equation (17) can be cast with either c_i or u_i as the dependent variable using Equations (18) through (24). This means any numerical solution of the multicomponent chemical transport model must solve N_c-coupled, nonlinear partial differential equations. Clearly, even moderate-sized cases of this class of problem represent a challenge for even the most powerful supercomputer (Barry, 1990b).

There are a variety of ways in which the governing model of reactive chemical transport can be tackled numerically. Kirkner and Reeves (1988) detail some analytical results, while Reeves and Kirkner (1988) provide case studies solved using different numerical schemes. There is, apparently, no single numerical scheme that is most efficient for all cases, i.e., the efficiency of the scheme is dependent on chemical characteristics. Perhaps more interesting are the results of the various cases considered by Reeves and Kirkner (1988). Reactions that involve relatively high

rates of complexation or adsorption represent the most difficult numerical challenge. Such cases also lead to the most dramatic rates of formation or disappearance of species within the porous medium. For instance, chemical reactions may lead to the presence of relatively high concentrations of a particular species within a given soil volume, whereas at the boundaries where fluxes are measured, the species concentration may be low. Thus, assumptions concerning the concentration of species within a medium, based on surface measurements, may be erroneous if the chemical reactions taking place favor the production of that species.

The flow of the transporting fluid has not been considered yet. Fluid flow in the unsaturated zone is governed by Richards' equation (Richards, 1931), while in the saturated zone it is a parabolic equation mathematically similar to Equation (17). Because the Darcy flux is dependent on the density of the fluid, the chemical transport equations, Equation (17), and the flow equation are coupled through the density equation of state. Similarly, if the transport of heat is important then the appropriate governing model is again similar in form to Equation (17). Temperature changes induce density changes in the fluid, so again there is coupling between the equations. The purpose to which the model is to be put is the determining factor to be used in model formulation and selection.

The theory used for quantifying chemical reactions and transport in porous media has been outlined and the main features of the theory demonstrated. The development of computer codes for chemical reactions and transport varies markedly in scope and complexity. Geochemical codes, for instance, are usually limited in usefulness by their accompanying databases of thermodynamic information. Transport codes for chemical species and fluid movement are likewise subject to a variety of numerical approaches. Many specialized geochemical and transport and flow codes are available. The nature of multicomponent chemical transport models is such that it is convenient to combine available codes for geochemistry and for flow and transport into a complete model. Below we look sequentially, therefore, at the available geochemical codes and then at existing multicomponent transport codes. The latter quantify the combined effects of the physics of flow and the chemical reactions of the transported species. As stated at the outset of this chapter, the variety of chemical transport scenarios is enormous. We describe also less complex computer codes that are used to simulate more simplified cases of transport, usually with correspondingly simplified chemical processes. To begin with, geochemical computer codes are discussed.

3.5 GEOCHEMICAL MODELS

3.5.1 Major Computer-Based Geochemical Codes

Many geochemical computational codes have been developed. Over time, code developments have continued, and improved versions of the various codes have been released. Jenne (1981) provides an overview of such developments. A list and brief description of major computer-based geochemical codes is presented in Table 3.2. This list is not meant to be exhaustive, rather it indicates the wide spectrum of available programs. Some of these codes are described in more detail below.

Table 3.2   Summary of Computer-Based Geochemical Models[a]

Name	Description	Ref.
CHEMIST	CHEMIST uses the Gibbs free energy minimization method to compute the equilibrium concentration distribution in a closed system. Alternatively, the steady state distribution in an open system can be determined	Deland (1967)
CHILLER	Computes multicomponent heterogeneous equilibria in all phases considering variations in temperature, pressure, and enthalpy	Reed (1991)
EQQYAC	EQQYAC uses the ion-association model. Activity coefficients depend on total concentration (assumed less than 1 molal). Thermodynamic data include temperature-dependent equilibrium constants	Barragan and Nieva (1989)
EQUILIB	Equilibrium concentrations between gaseous, aqueous, and solid phases are calculated. Aqueous speciation, redox, and pH can be determined in either open or closed systems	Morrey (1981)
EQ3/6	Computes distributions of ions, neutral species, ion pairs, and complexes in natural waters using a database. Irreversible reactions in solid rock systems and the effects of heating and cooling of solutions are included	Wolery (1979)
GEOCHEM	A modification of REDEQL-2, this code is able to compute chemical equilibria in natural soil solutions, including precipitation/dissolution, redox reactions, and adsorption. It includes a database	Sposito and Mattigod (1980)
MINTEQ	MINTEQ allows computation of ion speciation, activity coefficients, adsorption, and mass transfer. It is accompanied by a well-documented database. It is a partial descendent of WATEQ	Felmy et al. (1984)
PENALTY	The precipitation/dissolution reaction portion of the equilibrium speciation problem is handled with a penalty function method	Kirkner and Reeves (1990)

Table 3.2   Summary of Computer-Based Geochemical Models[a] (continued)

PHREEQE	This is an evolution of WATEQ and MIX2. Equilibrium calculations are based on aqueous phase concentrations and charge neutrality. No mass constraints are imposed on hydrogen and oxygen	Parkhurst et al. (1980)
SOLMNEQ	Calculates speciation for 162 inorganic aqueous phase species found in natural waters in the temperature range 0–350°C	Kharaka and Barnes (1973)
SOLVEQ	Computes multicomponent homogeneous equilibria of aqueous chemical species. For a known chemical composition and temperature, aqueous species activities, saturation indices, and gas fugacities are calculated	Reed (1982)
STEADYQL	Chemical speciation and composition in soil-water systems are calculated for reactions at three time scales: very fast reactions (equilibrium model), moderate (kinetic equations), and very slow (no reaction at the time scale of interest)	Furrer et al. (1989)
WATEQX	A modification of WATEQF that generalizes the program by extending the ionic strength range and updates the database using a commercial database program	van Gaans (1989)
WATEQ3	This is part of a series of improvements to the original WATEQ model, and includes an extensive thermodynamic database. Equilibrium distributions in natural waters are calculated with effects of temperature, pH, and redox potential included	Ball et al. (1981a,b)

[a] Cf. Kincaid et al. (1984a,b).

3.5.2   Descriptions of Some Geochemical Codes

3.5.2.1   EQ3/6

This package consists of two main parts: EQ3NR and EQ6, together with a shared thermodynamic database. EQ3NR is a speciation-solubility code that models the state of an aqueous solution. Reaction paths are calculated by EQ6, wherein aqueous systems are modeled as they move toward equilibrium, for example, reaction paths for reactions modeled by kinetic rate laws. Two scenarios are modeled by EQ6: (1)

a closed system and (2) a parcel of fluid traversing a reactive medium. Case (2) represents a crude transport model. EQ3/6 has been used to model tuff-groundwater interactions (Kerrisk, 1984) and crust and sea-water interactions (Bowers et al., 1985).

3.5.2.2   EQQYAC

This code consists of a main program and four subroutines (Barragan and Nieva, 1989). One subroutine computes temperature-dependent activity coefficients using Debye-Hückel theory (Henley et al., 1984). Another contains expressions for mass action equilibrium constants (Giggenbach, 1980). The subroutine ENTHALPIA computes specific enthalpy of steam and liquid phases (Fournier and Potter, 1982) while the final subroutine determines the steam fraction using the Fisher-Tropsch reaction (Nieva et al., 1987). EQQYAC has been used to calculated equilibrium concentrations of inorganic ions in a geothermal reservoir. CHILLER, which uses the data base SOLTHERM (Reed and Spycher, 1989), is another geochemical code that was designed for geothermal reservoir modeling. In most nongeothermal applications, such extensive temperature-dependent data sets will not be necessary.

3.5.2.3   GEOCHEM

This code is specifically aimed at calculating equilibria in soil solutions. Both redox reactions and solid phases can be included or excluded, and exchange coefficients can be estimated. The user can choose to have variable pH and ionic strength. Considerable effort has been devoted to compiling the thermodynamic database that draws on the work of Martell and Smith (1976–1977), Baes and Mesmer (1976), Robie et al. (1978), and Sadiq and Lindsey (1979), although the authors emphasize that there remains the possibility of uncertainty in the data. Parker et al. (1988) used a modified version of GEOCHEM to determine aluminium speciation in a soil solution with the results used to indicate aluminum toxicity to plants. They found, for example, that the activity of Al^{3+} has a detrimental effect on root growth in wheat. GEOCHEM was evaluated by Kincaid et al. (1984b), who concluded that the code and its accompanying documentation is very well suited to users who are disinclined to modify the code. On the other hand, documentation was not suited to those whose applications required that modifications be made. GEOCHEM has recently been updated and renamed SOILCHEM (Sposito and Coves, 1988).

3.5.2.4   MINTEQ

MINTEQ computes chemical equilibria in aqueous solutions, gases, and solids. The thermodynamic database contains information on numerous elements and complexes. It can model adsorption by the linear, Freundlich, or Langmuir isotherms. Alternatively, surface complexation models can be used, e.g., the constant capacitance or triple layer models. Surface complexation models are based on an assumed model of ion behavior at the local level (Sposito, 1984b, Ch. 5). In MINTEQ, the Davies and Debye-Hückel equations are used to calculate activity coefficients for aqueous species. The nonlinear set of equations set up by MINTEQ are solved using the Newton-Raphson procedure. The model has been used to simulate reactions in leaching of mining wastes (Peterson and Krupka, 1981).

A reduced version of MINTEQ, called MININR, has been produced by Felmy et al. (1984) for incorporation in flow and transport models. In essence, MININR is MINTEQ without the user interface. MININR was combined with a simple model for saturated flow by Felmy et al. (1984). This flow, transport, and chemical reaction model was tested against data from a laboratory column experiment where water was percolated through retorted oil shale. The combined model was able to predict with reasonable accuracy the pH, and concentrations of Ca^{2+}, SO_4^{2-}, Na^+, and K^+.

3.5.2.5   WATEQX

WATEQX is a version of the WATEQ family (e.g., Garrels and Thompson, 1962; Truesdell and Jones, 1974; Plummer et al., 1976). This family is used to find equilibrium speciation in natural waters using mass balance on all components except the solvent. The pH is a required input parameter, as is the temperature and redox potential. The main change incorporated in WATEQX is that data for reactions not contained in the present database can be incorporated quite easily. Activity coefficients can be computed using the extended Debye-Hückel and Davies formula, or the mean salt method of Pitzer (1973), Pitzer and Mayorga (1973), and Millero and Schreiber (1982), thereby extending the model to more electrolytes than previously possible.

3.6   MULTICOMPONENT TRANSPORT AND REACTION MODELS

3.6.1   A List of Major Codes

The number of combined chemical reaction-transport models developed remains relatively small. Many of those available have been developed at the Lawrence Berkeley Laboratory. A catalog of the major codes presently existing is given in Table 3.3. We observe that many of these codes have been developed to handle particular problems, especially those related to nuclear waste management. However, the generality of the codes, which depends in part on the geochemical data base incorporated in the model, makes them applicable, in principle, to other transport problems, e.g., transport of nonradioactive contaminants.

3.6.2   Descriptions of Some Multicomponent Chemical Transport Codes

The codes differ in the their complexity. This is displayed schematically in Figure 3.3, which considers mainly codes developed at the Lawrence Berkeley Laboratory. CHEMTRN, for example, models one-dimensional solute transport coupled with equilibrium chemical reactions. Thus, CHEMTRN can be considered to model a subset of the processes simulated by THCC because THCC includes the processes modeled by CHEMTRN in addition to heat transport. Some of the codes in Table 3.2 are described in more detail below.

3.6.2.1   CHEMTRN

This model simulates one-dimensional solute transport in a saturated porous medium. The processes of advection, dispersion, sorption, aqueous phase complex

Table 3.3   Combined Flow and Multicomponent Chemical Transport Models

Name	Description	Ref.
CHEMTRN	One-dimensional advective-dispersive transport code with equilibrium chemical reactions of speciation, precipitation/dissolution, cation exchange, and surface speciation	Miller and Benson (1983)
CHMTRNS	A nonequilibrium, temperature-dependent transport model, evolved from the CHEMTRN code	Noorishad et al. (1987)
DYNAMIX	Couples PHREEQE (Table 3.2) with the multidimensional transport code TRUMP. Now extended to include acid-base reactions, aqueous complexation, redox reactions, and precipitation/dissolution reactions	Liu and Narasimhan (1989a)
FASTCHEM	This is a suite of seven codes to model coupled flow and transport. The flow code, EFLOW, is a 2-D finite element solution of the flow equation, while the chemistry and transport codes are descendents of the MINTEQ geochemical code and the SATURN transport code	Hostetler et al. (1988)
FIESTA	Predicts the migration of subsurface pollutants that undergo convection, dispersion, soluble complexation, and sorption	Kirkner et al. (1984)
PHREEQM	Uses PHREEQE (Table 3.2) to model chemical reactions with a mixing cell concept to simulate transport	Nienhuis and Appelo (1988)
REACTRAN	Couples chemical reactions to mass transport and computes porosity changes due to precipitation and dissolution	Ortoleva et al. (1987)
SATRA-CHEM	Multidimensional flow with sorption, ion exchange, and equilibrium speciation	Lewis et al. (1986)
THCC	An extension of CHMTRNS in which heat transport is included but not coupled to mass transport	Carnahan (1987b)
TIP	Solves the coupled equations of solute, heat, and fluid transport, including equilibrium chemical reactions	Carnahan and Jacobsen (1988)

formation, and the dissociation of water are included in the model. Miller and Benson (1983) showed that the CHEMTRN predictions compared well with field data on the transport and exchange of Na^+, Ca^{2+}, and Mg^{2+} (Valocchi et al., 1983).

3.6.2.2 DYNAMIX

Liu and Narasimhan (1989a,b) consider that redox reactions are important not only in both organic and inorganic contaminant transport, but also in diagenesis of sedimentary rock, formation of oil and gas, and metal corrosion (cf. Sillen, 1967). The chemical reaction portion of DYNAMIX solves a nonlinear set of equations composed of mass balance equations, a charge balance equation, a conservation of redox state equation, and mineral solubility equations. The mineral assemblage within the system is determined by minimizing the Gibbs free energy. Oxygen is treated as a secondary, dependent species to account for changes in redox potential in the aqueous solution, and so oxygen transport is computed as part of the solution. As already stated in Table 3.3, the chemical reaction model is coupled with the transport model TRUMP (Edwards, 1972) to form DYNAMIX. A two-step solution approach is followed. As the numerical solution steps through time, the transport model is solved by explicit finite differences. Then, the chemical submodel computes the chemical distribution under dynamic partial equilibrium conditions. Liu and Narasimhan (1989b) verify the model by comparison with THCC and PHASEQL/ FLOW (Walsh et al., 1984). They provide two example applications of the model, both of which involve numerous chemical components. A solution was provided to a two-dimensional contamination problem involving selenium and arsenic but including also 16 aqueous components, 26 minerals, and over 76 aqueous complexes. They found that arsenic was strongly retarded by precipitation as As_2S_3. On the other hand, selenium was relatively more mobile, being transported in the aqueous phase. Not surprisingly, a Cray XMP/14 supercomputer was used to perform the calculations.

3.6.2.3 FASTCHEM

The two-dimensional FASTCHEM (*Fly Ash* and *Flue Gas Desulfurization Sludge Transport* and *Geochemistry*) package consists of separate modules including a two-part thermodynamic database (Krupka et al., 1988), groundwater flow code (Huyakorn et al., 1988), streamtube code (Kincaid, 1988), and equilibrium geochemical code (Morrey, 1988). The separate modules can be run independently if desired. Other codes are used to link the modules and solve the coupled transport and geochemical transformation equations.

3.6.2.4 FIESTA

This one-dimensional model combines the FEAP and MINEQL models (Kincaid et al., 1984a). It will handle six components with reactions including ion exchange, adsorption, and aqueous phase complexation (Theis et al., 1982). A detailed evaluation of FIESTA was performed by Morrey et al. (1986), who were interested in disposal problems faced by the electricity industry. They found that the construction of the code was sound, but concluded that its capabilities could be improved substan-
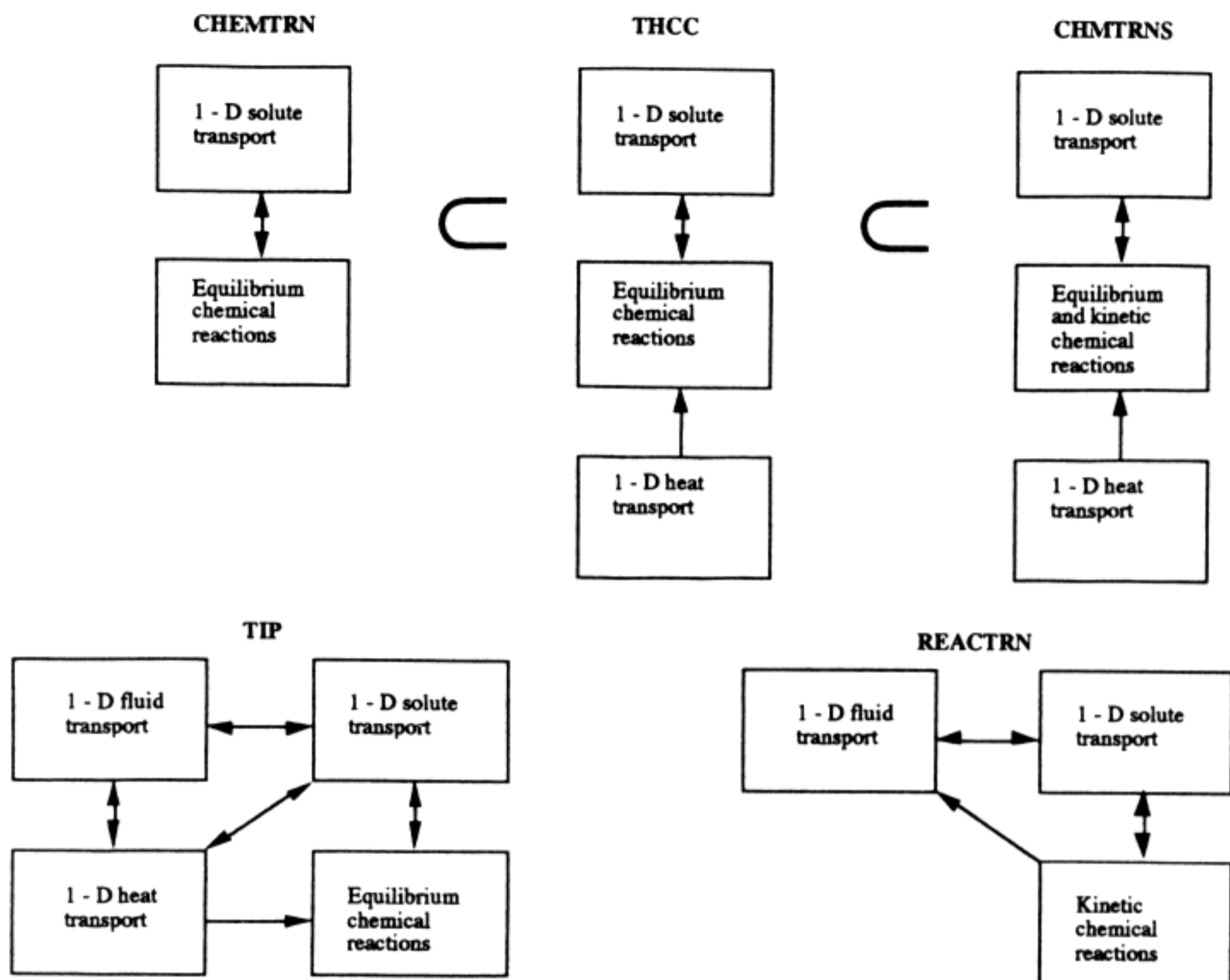
FIGURE 3.3. Processes modeled in various coupled flow, transport, and chemical reaction codes (cf. Carnahan, 1987). In the upper row the development of CHEMTRN is shown. In each box the processes modeled by the code are summarized. The arrows linking the boxes show the interaction between the various processes.

tially by, for example, increasing the number of components allowable, extending the adsorption, and allowing for variable dispersivity and velocity.

3.6.2.5 PHREEQM

PHREEQM combines the geochemical model PHREEQE with a one-dimensional mixing cell concept (Dance and Reardon, 1983; Schulz and Reardon, 1983), the latter to model the transport and dispersion of the solutes. Appelo and Willemsen (1987) performed a similar operation using the EQ3/6 (Wolery, 1983) geochemical model. In concept, the mixing-cell approach divides the domain into a group of cells. At each time step the fluid contained within each cell is advected and mixed between neighboring cells, with the mixing proportions between cells selected so that solute dispersion is simulated. Appelo et al. (1990) have used the model to simulate salt water transport and reactions in laboratory and field settings.

3.6.2.6 SATRA-CHEM

The flow and transport code, SATRA, a modified version of the SUTRA program (Voss, 1984), was combined with a mathematical formulation of the chemical reaction processes of sorption, ion exchange, and aqueous complexation to produce SATRA-CHEM (Lewis et al., 1987). These authors try explicitly to separate the

linear and nonlinear portions of the numerical calculations. Linear governing equations can then be solved separately from the nonlinear equations with, it is hoped, a consequent gain in efficiency. The model solved by Lewis et al. (1987) is a relatively simple one, and no general procedure of separating the numerical tasks is presented. Numerous one- and two-dimensional examples of SATRA-CHEM are presented, but no experimental data are analyzed.

3.6.2.7 TIP

This program is based on the thermodynamics of irreversible processes. It solves the coupled equations of flow of heat, fluid, and solute for spatially varying temperature, pressure, and solute concentration. The original code was modified (Jacobsen and Carnahan, 1988) to include the reactive chemical modeling contained in the THCC program (Figure 3.3).

3.7 SEMIANALYTICAL TRANSPORT MODELS

3.7.1 A List of Major Models

Unlike the relatively few multicomponent transport models discussed above, there exists a plethora of fully analytical or semianalytical models that can be used to simulate the transport of a single chemical species (usually) or, rarely, more than one species. The many physical and chemical scenarios encompassed by models in this class are too numerous to attempt more than an overview of the literature and computer codes in this area. Extensive summaries have been prepared by Grove and Stollenwerk (1987) and Miller (1987), who review the characteristics of many recent publications. Some of the more widely used and recent models implemented on computers will be considered here. These codes, for the most part, are based on relatively simple spatial domains and chemical reaction models. Their solution usually involves either calculation of an analytical solution or some simple numerical scheme, e.g., the numerical inversion of a Laplace domain solution. A brief summary of the available codes is given in Table 3.4. More detailed descriptions of the codes and their applications are presented below.

3.7.2 Descriptions of Some Semianalytical Codes
3.7.2.1 COLUMN2

COLUMN2 is an extension of the COLUMN program, developed by Bo (1978). The latest version of the code couples an explicit finite-difference solution to the one-dimensional convection-dispersion equation equilibrium sorption, aqueous phase reactions, and radioactive decay. The nonlinearity of the chemical reactions is ignored by using previously calculated concentrations for the components in the calculations. Nielsen et al. (1985) provide a number of examples involving the use of COLUMN2, but no examples were compared with actual experimental data.

3.7.2.2 CXTFIT

CXTFIT consists of a suite of one-dimensional transport models to which data can be fitted to determine parameters. Concentration profiles or breakthrough curves can be produced if parameters are known. Any of the following models can be selected.

Linear Equilibrium Adsorption Models

$$R\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} - \mu c + \lambda \tag{26}$$

Equation (26) is just the familiar convection-dispersion equation with first-order decay and zero-order production terms. It applies whether resident or flux concentrations (Barry and Sposito, 1988; Kreft and Zuber, 1978, 1986; Parker and van Genuchten, 1984b, 1986; Sposito and Barry, 1987) are considered.

Two-Site/Two-Region Nonequilibrium Models. This class of model considers "two-site" adsorption to be composed of equilibrium adsorption and first-order kinetic nonequilibrium adsorption (Selim et al., 1976; Rao et al., 1979). These adsorption sites are referred to as type-1 and type-2 sites, respectively. The governing model is

$$\left(1 + \frac{F\rho_b}{\theta}\right)\frac{\partial c}{\partial t} + \frac{\rho_b}{\theta}\frac{\partial s_2}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \tag{27a}$$

where

$$\frac{\partial s_2}{\partial t} = \alpha\left[(1 - F)kc - s_2\right] \tag{27b}$$

Equation (27b) defines the model for the nonequilibrium, type-2 sites, with concentration s_2. The constant k is defined by the equilibrium relationship between the adsorbed and aqueous phase concentration:

$$s_1 + s_2 = kc \tag{28}$$

The "two-region" model is mathematically equivalent to the two-site model although it is based on a physical interpretation of the transport process, in contrast to the chemical adsorption model upon which the two-site model rests (van Genuchten, 1981). In the physical interpretation, the soil is subdivided conceptually into two regions, one labeled mobile and the other immobile. Flow takes place in the mobile region, but not in the immobile zone. However, solute moves into the immobile zone at a rate proportional to the local difference in concentration in each zone. Thus, even if experimental data are fitted well by the two-site or two-region model, additional information is needed to determine which interpretation is applicable.

Regional Transport Model. Many different models of field-scale transport models have been developed (e.g., Bresler and Dagan, 1983; Jury, 1982; Persaud et al., 1985; van der Zee and van Riemsdijk, 1986; van der Zee, 1990). Parker and van Genuchten (1984b) assume the field can be subdivided into one-dimensional, inde-

Table 3.4   Semianalytical Chemical Transport Models

Name	Description	Ref.
COLUMN2	One-dimensional transport code incorporating dispersion, sorption, ion exchange, and first and second order homogeneous chemical reactions	Nielsen et al. (1985)
CXTFIT	Code used to fit transport parameters for a number of one-dimensional models	Parker and van Genuchten (1984a)
MIGRATE	Quasi-two-dimensional transport with a linear adsorption isotherm	Rowe and Booker (1985)
MYGRT	Two-dimensional transport under steady flow conditions with retardation and linear decay	Summers et al. (1989)
PESTAN	One-dimensional convective transport with various simplified chemical processes	Enfield et al. (1982)
POLLUTE	Solves the one-dimensional solute transport equation for layered profiles	Rowe et al. (1984)
PRZM	This is composed of a hydrology component (runoff, erosion, evapotranspiration) and a chemical transport component (chemical uptake, decay, transformation, retardation)	Carsel et al. (1985)
SESOIL	A seasonal compartmental model of water flow, sediment, and solute transport applicable at the watershed scale	Bonazountas and Wagner (1984)
TFMFIT	Fits transport and chemical parameters for an areally averaged three-dimensional convection-dispersion model.	Barry et al. (1988)
TRANSS	A simple model for transport of a decaying radionuclide along a collection of streamtubes	Simmons et al. (1986)

pendent, parallel soil columns, with the solute transport in each governed by a convection-dispersion equation with its own transport parameters. The distribution of pore water velocity is described by the log-normal distribution:

$$f(v) = \left(v\sigma_{\ln}\right)^{-1}(2\pi)^{-1/2} \exp\left\{-\frac{\left[\ln(v) - \mu_{\ln}\right]^2}{2\sigma_{\ln}^2}\right\} \tag{29}$$

The distribution of the dispersion coefficient is taken as being uniform because transport effects due to this mechanism are small in comparison to velocity variability (Amoozegar-Fard et al., 1982). Under these assumptions, the mean field-scale resident solute concentration is calculated from

$$\bar{c} = \int_0^\infty cf(v)\,dv \tag{30}$$

The inlet condition, which is the local flux density at the inlet of each column, is

$$M(t) = \begin{cases} v\theta c_0 t, & 0 < t \le t_0 \\ v\theta c_0 t_0, & t > t_0 \end{cases} \tag{31}$$

Define M_0 by $M_0 = v\theta c_0 t_0$, so that M_0 is the total mass applied per unit area. Solutions are provided for the following combinations:

1. Sure t_0, θ, c_0; stochastic M_0, v
2. Sure M_0, θ, c_0; stochastic t_0, v

The fitting algorithm of CXTFIT is that of Marquardt (1963). Examples showing the uses of CXTFIT include fitting to various models (1) laboratory column data of Parker (1984) and van Genuchten (1974), and (2) the field data of Jury (1982). Barry and Parker (1987) extended CXTFIT to account for layered profiles. They obtained accurate predictions of breakthrough curves for experimental data presented by Shamir and Harleman (1967) and Panigatti (1970).

3.7.2.3 MIGRATE

This model is intended to be applied for contamination problems involving leachate emanating from a landfill. A quasi-two-dimensional vertical slice of the landfill is modeled. It is assumed that an initial, known quantity of leachate is stored in the landfill at a given concentration. It moves downward at a steady velocity through a clay layer until it encounters a more permeable layer in which the flow is horizontal. Only linear equilibrium solute adsorption is included in the model. The Laplace domain solution derived by Rowe and Booker (1985b) is solved using the numerical inversion routine of Talbot (1979). Hensley (1989) and Hensley and Schofield (1991) compared MIGRATE with experimental data from a centrifuge experiment simulating a landfill leachate plume, and found that it was not able to

replicate the experimental results at all points in the centrifuge. In particular, MIGRATE predicted poorly transverse solute transport.

3.7.2.4 MYGRT

This code is based on the two-dimensional convection-dispersion equation with a linear decay term on a semiinfinite domain. A one-dimensional version of the same governing equation can be selected as well. In both cases analytical solutions are available (Cleary and Ungs, 1978; Javandel et al., 1984). The main computations performed are integrations that are carried out numerically. Solutions for an impermeable base at the lower boundary of the profile are obtained using the method of images.

3.7.2.5 PESTAN

This is a one-dimensional model that accounts for aqueous-phase transport and transformations under steady flow in homogeneous soil profiles. Three solutions are provided. These are (1) linear sorption and first-order decay without dispersion, (2) dispersion and linear sorption without decay, and (3) adsorption modeled using the Freundlich isotherm with first-order decay but no dispersion. Cases (1) and (2) are solved analytically while case (3) is solved numerically. PESTAN has been used by the U.S. Environmental Protection Agency Office of Pesticide Programs (Donigian and Rao, 1986a) and by Jones and Back (1984) to model aldicarb transport in a Florida soil. Donigian and Rao (1986b) compared the predictions of PESTAN with aldicarb data presented by Hornsby et al. (1983). They found reasonable agreement for leaching predictions in this case.

3.7.2.6 POLLUTE

This code is essentially a one-dimensional version of MIGRATE. It simulates one-dimensional vertical flow from a finite source of solute with linear adsorption as the only chemical reaction considered (Rowe and Booker, 1985a). Below this finite (clayey) layer is another, more permeable layer. The more permeable layer is perfectly mixed in the vertical direction and ignores dispersion in the horizontal direction. The lower boundary condition is obtained by conservation of mass of solute entering the permeable layer. The experiments described by Hensley and Schofield (1991) produced a flow field that was essentially unidimensional for at least part of the flow domain. Data obtained from this subdomain were predicted well using POLLUTE.

3.7.2.7 PRZM

Flow in PRZM is modeled using an empirical model (Donigian and Rao, 1986b). PRZM is a compartmental model, with the chemical submodel including plant uptake of solute, transport by surface runoff and erosion, solute decay, retardation, and transformation, as well as transport by dispersion. The profile is divided into layers, with a one-dimensional convection-dispersion model applicable in each layer. In the surface layer, the model accounts for erosion and runoff-induced chemical transport. A numerical solution is obtained using the finite-difference method. It has been used

for the modeling of pesticide transport in the analysis of several field studies (Jones et al., 1983; Jones, 1983; Carsel et al., 1985, 1986).

3.7.2.8 SESOIL

SESOIL is a compartmental model aimed at predicting solute distribution in both the soil profile and watershed on a seasonal basis. The code has a hydrologic cycle component based on the theory of Eagelson (1978). Both sediment and chemical transport are modeled by SESOIL. Chemical transformations and reactions included are volatilization, sorption, degradation, hydrolysis, oxidation, and cation exchange, with extensions to include other chemical processes planned (Donigian and Rao, 1986a). Donigian and Rao (1986a) report on a comprehensive evaluation of SESOIL. It was concluded that several improvements could be made to the chemical transport part of the code. Large variations in the hydraulic properties of the profile could not be handled well. The estimate of the time necessary for a chemical to leach to groundwater did not include sorption of the chemical, only the water movement in the profile. Donigian and Rao (1986b) used SESOIL to predict aldicarb movement to groundwater. They found that SESOIL overpredicted the mass of the pesticide leached. They also noted an error in the hydrolysis algorithm in the model.

3.7.2.9 TFMFIT

TFMFIT is based on the following convection-dispersion model (cf. Sposito and Jury, 1988):

$$BR\frac{\partial c_m}{\partial t} + (1-B)\frac{\partial c_m}{\partial t} = \sum_{i=1}^{3}\frac{1}{P_i}\frac{\partial^2 c_m}{\partial X_i^2} - \frac{\partial c_m}{\partial X_3} - BCc_m - (1-B)Dc_{im} \qquad (32a)$$

with

$$(1-B)R\frac{\partial c_{im}}{\partial t} + (1-B)Dc_{im} = W\left(c_m - c_{im}\right) \qquad (32b)$$

where

$$B = \frac{\theta_m + f\rho_b K_d + \theta_{gm}K_H^{-1}}{\theta + \rho_b K_d + \theta_g K_H^{-1}} \qquad (32c)$$

$$C = \frac{\left(\theta_m\beta_m^l + fK_d\beta_m^s + \theta_{gm}K_H^{-1}\beta_{im}^g\right)L}{\theta_m v(1-B)} \qquad (32d)$$

$$D = \frac{\left(\theta_{im}\beta_{im}^{l} + (1-f)K_d\beta_{im}^{s} + \theta_{im} + \theta_{gim}K_H^{-1}\beta_{im}^{g}\right)L}{\theta_m v(1-B)} \tag{32e}$$

and

$$W = \frac{\left(\alpha^{l} + \alpha^{g}K_H^{-1}\right)L}{\theta_m v} \tag{32f}$$

This model represents the following processes (Barry et al., 1988):

1. Solute is free to move in any spatial direction through a porous medium with uniform porosity, with steady flow along the X_3 axis.
2. Solute dispersion is anisotropic.
3. Solute can be partitioned between the gas phase, the mobile and immobile portions of the liquid phase, and the solid phase, with biodegradation possible in all phases.

Barry et al. (1988) provided both real-time and Laplace domain solutions for Equation (29) averaged over a window that corresponds, approximately, to the sampling region of an experiment. TFMFIT can fit experimental data or produce concentration profiles or breakthrough curves for specified parameter sets. Like CXTFIT, TFMFIT uses the Marquardt (1963) algorithm to carry out the fitting portion of the computations. The user can choose to use either the numerically inverted Laplace domain solution or the real time solution.

TFMFIT was used to fit carbon tetrachloride breakthrough curve data from the Borden aquifer experiment (Roberts et al., 1986). As shown in Figure 3.4, the model fitted to the data very well, and found, for example, that a retardation coefficient of 1.74 was appropriate. TFMFIT assumes a Dirac source term, so it computes the probability density function of the solute transport to a particular location. Finite duration, non-Dirac source terms are permissible so long as the distance from the source is relatively large. Tetrachloroethylene breakthrough curve data for the same experiment, described by Curtis et al. (1986), were also fitted. Again a good model fit was found (Figure 3.5), and it was shown conclusively that, in terms of the model used, tetrachloroethylene is more strongly retarded ($R = 2.47$) than carbon tetrachloride.

3.7.2.10 TRANSS

The basic concept behind TRANSS bears some similarity to the regional transport model contained in CXTFIT. The transport domain is conceptualized as a collection of streamtubes, each with different transport properties. A one-dimensional convection-dispersion equation is assumed to apply in each streamtube. The final concentration through the exit surface is a probability-weighted average over all the streamlines, with the weighting predetermined by the user. The model can treat radioactive or conservative solutes, with decay in both the source and streamtube. The only
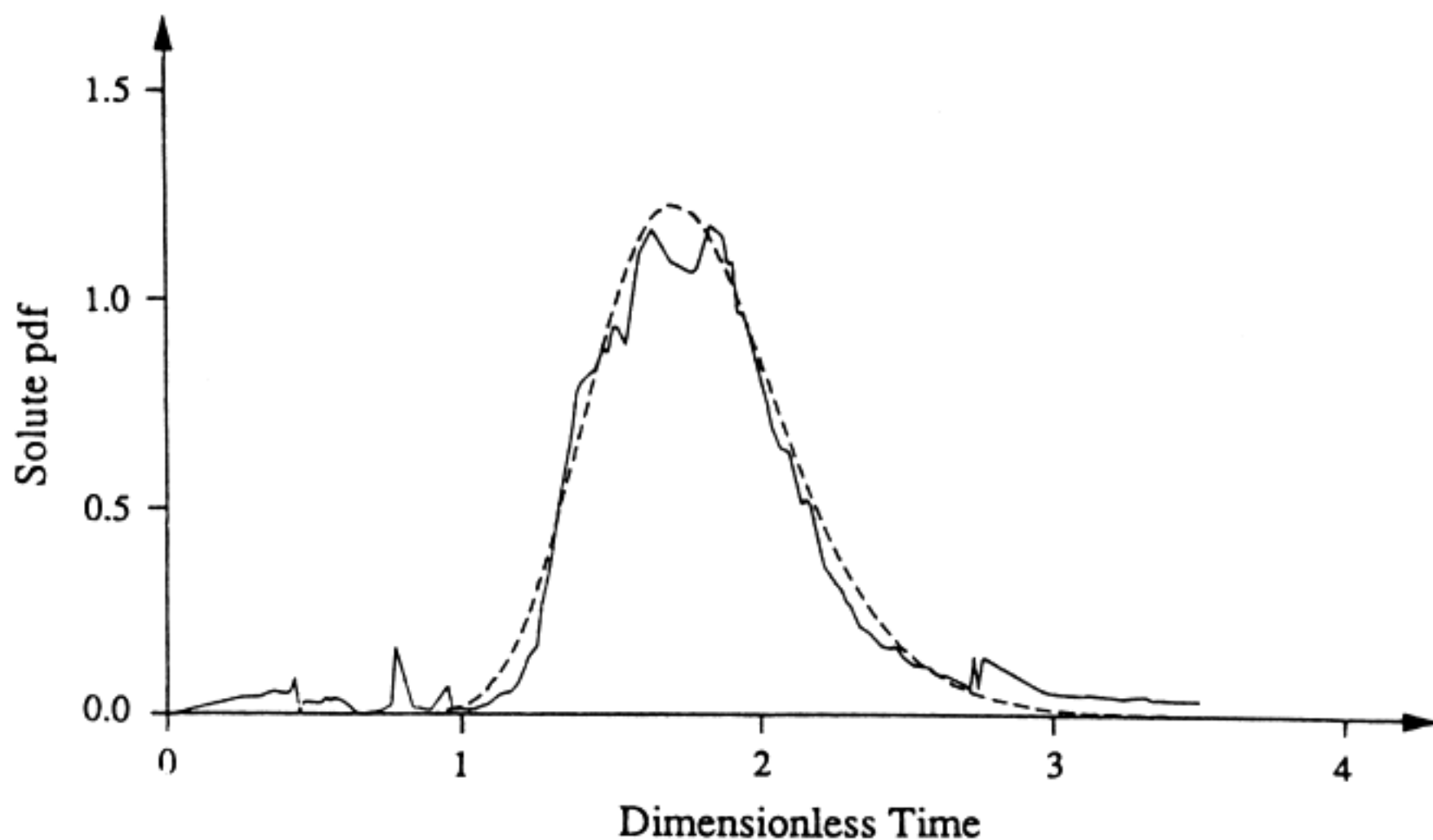
FIGURE 3.4.   Fit of the convection-dispersion model, Equation (32) (---), to the carbon tetrachloride breakthrough curve data (—) from the Borden aquifer experiment, as performed by TFMFIT.
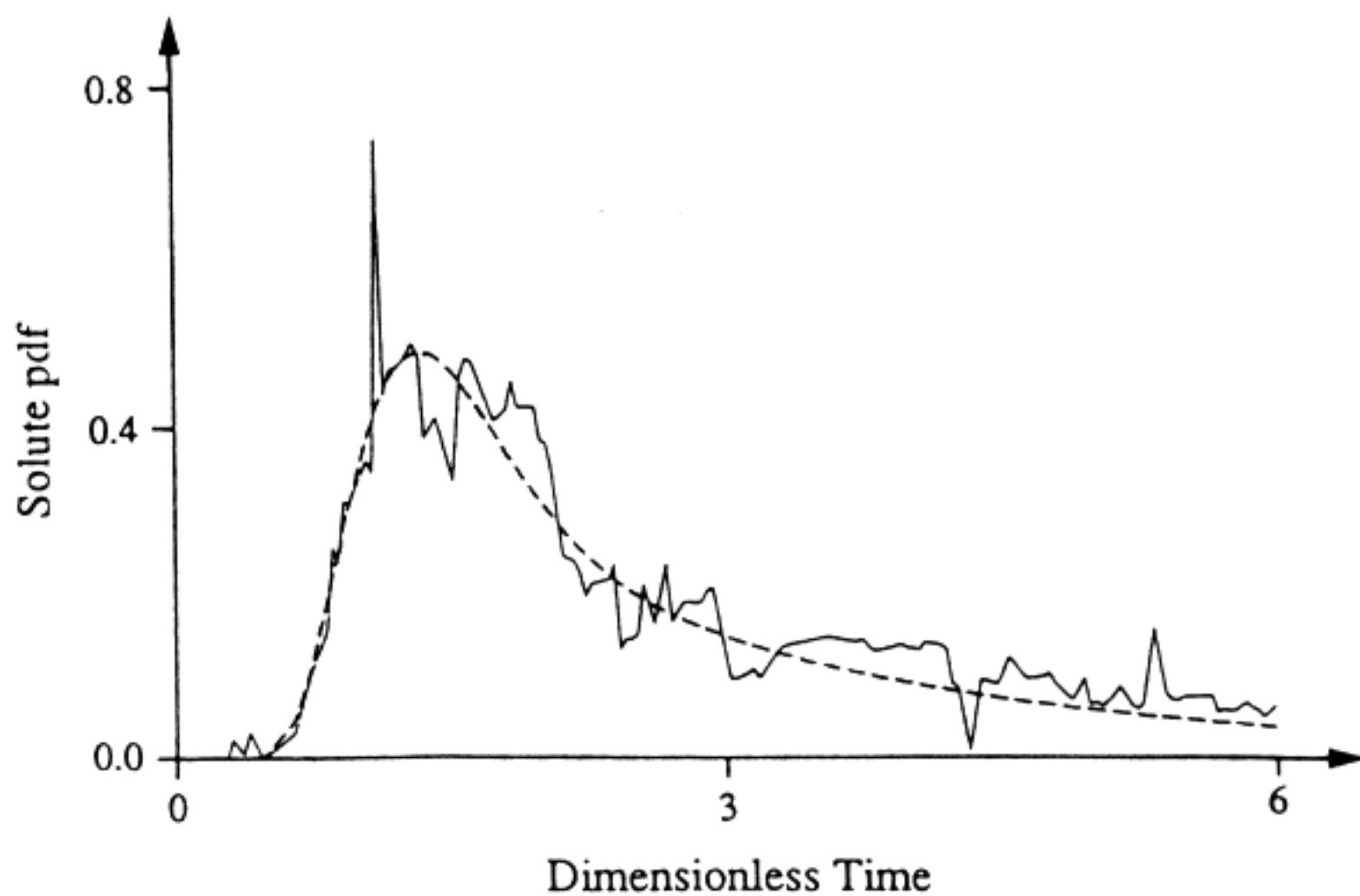
FIGURE 3.5.   Fit of the convection-dispersion model, Equation (32) (---) to the tetrachloroethylene data (—) collected from the Borden aquifer experiment as perfored by TFMFIT.

chemical reaction included is retardation due to solute sorption. Input concentrations can be stochastic or sure. Solute release from the source can be modeled in four different ways: (1) constant release rate, (2) solubility-controlled release, (3) adsorption-equilibrium-controlled release, and (4) diffusion-controlled release from below an infiltration barrier.

3.8 SUMMARY

The emphasis of many hydrologic modelers has been on the physical processes of convection and dispersion of solutes. At the same time, many batch-type geochemical models have been implemented. It is easy to imagine situations requiring both aspects of contaminant transport to be incorporated in a single model. Thus, this chapter began with the premise that it is necessary to quantify both chemical and physical processes in contaminant transport models.

The basic structure of the geochemical models was outlined. This structure can be incorporated into a flow and transport model, yielding a set of coupled nonlinear partial differential equations to be solved. The number of computer codes that have been developed for the multicomponent transport model is small. Even fewer models have been developed for multidimensional spatial domains. The reason is that any problem involving a significant number of chemical reactions will require the availability of a powerful computer. In some cases a supercomputer will be necessary. In cases where it is thought that only a single or a few chemical components are involved, numerical solutions can be obtained with a much more modest computer.

3.9 LIST OF SYMBOLS

$a_{i,j}$	$i = 1, \ldots, N$; $j = 1, \ldots, M$, stoichiometric coefficient of the jth component in the ith species
A	Empirical constant in the activity coefficient formula
A_{ij}	Stoichiometric coefficient
B	Empirical constant in the activity coefficient formula
B	Dimensionless constant
c, c_i	$i = 1, \ldots, N$; species molarity, $M\,L^{-3}$
c_i^{T}	Total concentration of the ith component, $M\,L^{-3}$
c_{im}	Concentration in the immobile region, $M\,L^{-3}$
c_m	Concentration in the mobile region, $M\,L^{-3}$
c_0	Solute concentration of the influent fluid, $M\,L^{-3}$
C	Dimensionless parameter
D	Hydrodynamic dispersion coefficient, $L^2\,T^{-1}$
$\mathbf{D}$	Hydrodynamic dispersion tensor, $L^2\,T^{-1}$
E_F	Equivalent fraction of F in the solid phase
$\tilde{E}_F$	Equivalent fraction of F in the liquid phase
f	Probability density function
f	Fraction of adsorbing solid phase in contact with mobile liquid
f^{cu}	Nonlinear function of u_i, $i = 1, \ldots, N_c$, $M\,L^{-3}$
f^{su}	Generalized adsorption isotherm, $M\,L^{-3}$
F	Exchange cation with valence f
F	Fraction of type-1 sorption sites
G	Exchange cation with valence g
k	Proportionality constant between adsorbed and fluid phase concentration

k_i	$i = 1, 4$; adjustable parameters
k_i	$i = 2, 5$; adjustable parameters, $L^3 M^{-1}$
k_3	Adjustable parameter, $L^{3(k_1-1)} M^{1-k_1}$
k_6	Adjustable parameter, $L^{3/2} M^{-1/2}$
k_7	Adjustable parameter, ML^{-3}
k_8	Adjustable parameter, $M^{k_1} L^{-3k_1}$
k_9	Adjustable parameter, $L^{3(1-k_1)} M^{k_1-1}$
k_{10}	Adjustable parameter, $L^{3(c^{k_1}/k_8-1)} M^{1-c^{k_1}/k_8}$
K_d	Distribution coefficient for adsorption, $L^3 M^{-1}$
$K_e, K_i, K_{e,i}$	$i = 1, \ldots, N$; equilibrium constants
K_H	Henry's law constant for solute partitioning between the liquid and air
K_{s_i}	Equilibrium constant for adsorption reaction
K_{sp}	Solubility product
$\mathbf{L}$	Convection-dispersion differential operator, T^{-1}
L	Distance form solute input point to monitoring point, L
m, m_i, etc.	Molality
m_{sol}	Mass of solvent, M
m_{sp}	Mass of a chemical species, M
$M(t)$	Cumulative flux of solute at time t, $M L^{-2}$
M_0	Total amount of solute added to profile, $M L^{-2}$
M_{Tw}	Mass of water, M
N_c	Number of chemical components
N_x	Number of chemical complexes
P_i	Peclet number in the ith direction
q	Excess of chemical adsorbed
$\mathbf{q}$	Fluid flux, $L T^{-1}$
r_i	$i = 1, \ldots, N$, stoichiometric coefficients
R	Retardation coefficient
R_i	$i = 1, \ldots, N$; reacting chemical species
s	Concentration of adsorbed solute, $M L^{-3}$
s_1, s_2	Solute concentration on type-1 and -2 sites, respectively, $M L^{-3}$
s_i	$i = 1, \ldots, M$; stoichiometric coefficients
S_i	$i = 1, \ldots, M$; product of reacting chemical species
t	Dimensionless time coordinate
t_i	$i = 1, \ldots, N$; stoichiometric coefficients
TN	Total normality of a solution
u_i	Total aqueous phase concentration of the ith component, $M L^{-3}$
v	Mean pore water velocity, $L T^{-1}$
V_{sol}	Volume of solution, L^3
w	Sorbed concentration, $M L^{-3}$
x_i	Concentration of the ith complex, $M L^{-3}$
x_T	Total number of surface sites in moles per unit volume of solution
X	Anion with valence -1
X_j	$j = 1, \ldots, M$; concentration of the jth component, $M L^{-3}$

X_i	Dimensionless distance in the ith direction
$X_{T,j}$	$j = 1, \ldots, M$; total concentration of the jth component in the system, $M\,L^{-3}$
Y	Anion with valence -1
z, z_i, etc.	Valence
Z^{z_z}	Exchange ion with valence z_Z
α	First-order rate coefficient, T^{-1}
α^i	Linear solute transfer coefficient for the ith (gas, g; liquid, l) component into the immobile portion of the liquid phase, T^{-1}
β^i_j	First-order solute decay constant for the ith (gas, g; liquid, l; solid, s) component in or contacting the jth (mobile, m; immobile, im) portion of the liquid phase, T^{-1}
γ	Activity coefficient, $L^3\,M^{-1}$
θ	Volumetric moisture content
θ_{im}	Volumetric moisture content of the immobile region
θ_{gim}	Volumetric air content in contact with the immobile region
θ_{gm}	Volumetric air content in contact with the mobile region
θ_m	Volumetric moisture content of the mobile region
λ	Zero-order production coefficient, $M\,L^{-3}\,T^{-1}$
μ	Rate constant for first-order decay, T^{-1}
μ_{ln}	Mean of $\ln(v)$
ρ_b	Bulk density, $M\,L^{-3}$
σ_{ln}	Standard deviation of $\ln(v)$
$\{\bullet\}$	Activity of $\bullet$
$\bullet_l$	In the liquid phase
$\bullet_s$	In the solid phase
$\bar{\bullet}$	Mean of $\bullet$

3.10 APPENDIX: CHEMISTRY CONCEPTS

The term *chemical species* may refer to either single ionic species or chemical *complexes*, i.e., ionic species acting as a single unit. The concentration of a solute can be expressed in various ways. Perhaps the most general, because it is independent of temperature or pressure changes, is the *molality*, which is simply the ratio of the mass of the chemical species to the mass of the solvent (Sposito, 1989, p. 264), i.e.,

$$m = \frac{m_{sp}}{m_{sol}} \tag{A1}$$

Molality is usually measured in units of moles per kilogram of solvent. More commonly, the molarity is used as the concentration measurement. *Molarity* is defined by (Sposito, 1981, §2.2):

$$c = \frac{m_{sp}}{V_{sol}} \qquad (A2)$$

and is usually expressed as moles per cubic meter. The concentration of a solute does not necessarily define its capacity to react. This is because of interaction between solute particles themselves or interactions with the solvent. The *activity* is a measure of the effective concentration of a solute (Tan, 1982, §3.15). If a solute has concentration c, then its activity is given by

$$\{c\} \equiv \gamma c \qquad (A3)$$

The *activity coefficient*, γ, has units of liters per mole, so that the activity is dimensionless (Sposito, 1989, §4.5). One can also define single ion activity coefficients by analogy with Equation (A3), although Sposito (1984b) points out that the meaning of such coefficients is purely operational. Activity is a measure of the chemical potential of the solute (Schay, 1969, §B). The activity coefficient is less than unity, although it approaches unity for dilute solutions. Thus, because many contaminant problems concern dilute solutes, the concentration of a species will be a good approximation to its activity. When the species is adsorbed onto the solid phase, the concentration variable changes to mole fractions. Mole fraction is defined as the ratio of the number of moles of the species under consideration to the total number of moles of adsorbed species. In this case the activity coefficient is termed a *rational activity coefficient* (Sposito, 1979, §9.4). In multicomponent solutions of electrolytes, the activity coefficient can be calculated using the equation

$$\log(\gamma) = BI - \frac{Az^2 I \sqrt{I}}{1 + I\sqrt{I}} \qquad (A4)$$

where the *ionic strength*, I, of the solution is given by

$$I = \frac{1}{2} \sum_{i=1}^{n_s} z_i^2 m_i \qquad (A5)$$

There are various versions of Equation (A4) available, depending on the (temperature-dependent) values of A and B (see Sposito, 1981, §2.6 for a range of values). Davies (1962) has produced an expression that is accurate for ionic strengths less than 0.5 mol/kg (Sposito, 1984b). If a reaction occurs in an aqueous solution without precipitation or adsorption, then at equilibrium the *law of mass action* asserts that the ratio of activities of the products to reactants is constant. The factor of proportionality is the *equilibrium constant* (Tan, 1982, §3.5). Ions that become associated in a reaction form a *complex* (Sposito, 1989, §4.2). Suppose the species $R_1, \ldots, R_N$ react to form products $S_1, \ldots, S_M$, according to

$$r_1 R_1 + \cdots + r_N R_N \rightleftarrows t_1 S_1 + \cdots + t_M S_M \qquad \text{(A6)}$$
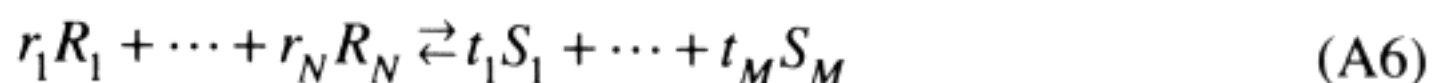
then the equilibrium constant, K_e, which is temperature dependent, is given by

$$K_e = \frac{\{R_1\}^{r_1} \times \cdots \times \{R_N\}^{r_N}}{\{S_1\}^{t_1} \times \cdots \times \{S_M\}^{t_M}} \qquad \text{(A7)}$$

If we make use of Equation (A3), then Equation (A7) may be rewritten as

$$K_e = \frac{\gamma_{R_1}^{r_1} R_1^{r_1} \times \cdots \times \gamma_{R_N}^{r_N} R_N^{r_N}}{\gamma_{S_1}^{t_1} S_1^{t_1} \times \cdots \times \gamma_{S_M}^{t_M} S_M^{t_M}} \qquad \text{(A8)}$$

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