

MODELING THE SORPTION OF HYDROPHOBIC CONTAMINANTS BY AQUIFER MATERIALS—II

COLUMN REACTOR SYSTEMS

CASS T. MILLER¹ and WALTER J. WEBER JR²

¹Water Resources Engineering, Department of Environmental Sciences and Engineering, The University of North Carolina, Chapel Hill, NC 27514, U.S.A. and ²Environmental and Water Resources Engineering, Department of Civil Engineering, The University of Michigan, Ann Arbor, MI 48109, U.S.A.

(Received December 1986; Accepted in revised form November 1987)

Abstract—This is the second of a two-part series describing laboratory investigations and mathematical modeling of the sorption of hydrophobic solutes by aquifer materials. An evaluation is made of several rate and equilibrium models for description of solute sorption as a rational basis for predicting sorption processes in groundwater systems. The first paper presents and compares sorption in completely mixed batch-reactor systems while this paper addresses column-reactor systems. The results show that accurate representation of the sorption process can be obtained with either a dual-resistance diffusion model or an equilibrium/first-order sorption rate model. Changes in velocity of the fluid phase affect the magnitude of fitted model parameters, but changes in concentration have negligible influence on these parameters.

Key words—sorption/desorption, groundwater modeling, pollutant transport, partitioning, aquifer materials, soils

NOMENCLATURE

- b = Langmuir isotherm sorption-energy constant (L^3M^{-1})
 C = solution-phase solute concentration (ML^{-3})
 C_e = equilibrium solution-phase solute concentration (ML^{-3})
 C_0 = initial solution-phase solute concentration (ML^{-3})
 C_s = fluid-phase equilibrium-isotherm solute concentration corresponding to the solid-phase concentration at the particle boundary (ML^{-3})
 D_h = second-rank hydrodynamic-dispersion tensor (L^2T^{-1})
 D_h = longitudinal hydrodynamic-dispersion coefficient (L^2T^{-1})
 D_s = intraparticle surface-diffusion coefficient for dual-resistance model (L^2T^{-1})
 k_f = film mass-transfer coefficient for dual-resistance model (LT^{-1})
 k_s = second-order Langmuir model rate constant ($L^3M^{-1}T^{-1}$)
 K_F = Freundlich isotherm sorption-capacity constant [$(L^3M^{-1})^n$]
 $K_{F,r}$ = Freundlich isotherm sorption-capacity constant for the rapid-rate component of the equilibrium/first-order rate model [$(L^3M^{-1})^{n_r}$]
 $K_{F,s}$ = Freundlich isotherm sorption-capacity constant for the slow-rate component of the equilibrium/first-order rate model [$(L^3M^{-1})^{n_s}$]
 K_p = linear sorption isotherm model coefficient (L^3M^{-1})
 l = characteristic length (L)
 L = length of the column (L)
 n = Freundlich isotherm sorption-energy constant (dimensionless)
 n_r = Freundlich isotherm sorption-energy constant for the rapid-rate component of the equilibrium/first-order rate model (dimensionless)
 n_s = Freundlich isotherm sorption-energy constant for the slow-rate component of the equilibrium/first-order rate model (dimensionless)
 P_e = Peclet number—equation (3) (dimensionless)
 q = volume-averaged solid-phase solute mass normalized by the solid-phase mass (MM^{-1})
 q_e = equilibrium volume-averaged solid-phase solute mass normalized by the solid-phase mass (MM^{-1})
 q_r = volume-averaged solid-phase solute mass normalized by the solid-phase mass for the rapid sorption-rate component of the equilibrium/first-order model (MM^{-1})
 q_s = volume-averaged solid-phase solute mass normalized by the solid-phase mass for the slow sorption-rate component of the equilibrium/first-order model (MM^{-1})
 $q_{s,e}$ = equilibrium volume-averaged solid-phase solute mass normalized by the solid-phase mass for the slow sorption-rate component of the equilibrium/first-order model (MM^{-1})
 Q^0 = Langmuir isotherm sorption-capacity constant (MM^{-1})
 r = radial distance variable for dual-resistance model (L)
 R = solid-phase particle radius (L)
 R_r = retardation factor—defined by equation (5) (dimensionless)
 rxn = subscript denoting a general chemical or mass-transfer reaction (dimensionless)
 t = time (T)
 v = pore-velocity vector (LT^{-1})
 v_z = pore velocity in the longitudinal direction (LT^{-1})
 α = equilibrium/first-order model rate constant (T^{-1})
 $\Gamma(C)$ = fluid-phase solute source ($ML^{-3}T^{-1}$)
 θ = volume void fraction of the media (dimensionless)

ρ = density of the solid particle (ML^{-3})
 ρ_b = bulk density of the solid phase (ML^{-3})

INTRODUCTION

The transport and fate of hydrophobic organic contaminants in groundwater systems involve complex phenomena that are influenced by many processes. One important process is sorption/desorption (herein referred to simply as "sorption"). Accurate assessment of the effect of sorption requires definition not only of eventual interphase equilibrium conditions, but also of rates of approach to equilibrium. If progress is to be made in the prediction of hydrophobic contaminant fate and transport, more accurate methods for modeling the sorption process and for determining associated model parameters are required. This is the second of a two-part series presenting the results of laboratory studies and comparisons of several rate and equilibrium sorption models. The first part describes investigations of equilibrium and sorption rate models for completely mixed batch-reactor (CMBR) systems. This part presents laboratory column-reactor system (CRS) experimental results and extends the batch-reactor equilibrium and rate models to equivalent CRS advection-dispersion-reaction forms.

BACKGROUND

The movement of a solute in groundwater is generally described by the advection-dispersion-reaction (ADR) equation

$$\frac{\partial C}{\partial t} = \text{div}(\mathbf{D}_h \text{grad } C) - \mathbf{v} \cdot \text{grad } C + \left(\frac{\partial C}{\partial t} \right)_{rxn} + \Gamma(C) \quad (1)$$

where C is the solution-phase solute concentration, t is time, \mathbf{D}_h is a second-rank hydrodynamic dispersion tensor, \mathbf{v} a pore-velocity vector, $\Gamma(C)$ a fluid-phase solute source term, and the subscript rxn denotes reactions that affect the solute concentration. The reaction under consideration here is sorption—a heterogeneous-phase mass-transfer process. Simplification of the general ADR equation to one spatial dimension (z) for a single solute, subject only to sorption, yields

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \frac{\rho_b}{\theta} \frac{\partial q}{\partial t} \quad (2)$$

where D_h is the hydrodynamic dispersion coefficient, v_z the one-dimensional fluid-phase pore velocity in the z direction, ρ_b the bulk density of the soil, θ the volumetric fraction of the aqueous phase, and q the volume-averaged solid-phase solute mass normalized by the solid-phase mass.

Various methods can be used to characterize the sorption reaction given by the third term on the

right-hand side of equation (2). All methods consist of describing two general components: the aqueous-solid equilibrium phase distribution relationship, and the rate at which this equilibrium distribution is approached. The most simple sorption model assumes that the equilibrium distribution between the solid phase and the fluid phase is linear and that the equilibrium condition is approached rapidly. This model is termed the linear-local-equilibrium (LLE) model. The LLE sorption model is a common method for approximating solute retardation by sorption in groundwater systems (Metry, 1977; Faust and Mercer, 1980; McCarty *et al.*, 1981; Enfield *et al.*, 1982; Pinder, 1984; Dragun *et al.*, 1984). The popularity of the method is due, in part, to the simplicity of its solution, which differs simply by a constant from any solution to the conservative form of the advection-dispersion equation.

The first paper in this series (Weber and Miller, 1988) cites previous findings of nonlinear sorption equilibrium and describes nonlinear sorption isotherms for a matrix of six hydrophobic solute-solid systems—the greatest nonlinearity being observed for the most strongly sorbing systems. A nonlinear equilibrium isotherm generally precludes analytical solution of equation (2), thereby complicating model development and application. It is also reported in the first part of this series that the sorption reaction requires several days to approach equilibrium for the hydrophobic solute-solid combinations investigated (Weber and Miller, 1988). Rate dependency alone does not necessarily preclude analytical solutions to the ADR equation. This point is explored further in the CRS modeling section of this paper. The rate dependency can however significantly change the form of the solute concentration profile, and markedly affect the estimation of fate and transport in groundwater systems.

MATERIALS AND METHODS

Materials used for the experimental studies described in this paper included four combinations of three glacially deposited aquifer sands and two hydrophobic solutes, lindane, and nitrobenzene. The physical and chemical properties of these materials are characterized elsewhere (Miller and Weber, 1986).

Columns consisting of aquifer sands packed in glass tubes of 2.5-cm dia were used to investigate contaminant sorption characteristics in systems involving both advective and dispersive flow. Borosilicate glass was used for all columns, tubing, valves, and sampling vessels to minimize extraneous sorption. The aquifer material was packed between thin end layers of glass beads to prevent particle migration from the column. Effluent concentrations were monitored continuously using a time-or-volume regulated fraction collector to obtain samples. Discrete influent sampling was done by valve regulation. A peristaltic pump provided a constant flow to the columns; adjustments in flow rate were accomplished by varying the pump tube size and motor speed.

Chloride was used as a nonreactive tracer to determine the hydrodynamic characteristics of each CRS. This was accomplished by first equilibrating a column with a flow of

an organic-free feed solution (0.01 N calcium sulfate) and then introducing an organic contaminant solution that was also 0.01 N in calcium chloride. Chlorides were analyzed with an internally-referenced, specific-ion electrode (Orion®) and a digital pH meter. A second tracer front was measured after the sorption interval, by halting the input of the organic-contaminant, calcium-chloride solution and reinitiating the feed of organic-free, calcium-sulfate solution.

COLUMN REACTOR MODELING

The purpose of the investigation was to compare methods for quantifying the sorption of hydrophobic compounds on aquifer solids and to evaluate factors affecting model variables. Four sorption models were investigated: (1) a linear-local-equilibrium model, (2) a parallel equilibrium/first-order rate model, (3) a Langmuir-type second-order rate model, and (4) a dual-resistance diffusion model. The first of these models is the most frequently used, while the remainder are sorption models used in Part I (Weber and Miller, 1988).

Because it was intended to develop and evaluate a flexible modeling approach, numerical models were developed for each of the sorption rate cases. Typical problems in solving the advection-dispersion equation using standard Eulerian methods include solution oscillations, smearing of sharp fronts, and phase errors. A thorough review of such difficulties is beyond the scope of this paper, but related discussions are available (Pinder and Gray, 1977). These numerical problems are usually associated with advection-dominated flow and were overcome in this work through mesh refinement.

The standard measure of the relative ratio of the advection and dispersion components of transport is given by

$$P_e = \frac{v_z l}{D_h} \quad (3)$$

where P_e is the Peclet number and l is a characteristic length.

The spatially centered finite-difference method was used in this work to develop a general numerical solution to the ADR equation to facilitate investigation of cases that are not analytically solvable. The finite-difference method proved to be an accurate, efficient method. Numerical model solution accuracy was evaluated in each case by comparing the formulation of a given model with a known analytical solution. This procedure does not in itself validate the inherent conditions and assumptions of a particular model, but when coupled with routine mass-balance checks, it does provide a "reasonable" assurance of the integrity of the model algorithm structure.

The linear-local-equilibrium model

This model differs from the conservative advection-dispersion model by only a constant, so

the model can be used to simulate various degrees of sorption simply by adjusting the value of a "retardation factor". The form of the ADR equation resulting from assuming local equilibrium is

$$R_f \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} \quad (4)$$

$$R_f = 1 + \frac{\rho_b}{\theta} \frac{\partial q}{\partial C} \quad (5)$$

for the initial and boundary conditions described by

$$C(z \geq 0, t \leq 0) = 0 \quad (6)$$

$$C(z = 0, t > 0) = C_0 \quad (7)$$

$$\left. \frac{\partial C}{\partial z} \right|_{z=L, t>0} = 0 \quad (8)$$

where R_f is the retardation factor. Equations (6)–(8) are boundary and initial conditions for all models considered in this paper.

Solutions of equation (4) for a linear isotherm mimic solutions of the nonreactive form of the advection-dispersion equation, with the spatial solute profile delayed in time by the factor R_f . For sorption reactions involving nonlinear isotherms, the retardation factor is not constant, but local equilibrium modeling can still be applied.

Figure 1 shows a comparison of an analytical solution for a semi-infinite domain (Bear, 1979) and the finite-difference numerical solution for the LLE sorption case. This example is for a system Peclet number of 100 but a numerical discretization mesh Peclet number of 2. The agreement between the analytical and numerical solution confirms the adequacy of the finite-difference method for laboratory-scale simulations.

The equilibrium/first-order model

The equilibrium/first-order model was considered by extending the mass-transfer form of the model used in batch-reactor systems (Weber and Miller, 1988) to a column-reactor system. The governing ADR equation for an arbitrary equilibrium function is

$$\left(1 + \frac{\rho_b}{\theta} \frac{\partial q_f}{\partial C} \right) \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \frac{\rho_b}{\theta} \alpha (q_{s,e} - q_s) \quad (9)$$

where q_f is the solid-phase concentration associated with the "fast" or instantaneous sorption component, α is a mass-transfer coefficient, and q_s is the solid-phase concentration associated with the "slow" or rate-controlled reaction component.

The Freundlich isotherms for the fast and slow components are then

$$q_f = K_{F,f} C^{n_f} \quad (10)$$

$$q_s = K_{F,s} C^{n_s} \quad (11)$$

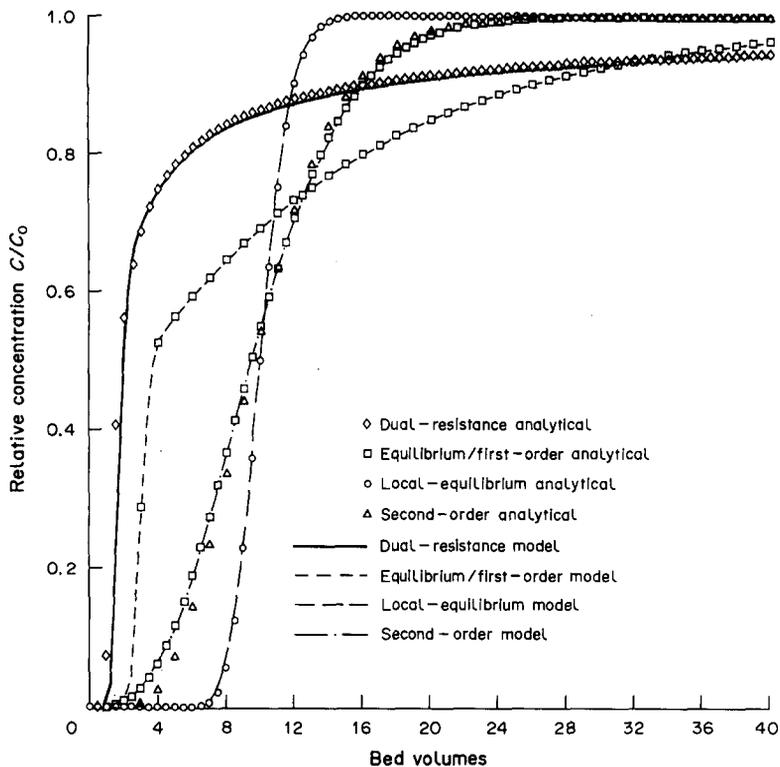


Fig. 1. Validation of numerical algorithms with analytical solution.

where $K_{F,f}$ is the Freundlich capacity constant for the fast sites, $K_{F,s}$ for the slow sites, n_f is the Freundlich energy constant for the fast sites, and n_s for the slow sites.

The general form of the equilibrium/first-order rate equation incorporating Freundlich equilibrium models for both the fast and slow components was solved using a spatially-centered finite-difference formulation. Figure 1 illustrates the agreement of the numerical model solution with an analytical solution (Cameron and Klute, 1977) for the case of linear equilibrium relationships. Sensitivity analyses in dimensionless form have been presented for the linear-isotherm case (Cameron and Klute, 1977) and both linear- and nonlinear-equilibrium versions of the mass-transfer form of the model (Miller, 1984).

The second-order model

The "second-order" model investigated here is a Langmuir-type rate model, which is actually second order with respect to sorption and first order with respect to desorption. The ADR equation incorporating a Langmuir second-order sorption-rate model has the form

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \frac{\rho_b}{\theta} k_s \left[C(Q^0 - q) - \frac{q}{b} \right] \quad (12)$$

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (13)$$

where k_s is the second-order sorption-rate coefficient, Q^0 the Langmuir isotherm capacity constant, and b the Langmuir isotherm energy constant (Weber and Miller, 1988).

Figure 1 presents a comparison of an analytical solution (Keinath and Weber, 1968) to the numerical solution for the second-order rate model with a Peclet number of 100. Because the analytical solution neglects dispersion, the agreement shown is considered reasonable; that is, the deviation observed is consistent with the expected effect of dispersion. As a second check of the validity of the model algorithm, the previously presented analytical solution for the equilibrium/first-order model was used to approximate the second-order solution. The two models are roughly equivalent when the instantaneous portion of the equilibrium/first-order model vanishes, and the equilibrium solid-phase concentration is much less than the Langmuir sorption-capacity constant. Results of this check, included in Fig. 1, provide a further validation of the numerical model accuracy.

The dual-resistance diffusion model

Different diffusion models have been applied to describe transport phenomena for a variety of boundary conditions and conceptual process variations in rock systems (Rasmuson, 1981; Rasmuson *et al.*, 1982) and in natural sorbent systems (Van Genuchten and Wierenga, 1976, 1977; Van Genuchten *et al.*,

1977; Valocchi, 1985; Crittenden *et al.*, 1986; Goltz and Roberts, 1986; Hutzler *et al.*, 1986). These diffusion-modeling approaches have generally relied on physical interpretations of the process involving the concept that one portion of the solid void-space fluid is "mobile", and another portion is "immobile". This approach, while able to describe the "tailing" frequently observed in a solute concentration breakthrough curve (BTC), still involves a local-equilibrium assumption. Sorption data collected from CMBR experiments have shown that this process can occur slowly, frequently extending over several days (Miller and Weber, 1986; Weber and Miller, 1988), or more (Karickhoff, 1980).

The dual-resistance diffusion model employed in this work incorporates mass transfer through a boundary film surrounding an individual solid particle coupled with diffusion within the particle. It is unlikely that the intraparticle diffusion process occurs uniformly within an entire solid particle. Instead, it probably occurs within agglomerations of organic material associated with the particle. The difference between the mechanistic concept and physical reality does not limit the practical application of the dual-resistance model because the volume average of the solid-phase concentration is the macroscopic property that effects the BTC.

Inclusion of the dual-resistance diffusion model with a Freundlich equilibrium isotherm model in the ADR equation gives

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \frac{3(1-\theta)k_d}{\theta R} (C - C_s) \quad (14)$$

$$\frac{\partial q_r}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_r}{\partial r} \right) \quad (15)$$

$$\frac{\partial q_r}{\partial r} \Big|_{r=R} = \frac{k_f}{D_s \rho} (C - C_s) \quad (16)$$

$$\frac{\partial q_r}{\partial r} \Big|_{r=0} = 0 \quad (17)$$

$$C_s = \left(\frac{q_r}{K_F} \right)^{1/n} \quad \text{for } r = R \quad (18)$$

where ρ is the solid-particle density, k_f the external-film mass-transfer coefficient, q_r the solid-phase concentration as a function of radial position, D_s the intraparticle surface-diffusion coefficient, C_s the solution-phase concentration corresponding to the solid-phase external-surface concentration at radius R , and K_F and n are characteristic Freundlich isotherm coefficients.

An analytical solution (Rasmuson and Neretnieks, 1980) of the dual-resistance diffusion model is compared in Fig. 1 to the general numerical solution for the special case of a linear isotherm. The general agreement between these solutions is good. It is interesting that the numerical solution requires less computational effort than the rather involved analytical solution, at least for the case where 50 points are used to define the BTC.

COLUMN REACTOR EXPERIMENTS

The column apparatus described in the experimental section was used to collect a series of conservative-tracer and organic-solute breakthrough curves. Table 1 summarizes CRS experimental conditions. The combinations investigated included: Ann Arbor aquifer material with nitrobenzene; and Ann Arbor, Michaywe, and Delta aquifer materials with lindane. The Peclet numbers tabulated in Table 2 were derived by fitting the numerical model to chloride tracer data. Figure 2 shows a typical example of a chloride BTC and the resultant model fit. The characteristic tailing of the BTC, which is well

Table 1. Experimental CRS conditions

Run	Aquifer material	Solute	Solute concentration ($\mu\text{g l}^{-1}$)	Column length (cm)	Pore velocity (cm h^{-1})	Column porosity
6-3	Ann Arbor	Lindane	576	3.70	3.25	0.400
9-4	Ann Arbor	Lindane	250	2.25	2.65	0.409
11-1	Ann Arbor	Lindane	594	3.00	2.21	0.384
11-2	Michaywe	Lindane	540	4.65	2.64	0.404
11-4	Delta	Lindane	494	8.00	2.01	0.423
13-1	Ann Arbor	Lindane	513	2.25	5.30	0.409
15-1	Ann Arbor	Nitrobenzene	1430	24.50	6.56	0.397

Table 2. CRS hydrodynamic dispersion fits

Run	Aquifer material	Solute	D_h ($\text{cm}^2 \text{h}^{-1}$)	P_e	Model variance
6-3	Ann Arbor	Lindane	1.6	7.4	9.9×10^{-4}
9-4	Ann Arbor	Lindane	0.53	11.0	3.0×10^{-4}
11-1	Ann Arbor	Lindane	0.17	38.0	2.8×10^{-3}
11-2	Michaywe	Lindane	0.40	30.0	1.7×10^{-4}
11-4	Delta	Lindane	0.23	70.0	8.8×10^{-4}
13-1	Ann Arbor	Lindane	1.3	9.4	4.8×10^{-3}
15-1	Ann Arbor	Nitrobenzene	3.0	54.0	2.4×10^{-4}

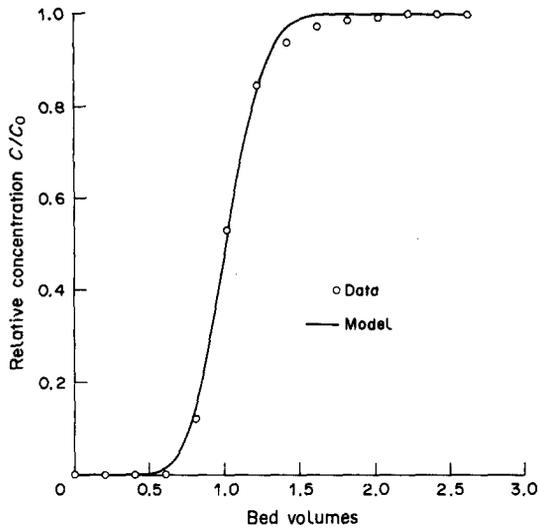


Fig. 2. Chloride tracer BTC (Run 15-1).

documented in the literature (Van Genuchten and Wierenga, 1976; Valocchi, 1985), was observed for all tracer experiments. Because the observed tailing was slight, and the rate of the sorption reaction was previously shown to be slow (Weber and Miller 1988), the mobile-immobile region approach was not used in this work.

The equilibrium parameters derived from independent CMBR experiments were employed in the various CRS models used for predicting and describing BTC behavior. These parameters were developed from the bottle-point tests discussed in Part I (Weber and Miller, 1988).

Local equilibrium modeling

To provide a basis for comparison with the rate models, data collected were analyzed for variance

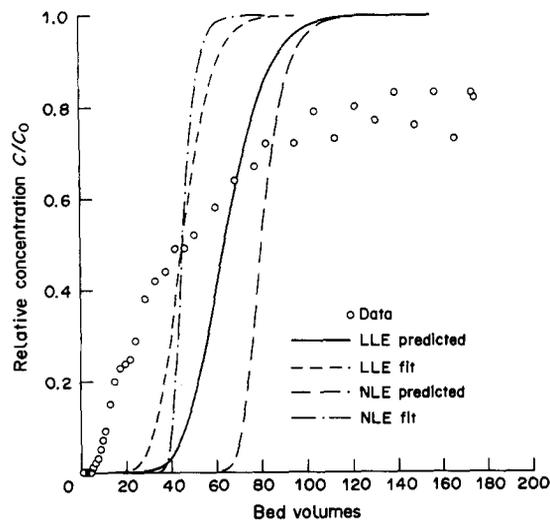


Fig. 3. CRS data and local equilibrium model projections for Ann Arbor aquifer material and lindane (Run 11-1).

using both linear-local-equilibrium (LLE) and nonlinear-local-equilibrium (NLE) models. For the NLE model the Freundlich isotherm was used to describe the sorption condition. This was done by substituting the derivative of the Freundlich isotherm model into equation (5) for $\partial q/\partial C$. All data sets were analyzed with respect to both prediction-based coefficients determined in CMBR experiments and best-fit coefficients from the CRS data by adjusting K_p or K_f to minimize variance. The results showed greater variance for all local-equilibrium simulations relative to the rate model simulations and higher variance for the equilibrium model predictions relative to the equilibrium model fits.

Figure 3 shows typical results for local-equilibrium modeling of the CRS data for uptake of lindane by Ann Arbor aquifer material. It is evident from Fig. 3 that the gradual nature of the Ann Arbor solid-lindane solute BTC reflects a much different response than can be predicted using equilibrium modeling approaches. A better fit could have been accomplished by adjusting the hydrodynamic dispersion coefficient, but that value was held constant at the level determined from tracer data fits.

Another point of interest relative to the application of local-equilibrium modeling is that the additional burden of solving the NLE model did not seem warranted. In every case investigated, the nonlinear local-equilibrium predictions and fits manifested greater variance than did their linear equilibrium counterparts. This was probably because the Freundlich isotherm was concave ($n < 1$) for all data sets studied, leading to a retardation factor that decreased as a function of increasing fluid-phase concentration. The results were sharper BTCs with less of a "tail" for Freundlich coefficients that were < 1 . The opposite result could be anticipated for solute-solid systems exhibiting Freundlich experimental coefficients greater than unity.

Single parameter fits

In addition to the equilibrium parameters, every model with the exception of local-equilibrium-based models requires definition of rate parameter values. Differences in hydrodynamic conditions between vigorously-stirred CMBRs and relatively low-velocity column reactors were expected to effect somewhat different absolute rate coefficients.

Column BTCs were fit for one parameter for each of the nonequilibrium models, with all other model parameters either measured or taken from independent tests. The parameters fit were: $K_{F,f}$, the equilibrium partition coefficient for the fast (instantaneous) sorption component of the equilibrium/first order model; k_s , the rate parameter for the second-order model and k_f , the film mass-transfer parameter for the dual-resistance model.

The models were fit to the data using a Golden-section direct-search algorithm (Himmelblau, 1972).

Table 3. CRS model single-parameter fits

Run	Equilibrium/first-order			Second-order		Dual-resistance		
	$K_{F,f}$ ($\text{cm}^3 \text{g}^{-1}$) ⁿ	α (h^{-1})	Variance	k_s ($\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$)	Variance	k_f (cm h^{-1})	D_s ($\text{cm}^2 \text{h}^{-1}$)	Variance
6-3	5.8×10^{-2}	1.8×10^{-2}	5.2×10^{-3}	9.4×10^3	7.6×10^{-3}	1.1×10^2	8.2×10^{-8}	5.6×10^{-3}
9-4	3.6×10^{-2}	1.8×10^{-2}	8.8×10^{-3}	8.2×10^3	1.1×10^{-2}	2.7×10^{-2}	8.2×10^{-8}	2.9×10^{-3}
11-1	3.6×10^{-2}	1.8×10^{-2}	4.8×10^{-3}	7.9×10^3	8.0×10^{-3}	6.6×10^{-2}	8.2×10^{-8}	1.7×10^{-3}
11-2	1.5×10^{-1}	1.9×10^{-2}	1.4×10^{-3}	6.0×10^3	2.8×10^{-2}	4.0×10^0	3.2×10^{-7}	3.1×10^{-2}
11-4	3.2×10^{-1}	4.4×10^{-2}	5.1×10^{-3}	1.4×10^4	2.5×10^{-2}	2.5×10^{-3}	1.9×10^{-6}	1.7×10^{-2}
13-1	2.5×10^{-2}	1.8×10^{-2}	7.0×10^{-3}	9.3×10^3	3.8×10^{-2}	1.9×10^{-2}	8.2×10^{-8}	6.3×10^{-3}
15-1	0.0×10^0	3.3×10^{-2}	2.0×10^{-3}	6.0×10^3	3.5×10^{-3}	7.5×10^{-2}	3.4×10^{-7}	7.7×10^{-4}

The objective function was to minimize the variance between observed and predicted model concentrations. The Golden-section algorithm typically required about 30 model solutions for each sorption-rate model for three significant-figure accuracy of the estimated parameter. The computational effort required for the Golden section method was greater than the computational effort required for the Newton derivative method but the former proved more robust.

Sorption rate parameters and model variances are summarized in Table 3. Figure 4 shows a typical solute BTC for the Delta aquifer material and the lindane solute along with corresponding model predictions. Each simulation had the highest variance associated with the second-order model. These results agree with the findings of the CMBR studies (Weber and Miller, 1988).

The dual-resistance model fits yielded the lowest variance for the Ann Arbor aquifer material, for both lindane and nitrobenzene solutes. The equilibrium/first-order model fits had uniformly less variance for the two data sets on soils with low organic carbon, the Delta and Michaywe solids.

For the Ann Arbor material, the dual-resistance model qualitatively provides the most satisfying

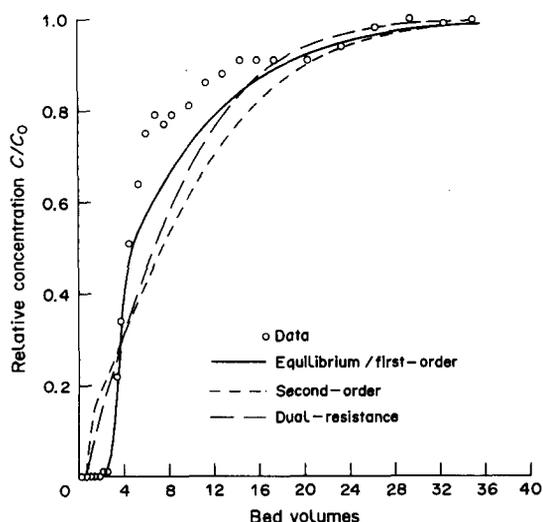


Fig. 4. BTC data and model projections for Delta aquifer material and lindane (Run 11-4).

representation of the observed BTCs. The equilibrium/first-order and second-order model fits are less satisfactory, largely because of the bifurcated BTCs resulting from minimization of variance with these models. The bifurcation is inherent to the structure of the equilibrium/first-order model because of the assumed fast and slow components. The second-order model bifurcation is attributed to the relatively large value of the best-fit rate parameter, relative to the mean column-retention time. The BTCs for the Delta and Michaywe aquifer materials were more accurately simulated by the equilibrium/first-order CTS model.

Factors affecting model fits

The four Ann Arbor solids-lindane experiments provide a basis for comparing the affects of variations in initial solute concentration and system hydrodynamic conditions on values of the fitted rate parameters. It would be expected that solute concentration changes do not influence sorption rate parameters, but changes in pore velocity may because of the potential velocity dependence of the fluid-film thickness surrounding solid particles in a CRS.

Comparison of Runs 9-4 and 11-1 shows that only a small change in fitted parameters resulted from a change in initial concentration alone. However, significant changes in velocity alone (Run 6-3) and velocity and concentration (Run 13-1) were observed to markedly affect fitted values for the model parameters $K_{F,f}$, k_s , and k_f relative to Run 11-1.

The best-fit value of k_f varied between Run 9-4 and Run 11-1 (by a factor of 2.4). The variance function was found to be insensitive to the film-transport coefficient in this range. To further investigate model sensitivity to k_f , an analysis was performed for each run by varying the film-transfer coefficient over four orders of magnitude, from 0.001 to 10 cm h^{-1} , while leaving all other parameters constant. Results from these simulations show that the dual-resistance model was relatively insensitive to the parameter k_f for most of the data sets presented. A notable exception was Run 15-1, the nitrobenzene solute run.

The film-transfer resistance plays a minor role for the one-parameter fit approach to modeling lindane solute sorption on the three aquifer materials studied. The film-transfer resistance for nitrobenzene plays a much more significant role, however, and suggests

Table 4. CRS model dual-parameter fits

Run	Equilibrium/first-order			Dual-resistance		
	$K_{F,r}$ ($\text{cm}^3 \text{g}^{-1}$) ^a	α (l h^{-1})	Variance	k_r (cm h^{-1})	D_s ($\text{cm}^2 \text{h}^{-1}$)	Variance
6-3	6.3×10^{-2}	1.6×10^{-2}	5.0×10^{-3}	1.1×10^2	1.2×10^{-7}	4.7×10^{-3}
9-4	5.8×10^{-2}	1.1×10^{-2}	3.4×10^{-3}	3.8×10^{-2}	7.5×10^{-8}	2.8×10^{-3}
11-1	5.7×10^{-2}	1.3×10^{-2}	2.4×10^{-3}	2.0×10^{-2}	1.1×10^{-7}	1.0×10^{-3}
11-2	1.6×10^{-1}	1.8×10^{-2}	1.3×10^{-3}	4.0×10^0	1.1×10^{-6}	1.0×10^{-2}
11-4	3.6×10^{-1}	2.2×10^{-2}	1.5×10^{-3}	2.5×10^0	4.1×10^{-7}	7.8×10^{-3}
13-1	2.8×10^{-1}	1.3×10^{-2}	4.1×10^{-3}	3.4×10^{-2}	4.0×10^{-8}	5.9×10^{-4}
15-1	4.2×10^{-2}	2.3×10^{-2}	6.3×10^{-4}	1.4×10^{-2}	2.7×10^{-7}	6.0×10^{-4}

that there are cases in which a two-resistance approach has merit. The dual-resistance model fit for Run 16-1 yielded the lowest total variance of any model fit to any data set, and is in close agreement with the required variance modeling assumptions—the errors have a mean of zero, are normally distributed, are not autocorrelated, and are homoscedastic (Beck and Arnold, 1977). The better fit of the nitrobenzene data is judged in part to be a result of the somewhat greater stability of nitrobenzene relative to lindane; the latter tends to undergo a slow degradation by hydrolysis. The hydrolysis of lindane was assumed to be small and therefore ignored in all of the modeling approaches. Nitrobenzene is more volatile, but care was taken in the experimental procedures to minimize losses to the atmosphere.

Multiple parameter fits

The validity of the one-parameter-fit approach was challenged by subjecting the data sets to a search of two parameters for the equilibrium/first-order model and the dual-resistance model. The second-order model was not searched for multiple parameters because the model contains only one rate parameter and it was assumed that the CMBR experiments had produced representative equilibrium parameters. $K_{F,r}$ and α were fit for the equilibrium/first-order model. For the dual-resistance model, k_r and D_s were fit. The results of the two-parameter fits are given in Table 4.

A Marquardt method was used for parameter estimation. This method proved satisfactory for all but the dual-resistance fits for Runs 6-3, 11-2 and 11-4. For these runs difficulty was encountered in finding a single value of k_r that minimized the variance. For two of these cases (Runs 6-3 and 11-2), the single-parameter-search value for k_r was used. In the case of Run 11-4, k_r was arbitrarily fixed in the range insensitive to variance by selecting a value that was three orders of magnitude greater than the single-parameter estimate. The variance was minimized for all three cases by adjusting only D_s .

The results from the dual-parameter search were similar to those from the single-parameter search. The dual-resistance model provided the most accurate fits to the Ann Arbor solids data while the equilibrium/first-order model gave the most accurate representations for low organic-carbon Delta aquifer material.

Several methods can be applied to interpret these

data. One method is to note differences in the parameter originally assumed constant. The equilibrium/first-order model fits for the Ann Arbor solids/lindane system yielded a range of α from 1.09×10^{-2} to $1.57 \times 10^{-2} \text{ cm h}^{-1}$, with two values very close to the mean of $1.31 \times 10^{-2} \text{ cm h}^{-1}$. The dual-resistance model fits of the same data sets yielded values of D_s in the range of 4.01×10^{-8} – $10.5 \times 10^{-8} \text{ cm}^2 \text{ h}^{-1}$, with a mean of $8.19 \times 10^{-8} \text{ cm}^2 \text{ h}^{-1}$. While the relative size of the D_s range was larger than that for α , the mean value for D_s was within 4% of the independently measured mean. The mean value of α differed from the independently determined value by about 26%.

The results of the dual-parameter search for Run 15-1 are illustrated in Figs 5 and 6. Figure 5 compares the one- and two-parameter fits for the equilibrium/first-order model, and Fig. 6 shows a similar comparison for the dual-resistance model.

Figure 5 includes results obtained by assuming that the instantaneous component of the equilibrium/first-order model is linear for both single- and dual-parameter fits. The overall nonlinear equilibrium condition was preserved by assuming that the instantaneous equilibrium model was correct and then solving for the slow equilibrium Freundlich isotherm coefficient $K_{F,s}$. Only a small difference was noted in

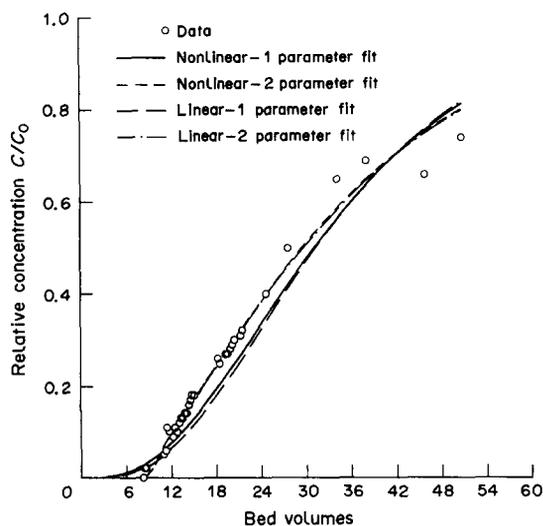


Fig. 5. CRS data and equilibrium/first-order model projections for Ann Arbor aquifer material and nitrobenzene (Run 15-1).

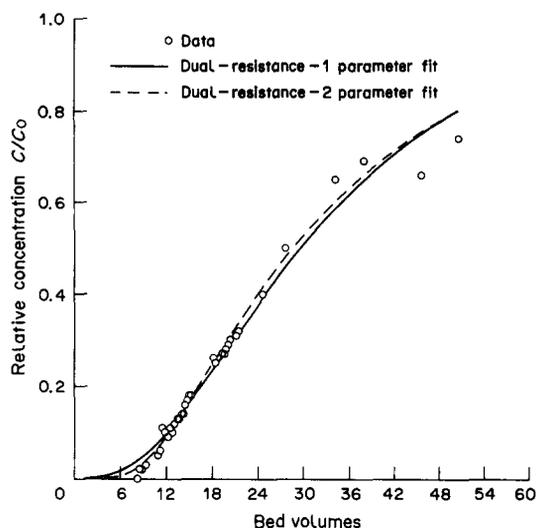


Fig. 6. CRS data and dual-resistance model projections for Ann Arbor aquifer material and nitrobenzene (Run 15-1).

the fits for the linear and nonlinear fast components. Description of the fast component of sorption as linear typically gave a slightly lower variance. This is consistent with the previous discussion concerning linear- and nonlinear-local-equilibrium modeling.

CONCLUSIONS

Seven sets of laboratory CRS breakthrough data were collected for sorption of lindane and nitrobenzene by three different aquifer sands. Several models were developed, validated, and used to predict and describe the experimental BTC data. Conclusions derived from these investigations are that:

(1) Local-equilibrium models were not effective for describing the observed tailing of the BTCs. Nonlinear-local-equilibrium model fits to the data exhibited higher variance than linear-local-equilibrium model fits for the solids tested, even though the solid-solute systems displayed nonlinear equilibrium isotherms.

(2) Of the three rate models tested, a dual-resistance diffusion model and an equilibrium/first-order model provided better fits of the observed data than did a second-order model.

(3) The dual-resistance model (coupled film and intraparticle diffusion) provided a better interpretation of CRS breakthrough behavior for more strongly sorbing systems, while the equilibrium/first-order model provided a better characterization of behavior for low organic-carbon solids that exhibited less sorption.

(4) The dual-resistance model fits for lindane were found to be relatively insensitive to the film-transfer coefficient, but sensitive for nitrobenzene for the data sets examined.

(5) Dual-parameter estimation methods support the notion that the mass-transfer coefficient in the

equilibrium/first-order model and the surface-diffusion coefficient in the dual-resistance model can be determined independently, that is, in separate CMBR experiments, and used in a "predictive" as well as a "fitting" modeling sense.

Acknowledgements—The authors thank Susan Chase, Pete Cooper, David Crompton and Joseph Pedit, graduate students in the Water Resources and Environmental Engineering Program at the University of Michigan when this work was conducted, for their contributions to the experimental analyses. The initial research described in this paper was supported partially by Grant 14-34-00001-2124 from the U.S. Department of the Interior through the Michigan State Institute of Water Research, and later stages partially by Grant ECE 8503903 from the U.S. National Science Foundation, Edward H. Bryan, program director.

REFERENCES

- Bear J. (1979) *Hydraulics of Groundwater*. McGraw-Hill, New York.
- Beck J. V. and Arnold K. J. (1977) *Parameter Estimation in Engineering and Science*. Wiley, New York.
- Cameron D. R. and Klute A. (1977) Convective-dispersive solute transport with a combined equilibrium and kinetic adsorption model. *Wat. Resour. Res.* **13**, 183-188.
- Crittenden J. C., Hutzler N. J., Geyer D. G., Oravitz J. L. and Friedman G. (1986) Transport of organic compounds with saturated groundwater flow: Model development and parameter sensitivity. *Wat. Resour. Res.* **22**, 271-284.
- Dragun J., Kuffner A. C. and Schneiter R. W. (1984) Transport and transformations of organic chemicals. *Chem. Engng* 26 November, 65-78.
- Enfield C. G., Carsel R. F., Cohen S. Z., Phan T. and Walters D. M. (1982) Approximating pollutant transport in ground water. *Ground Wat.* **20**, 711-722.
- Faust C. R. and Mercer J. W. (1980) Ground-water modeling: recent developments. *Ground Wat.* 569-577.
- Goltz M. N. and Roberts P. V. (1986) Three-dimensional solutions for solute transport in an infinite medium with mobile and immobile zones. *Wat. Resour. Res.* **22**, 1139-1148.
- Himmelblau D. M. (1972) *Applied Nonlinear Programming*. McGraw-Hill, New York.
- Hutzler N. J., Crittenden J. C., Gierke J. S. and Johnson A. S. (1986) Transport of organic compounds with saturated groundwater flow: experimental results. *Wat. Resour. Res.* **22**, 285-295.
- Karickhoff S. W. (1980) Sorption kinetics of hydrophobic pollutants in natural sediments. In *Contaminants and Sediments* (Edited by Baker R. A.), Vol. 2, pp. 193-205. Ann Arbor Science, Ann Arbor, Mich.
- Keinath T. M. and Weber W. J. Jr (1968) A predictive model for the design of fluid-bed adsorbers. *J. Wat. Pollut. Control Fed.* **40**, 741-765.
- McCarty P. L., Reinhard M. and Rittmann B. E. (1981) Trace organics in groundwater. *Envir. Sci. Technol.* **15**, 40-51.
- Metry A. A. (1977) The fate of pollutants in subsurface environments. *J. envir. Sci.* March/April, 27-31.
- Miller C. T. (1984) Modeling of sorption and desorption phenomena for hydrophobic organic contaminants in saturated soil environments. Ph.D. dissertation, University of Michigan, Ann Arbor, Mich., U.S.A.
- Miller, C. T. and Weber W. J. Jr (1986) Sorption of hydrophobic organic pollutants in saturated soil systems. *J. Contaminant Hydrol.* **1**, 243-261.

- Pinder G. F. (1984) Groundwater contaminant transport modeling. *Envir. Sci. Technol.* **18**, 108A–114A.
- Pinder G. F. and Gray W. G. (1977) *Finite Element Simulation in Surface and Subsurface Hydrology*. Academic Press, New York.
- Rasmuson A. (1981) Exact solution of a model for diffusion and transient adsorption in particles and longitudinal dispersion in packed beds. *A. I. Ch. E. JI* **27**, 1032–1035.
- Rasmuson A., and Neretnieks I. (1980) Exact solution of a model for diffusion in particles and longitudinal dispersion in packed beds. *A. I. Ch. E. JI* **26**, 686–689.
- Rasmuson A., Narasimhan T. N. and Neretnieks I. (1982) Chemical transport in fissured rock: verification of a numerical model. *Wat. Resour. Res.* **18**, 1479–1492.
- Valocchi A. J. (1985) Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Wat. Resour. Res.* **21**, 808–820.
- Van Genuchten M. T. and Wierenga P. J. (1976) Mass transfer studies in sorbing porous media I. Analytical solutions. *Soil Sci. Soc. Am. J.* **40**, 473–480.
- Van Genuchten, M. T. and Wierenga P. J. (1977) Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Sci. Soc. Am. J.* **41**, 272–278.
- Van Genuchten M. T., Wierenga P. J. and O'Connor G. A. (1977) Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,3,5-T. *Soil Sci. Soc. Am. J.* **41**, 278–285.
- Weber W. J. Jr and Miller C. T. (1988) Modeling sorption of hydrophobic compounds by aquifer materials—I. Rates and equilibria. *Wat. Res.* **22**, 457–464.