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Distributed-Rate Model Configured in Series to Simulate Sorption of Organic Pollutants to Natural Soil

J. A. Smith,[1] J. J. Deitsch[2]

[1] Program of Interdisciplinary Research in Contaminant Hydrogeology, Department of Civil Engineering, Post Office Box 4004742, University of Virginia, Charlottesville, VA, 22904, USA
[2] Geosyntec Consultants, 1100 Lake Hearn Drive, Atlanta, GA, 30342, USA

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The rate of organic pollutant and pesticide mass transfer between natural soil and water is a rate-limited process (Ball and Roberts 1991a, b; Brusseau *et al.* 1991; Laha and Luthy 1991; Wu and Gschwend 1986). If sorption kinetics are not properly accounted for in solute transport simulations, the transport of the solute can be significantly under-predicted (for sorption) or over-predicted (for desorption). Indeed, many pump-and-treat ground-water remediation systems that were designed assuming instantaneous desorption under-predict plume remediation times, sometimes by tens of years. Several research groups have developed distributed rate models (DRMs) to simulate pollutant mass-transfer between soil and water (Connaughton *et al.* 1993; Culver *et al.* 1997; Cunningham *et al.* 1997; Haggerty and Gorelick 1995; Pedit and Miller 1994). Instead of using a single mass-transfer coefficient, DRMs conceptually use an infinite number of mass-transfer coefficients. By assuming these mass-transfer coefficients follow a statistical distribution, such as a lognormal or gamma (γ) distribution, only two parameters are required to uniquely specify the distribution. The use of a continuum of mass-transfer rate coefficients is consistent with the heterogeneous nature of most natural soil samples. Distributed rate models have been shown to better simulate kinetic sorption data than models that employ a single mass-transfer coefficient or a single coefficient in combination with a fraction of "instantaneous equilibrium sites" (e.g. the popular two-site kinetic sorption model) (Culver *et al.* 2000; Culver *et al.* 1997; Deitsch and Smith 1999). In practice, the continuous distribution of mass-transfer coefficients is approximated by a discrete distribution with a finite number of mass-transfer coefficients, each associated with a specific sorption "site" or "compartment".

To date, DRMs have been configured in *parallel*. In other words, for each sorption site, the mass-transfer rate is assumed to be constant, each compartment is assumed to occupy an equal fraction of the soil, and each sorption site does not interact with adjacent compartments (i.e., no transfer of mass between adjacent compartments). Although parallel DRMs have been shown to simulate sorption data well, they are not mechanistically consistent with the most current view of organic pollutant sorption to natural soil and the structure of soil organic matter. Several researchers have hypothesized that the outer region of soil organic matter has an amorphous polymer-like structure (Carrol *et al.* 1994; Weber *et al.* 1992; Xing and Pignatello 1997). The inner regions are described as "condensed, glass-like humic polymer phases" (Carrol *et al.* 1994). A reasonable hypothesis is that there is a transition zone where the amorphous region condenses to become the more structured glass-like phase. For this model, we envision sorption to occur first by relatively rapid solute diffusion into the amorphous organic-matter polymer phase followed by slower diffusion into the deeper, condensed phases. In this regard, sorption proceeds by mass transfer through compartments that exist in series, rather than in parallel. In this paper, we present and test a new distributed-rate sorption model that is configured in series.

Correspondence to: J. A. Smith

MATERIALS AND METHODS

Previously published data for the time-varying sorption of 1,2-dichlorobenzene (DCB) to four natural soils in batch reactors was used to evaluate the performance of the series configuration of the DRM. Detailed descriptions of the experimental methods used to generate these data can be found in Deitsch (1998) and Deitsch et al. (2000). Briefly, the four natural soils (organic-carbon contents in parentheses) are: Picatinny Peat (14.6%), Picatinny Sand (0.53%), Woodburn Soil (1.23%), and the Army Corps of Engineers (ACE) Silty Clay (1.26%). Batch reactors (15-mL glass centrifuge tubes with Teflon-lined caps) containing soil and water with varying amounts of [^{14}C]-DCB (initially all in the aqueous phase) were gently mixed in the dark at 20 °C. Reactors were sacrificed over time and the aqueous-phase concentration of DCB was quantified by liquid scintillation counting. Sodium azide was added to each reactor to prevent aerobic biodegradation of DCB. The equilibrium condition was estimated from batch reactors with soil, water, and solute equilibrated for 7 d. Over the range of equilibrium aqueous concentrations studied (25 to 41,000 μg/L), sorption was approximately linear. Appropriate blank reactors (without sorbent) and background reactors (without solute) were included with each experiment for quality control. A total of 79 blank reactors incubated for times ranging from several hours to more than 100 d were used to define a first-order rate coefficient (equal to 6.2×10^{-4} d^{-1}) for DCB losses by processes other than sorption to soil (Deitsch and Smith 1999). Finally, for a subset of the batch reactors, sequential methanol extractions were performed to quantify the mass of DCB sorbed to the soil. This value was added to the mass of DCB in solution and compared to the mass of DCB added to the batch reactor. Average percent recoveries were 98% (Deitsch *et al.* 2000).

The two-site kinetic sorption model (Brusseau and Rao 1989; Parker and van Genuchten 1984; van Genuchten and Wagenet 1989) has been described previously. The two kinetic parameters for this model are f, the fraction of equilibrium sites, and α, the first-order mass-transfer coefficient (1/T). These two parameters are typically determined by fitting the model solution to experimental data (Culver *et al.* 1997; Parker and van Genuchten 1984).

The parallel configuration of the distributed rate model (DRM-PC) has also been described previously (Culver *et al.* 1997; Deitsch 1998; Deitsch and Smith 1999; Deitsch *et al.* 2000). For the DRM-PC, the continuous distribution of mass-transfer rates is approximated by a discrete distribution with a finite number of compartments, NK. The governing equations for the DRM-PC applied to a completely mixed batch reactor are as follows:

$$\frac{dS_T}{dt} = \sum_{i=1}^{NK} \alpha_i (fK_D C - S_i) \tag{1}$$

$$\frac{dC}{dt} = -\frac{M_s}{V}\left[\sum_{i=1}^{NK} \alpha_i (fK_D C - S)_i\right] - \frac{k}{V}C \tag{2}$$

where S_T is the total sorbed concentration (M/M), α_i is the first-order mass-transfer coefficient for compartment i (1/T), f is the fraction of sites in each compartment (equal to $1/NK$), S_i is the mass sorbed in compartment i with respect to the total mass of the soil (M/M), M_s is the mass of soil in the reactor (M), V is the volume of water in the reactor (L^3), K_D is the equilibrium sorption distribution coefficient (equal to S/C for linear sorption, as is assumed here), and k is a rate constant (L^3/T) that accounts for solute losses from sorption to glass/Teflon, volatilization, etc. Assuming that M_s, V, K_D, and k can be determined independently, equation (2) has NK adjustable parameters (the NK values for α_i).

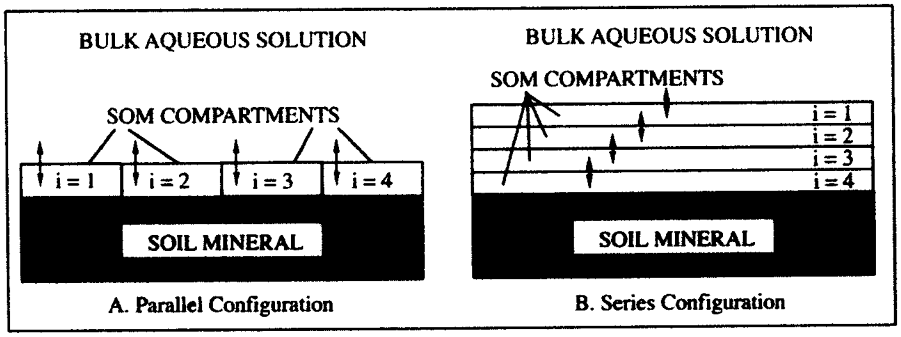

Figure 1. Conceptual diagrams of the distributed rate model configured in parallel (A) and series (B). SOM is soil organic matter.

By assuming that the α_i values follow a lognormal or γ distribution, the number of adjustable parameters is reduced to two. The lognormal probability distribution function (PDF) is uniquely defined by the mean, μ, and the standard deviation, s. The γ PDF is uniquely defined by the shape parameter, η, and the scale parameter, β. The mathematical form of the lognormal and gamma PDFs are presented in many probability texts (e.g. (Taylor and Karlin 1994).

The series configuration of the DRM (DRM-SC) is fundamentally different from the DRM-PC. In the DRM-PC, the *NK* compartments can be visualized as *NK* independent sorption regions that do not interact with each other. Each compartment does not have to be a contiguous sorption region. A compartment may represent numerous sub-compartments having identical mass-transfer properties. The only constraint is that the sum of the mass of the sub-compartments must equal the mass assigned to the idealized contiguous compartment. As a result, the individual contributions of the *NK* compartments to the sorption or desorption of a solute can be summed to give the total change in sorbed concentration. This is the summation that occurs in equation (2). A diagram of the parallel configuration with four SOM compartments is shown in Figure 1a.

Unlike the parallel configuration, where no assumption about the physical location of each site is necessary, the series configuration prescribes the arrangement of the sorption compartments. The development of the DRM-SC is based upon the assumption that the magnitude of the mass-transfer rate coefficient decreases in each subsequent compartment. As a result, the fastest rates of mass transfer will occur in the outer compartments of the sorbent and the slowest rates of mass transfer will occur in the interior compartments. The prescription of the lowest mass-transfer rates to the interior of the sorbent is consistent with recent research showing that soil organic matter transitions from an amorphous polymeric-like phase at the soil-water interface to a more condensed, crystalline phase near mineral/organic-matter interface (Carrol *et al.* 1994; Weber *et al.* 1992; Xing and Pignatello 1997). A distribution of mass-transfer coefficients configured in series is a reasonable approximation to the diffusive resistances encountered within the soil organic matter in this conceptualization.

The series configuration also differs from the parallel configuration in that the NK sorption compartments do not act independently. Figure 1b depicts the physical conceptualization of the DRM-SC for four compartments. Only compartment 1 can exchange solute mass with the aqueous phase. In addition, compartment 1 is capable of exchanging solute mass with compartment 2. Compartment two interacts with compartments 1 and 3. This sequence continues until compartment *NK* is reached. Compartment *NK* may only interact with compartment *NK*-1.

To derive the governing equations for the series configuration, we replace S_i with a new variable, S_i^*. In previous equations S_i has represented the sorbed solute mass in compartment *i* divided by the total mass of soil in the reactor. For the following derivation, S_i^* will be defined as the sorbed solute mass in compartment *i* divided by the mass of soil in compartment *i*. Given that the soil is divided into *NK* compartments, the governing equation for a batch reactor becomes

$$\frac{dC}{dt} = -\frac{1}{V}\left[\sum_{i=1}^{NK} M_{s,i}\frac{dS_i^*}{dt}\right] - \frac{k}{V}C \qquad (3)$$

where $M_{s,i}$ is the mass of soil in compartment *i* (equal to M_s/NK for our simulations). The *NK* equations for the *NK* dS_i^*/dt terms are given by following system of equations:

$$\begin{array}{lcr}
i=1: & \dfrac{dS_1^*}{dt} = -\alpha_1\left(S_1^* - K_D C\right) + \alpha_2\left(S_2^* - K_{1/2}S_1^*\right) & (4.1) \\
\downarrow & \downarrow & \downarrow \\
i=2: & \dfrac{dS_2^*}{dt} = -\alpha_2\left(S_2^* - K_{1/2}S_1^*\right) + \alpha_3\left(S_3^* - K_{2/3}S_2^*\right) & (4.2) \\
\downarrow & \downarrow & \downarrow \\
i=n: & \dfrac{dS_n^*}{dt} = -\alpha_n\left(S_n^* - K_{(n-1)/n}S_{n-1}^*\right) + \alpha_{n+1}\left(S_{n+1}^* - K_{n/(n+1)}S_n^*\right) & (4.n) \\
\downarrow & \downarrow & \downarrow \\
i=NK: & \dfrac{dS_{NK}^*}{dt} = -\alpha_{NK}\left(S_{NK}^* - K_{(NK-1)/NK}S_{NK-1}^*\right) & (4.NK)
\end{array}$$

where $K_{(n-1)/n}$ is defined as the sorption distribution coefficient between compartments *n*-1 and *n* (M/M). For this study, all the compartmental distribution coefficients were assigned a value of unity. Although experimental data and analyses suggest that the equilibrium distribution coefficients may increase as the SOM transitions from an amorphous to a condensed phase, there are no experimental methods available to accurately quantify this behavior at this time.

The system of equations given by (4) is substituted into equation (3) to give the governing equations for the DRM-SC assuming that each sorption compartment consists of an identical mass of soil. In order to numerically solve the governing equations for both the DRM-PC and DRM-SC, representative values for the mass-transfer rate coefficients were determined for the *NK* compartments from the chosen PDF. Following the example of Culver et al. (1997), the median value of the mass-transfer rate coefficient within each compartment was chosen as a representative value. The median mass-transfer rate coefficient for each compartment is determined from the cumulative probability distribution using a standard bisection search method.

Analytical solutions were developed for the two-site model and the DRM-SC. A standard fourth-order Runge-Kutta numerical integration technique was used to solve the system of ordinary differential equations arising from the DRM-PC. Deitsch (1998) provides additional details of the solution techniques and their verification.

RESULTS AND DISCUSSION

The DRM-SC was fit to the experimental data for DCB sorption to each of the four natural soils to minimize the percent error (as defined by Culver et al. 1997). These results were compared to previously published model fits for the two-site

Table 1. Optimal parameters fit to experimental sorption data for the series configuration of the distributed rate model. Parameters are for both lognormal and γ distributions of mass-transfer coefficients (units of d^{-1}).

	Lognormal model		γ model	
Soil Type	μ	σ	η	β
Picatinny Peat	8.72	5.32	0.202	3.94×10^5
Picatinny Sand	7.46	5.10	0.185	1.84×10^5
Woodburn Soil	4.50	5.28	0.127	0.55×10^5
ACE Silty Clay	8.99	4.35	0.242	2.69×10^5

Table 2. Minimum percent errors for the distributed-rate models for lognormal (LN) and γ distributions of the mass-transfer coefficients configured in parallel (PC) and in series (SC).

Soil Type	LN-PC	LN-SC	γ-PC	γ-SC	Two-Site
Picatinny Peat	2.52	2.88	2.66	2.66	7.19
Picatinny Sand	1.42	0.92	2.27	2.01	3.81
Woodburn Soil	2.81	2.20	3.95	3.67	4.26
ACE Silty Clay	1.64	0.84	1.56	1.08	1.36

model and the DRM-PC (Deitsch *et al.* 2000). The optimal parameters obtained from the sorption experiments for the lognormal DRM-SC (i.e., LN-DRM-SC) and the γ-DRM-SC are in Table 1. The percent errors for the LN-DRM-PC, the γ-DRM-PC, the LN-DRM-SC, the γ-DRM-SC, and the two-site model are in Table 2. For the lognormal distribution, the series configuration was able to simulate the experimental uptake data more effectively than the parallel configuration for three of the four data sets. For the γ-PDF, the series configuration simulated the experimental data more effectively than the parallel configuration for three of the four data sets. For the Picatinny Peat, the series and parallel models gave equal percent errors for the γ distribution. Comparing all models, the LN-DRM-SC had the lowest percent error for three of the four soils. With the possible exception of the ACE Silty Clay, the two-site model performed poorly compared to the DRM models.

Figure 2 shows sorption data for three of the soils and the associated optimal model simulations for the four DRMs. All four DRMs are able to simulate the transient sorption data well. There is little difference between the series and parallel configurations. The series model appeared to be better able to simulate the slow approach to equilibrium than the parallel model. The ability to simulate the later sorption data is more dependent on the probability distribution used to generate the mass-transfer coefficients than on the model configuration.

Figure 3 gives the optimal distributions of the mass-transfer coefficients for the Picatinny sand for the γ-DRM-PC and the γ-DRM-SC. The rate coefficients in the fast mass-transfer region for the series configuration were significantly higher than the corresponding rate coefficients for the parallel configuration, and this result is consistent with the distributions for the other soil samples. Based on these early analyses, it appears that the series model configuration simulates the experimental data as well or better than the parallel configuration. Unlike the parallel model, the series model can be solved with an analytical solution (Deitsch 1998) and is mechanistically more appropriate to current understanding of nonionic pollutant and pesticide sorption to natural soil. Although both the parallel and series configurations do a good job of fitting the sorption data, the mass-transfer coefficient distributions are distinctly different, reflecting the different mechanisms of mass transfer.

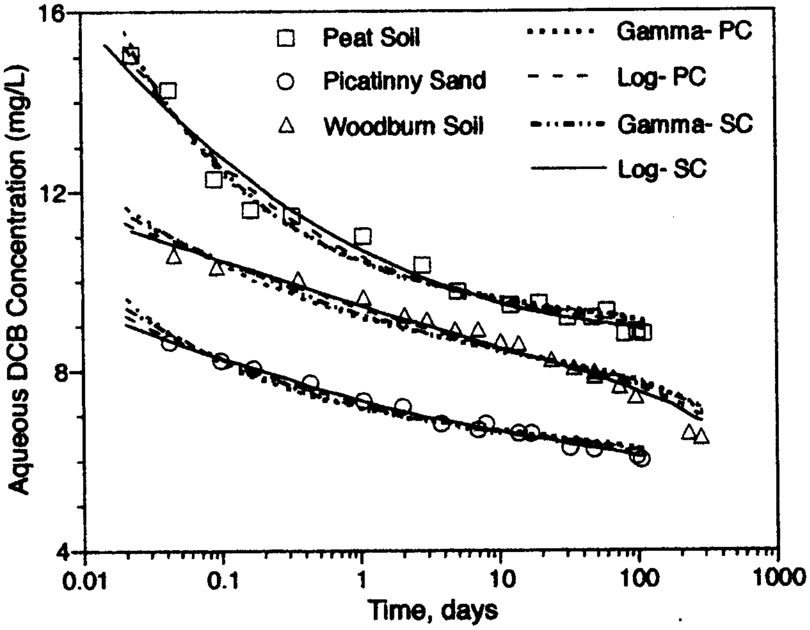

Figure 2. Aqueous concentrations and DRM simulations for 1,2-dichlorobenzene (DCB) sorption to peat, Picatinny sand, and Woodburn soil.

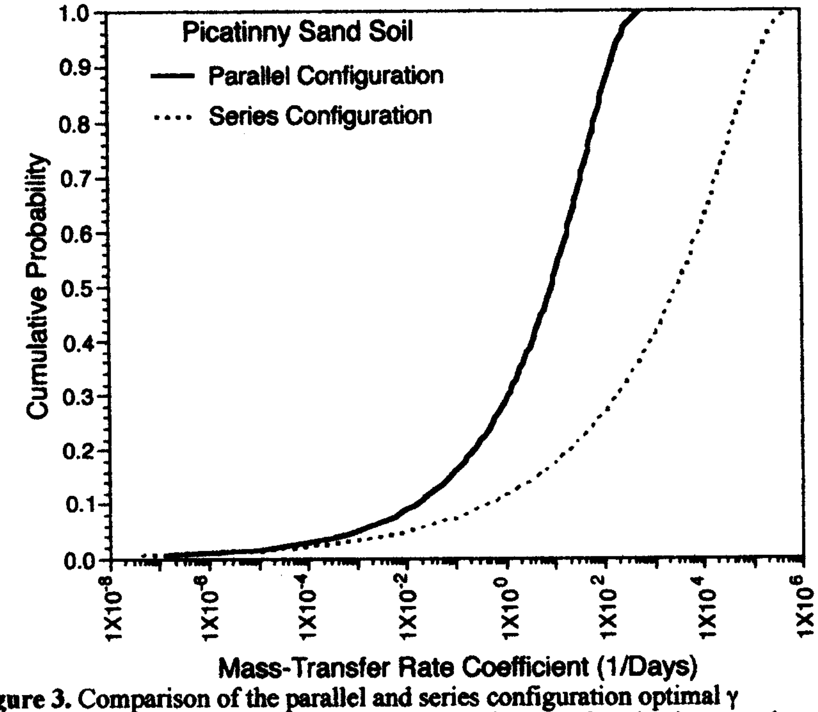

Figure 3. Comparison of the parallel and series configuration optimal γ distributions of mass-transfer rate coefficients for Picatinny sand.

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