

**Nonequilibrium Sorption of
Nonionic Organic Chemicals in Soils:
Experiments and Modeling**

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Vorwort

Da die folgenden Seiten eher nüchtern über das Resultat meiner wissenschaftlichen Arbeit berichten, nehme ich hier die Gelegenheit wahr, ein paar persönliche Eindrücke aus meinem vierjährigen Streben nach neuen Erkenntnissen zu berichten.

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Chapter 1

General Introduction

Introduction

During the last decades our knowledge on the processes governing the environmental fate of organic chemicals in soils and sediments has continuously increased. Research regarding the behavior of organic chemicals in soil was and still is driven by the quest to manage and prevent possible contamination of the environmental compartments (e. g. aquifers and surface waters) protected by this natural barrier. A key process for the fate of organic chemicals in soils is sorption. Sorption determines the chemical concentration in solution, which controls transport and degradation processes. Sorption is thus central to the environmental fate and must always be considered when the behavior of organic chemicals is investigated in soil.

The ideas on sorption behavior of nonionic organic chemicals have changed due to the development of more sophisticated measurement techniques as well as mathematical models. Especially mathematical models have proved to be a valuable tool in understanding sorption. Until the mid 1980s almost all research was based on the assumption that equilibrium between the solution and sorbent is reached within 24 to 48 h. Rate studies that showed complete solute uptake within the first 24 to 48 h appeared to confirm this. However, small concentration changes due to solute uptake over longer periods of time may have often remained unrecognized because experimental errors masked ongoing uptake. Beginning from the mid 1980s the research on slow sorption kinetics became more significant. Today it is widely accepted that sorption of nonionic organic chemicals proceeds slowly. As a consequence, it is now evident that it may take months or even years to establish true sorption equilibrium between solution and sorbent.

The believe in fast equilibration has however manifested the use of equilibrium isotherms to characterize the environmental behavior of organic chemicals until today. Linear as well as nonlinear isotherms determined after 24–48 h are still a popular choice for modeling purposes and play an important role in pesticide registration procedures. Any strategy based on this simplification limits however the reliance of predictions regarding fate and bioavailability of such chemicals. Considering the amount of scientific evidence regarding slow sorption of organic chemicals that has been gained in recent years, the common routine of assuming sorption equilibrium during solute transport may be called into question.

Mechanisms of sorption to soil organic matter

In soil, where it is relatively abundant the organic matter fraction is the main sorbent for nonionic organic chemicals. This is reflected in specific K_{oc} values which are used to approximate the extent to which a certain chemical is sorbed in soils with varying contents of organic carbon. Soil organic matter (SOM) consists of various bioresidues in different stages of microbial and chemical alteration. Classically it is divided into three fractions: insoluble humines, and soluble humic and fulvic acids. While humines have rarely been thoroughly investigated, the latter fractions have been subject to extensive research. In solution humic and fulvic acids form colloids which are likely to consist of molecules arranged in a coiled and/or aggregated structure. The true nature of these structures is controversial and they have been described as polymeric coils of macromolecules (Ghosh and Schnitzer, 1980; Stevenson, 1994)), self-associated aggregates of small heterogeneous molecules (Piccolo et al., 1996; Conte and Piccolo, 1999), or gel phases (Benedetti et al., 1996; Schaumann, 1998). Direct evidence for similar structures in the SOM parent material is scarce. However, Schaumann (1998) presents evidence that the chemical behavior of the whole SOM is similar to that of its subfractions. As for humic and fulvic acids, water uptake and release of SOM is hysteretic. When water-swollen, SOM contains three to five times its dry weight of water – humic and fulvic acids contain water at about a hundred times their dry weight when swollen. Compared to humic and fulvic acids it is likely that the hydrophobicity of SOM and the molecular weight of its segments is increased while the structure is more condensed. Throughout this thesis only the water-swollen stage of SOM will be dealt with as it is the environmentally relevant condition in relatively wet climates. However, effects of drying and rehydrating SOM especially for experimental purposes are discussed in chapter 2.

While the nature of water-swollen SOM is still subject to controversy, it is considered here to be a mesh of macromolecules with physicochemical properties similar to that of a polymer. Generally, sorption of organic chemicals by this mesh is driven by the hydrophobic effect resulting from a gain in free energy when diffusing from water into the sorbent. Diffusion within the SOM is believed to play an important role in slow sorption of organic chemicals.

This concept has been proposed by Brusseau et al. (1991a) and recently put forward by Pignatello (1998) and Weber and Huang (1996). The latter proposed two distinct domains within the SOM with different physicochemical properties. An outer domain which is flexible and “rubbery” and an inner domain that is condensed, rigid, and “glassy”. In the rubbery domain sorption is assumed to be linear, while in the glassy domain linear sorption is accompanied by a Langmuir type “hole-filling” sorption. This concept is however subject to controversy and other researchers request more direct evidence (Luthy et al., 1997). According to Pignatello (1998) the heterogeneity of SOM leads to two distinct sorption stages – a fast stage with an equilibration time of several hours and a slow stage lasting weeks, month, or even years. The occurrence of these stages has been validated by numerous experiments (Pignatello and Xing, 1996). Pignatello (1998) presents two possible mechanisms for slow kinetics such as a) slow diffusion within the “glassy” domain of SOM or b) an activated hole filling process in the same domain.

Process identification

When trying to identify microscopic processes by means of models we still have to rely on macroscopic evidence. There are currently no direct methods available which are suited to detect locations of organic chemicals within the SOM on the molecular level. An interpretation of macroscopic sorption data may be subject to erroneous model assumptions with regard to the underlying processes. There are some unsolved problems such as true or apparent S/D-hysteresis (or non-singularity)*, formation of bound residues and unexplained discrepancies in the results of different experimental techniques. Therefore, there is still a need to investigate sorption of organic chemicals and its kinetics at the laboratory scale. This is somewhat in contradiction to the fact that in recent years more and more

*Note that in chapter 2 the term hysteresis is used to refer to isotherm nonideality, as the investigation is limited to nonideality of sorption–desorption isotherms. In chapter 3 the term non-singularity is used to refer to isotherm nonideality as this phenomenon is studied in a more general manner. The investigation includes nonideality of isotherms which were measured by using successive sorption steps without inducing desorption – a phenomenon which is inconsistent with the meaning of hysteresis. However, considering that all nonideality phenomena discussed in this theses can be explained by sorption nonequilibrium, either term is misleading. Since both terms are well established in the literature their use is justified.

research effort has been focused on contaminant fate in field soils where soil heterogeneity and phenomena such as preferential flow have proved to be of great importance to contaminant transport. We need to fully understand sorption at the laboratory scale, first, to be able to interpret important aspects of sorption and transport behavior at the field or regional scale. In the field slow sorption may be the result of multiple processes. The separation of these processes is therefore of great importance to get reliable estimates for any model parameters. Laboratory techniques for the independent detection of slow sorption kinetics are available such as the commonly used batch or column techniques. As they more closely resemble field processes column techniques are often preferred to batch techniques especially as discrepancies between batch and column techniques have often been found.

The two distinct stages of solute uptake often observed when investigating kinetic sorption data (Pignatello, 1998) may be modeled by a two-stage approach, where the fast sorption stage is described by Freundlich equilibrium while the slow (diffusion) stage is approximated by a rate-limited mass transfer in a domain accessible from the fast domain. At equilibrium, the Freundlich isotherm describing sorption in the slow domain is the same as in the fast domain. This simple kinetic two-stage model with a total of four independent sorption parameters can be applied without knowledge on particle geometry and has been successful (most often in the linear form) in describing organic chemical behaviour in soil (Brusseau et al., 1991a; Streck et al., 1995). There are however limitations to this model which often cannot describe the uptake characteristic of a solute at very different time scales. This phenomenon probably arises because the mass transfer model is limited in its ability to describe the real diffusion process which takes place within the SOM. Approximating a spherical diffusion process over a broad range of time by means of a mass transfer model reveals that the rate parameter is time dependent (Gratewohl, 1998; Griffioen, 1998). This is usually ignored when applying the mass transfer model at different time scales.

To achieve a better agreement with measured data some authors extended the two-stage model to multiple sites of different accessibility (Boesten et al., 1989; Brusseau et al., 1989), or even to a continuous distribution of rate-limited sites (Chen and Wagenet, 1997; Culver et al., 1997). Another alternative is the direct use of diffusion models (Wu and Gschwend, 1986; Miller and Pedit, 1992). However, diffusion models are also subject to approximations as hypothetical as-

assumptions on the particle size distribution and geometry have to be made. None of the models is perfect and it is up to the researcher which model to use. All investigations in this thesis are limited to the two-stage model since all sorption phenomena described in the following chapters were readily described by this approach.

Scope and outline of this thesis

From the considerations given above the present situation concerning research on sorption of organic chemicals in soil is the following:

- Sorption of organic chemicals in soil is very slow. Equilibration takes weeks, months, or even years.
- Slow sorption in soil is most probably caused by diffusion into water-swollen SOM.
- Experimental methods, mainly batch and column techniques, used to investigate slow sorption show unexplained phenomena and have often found to yield ambiguous results.
- As true equilibrium is rarely reached, but often incorrectly assumed, some of these effects may be artifacts.
- The failure to reach equilibrium within reasonable time requires the rigorous examination of all experimental data by a kinetic model before one is able to discuss any unexplained effects.

Basically all chapters of this work are based on these ideas. In chapter 2 the principle relationship between sorption kinetics and sorption–desorption phenomena such as hysteresis is illustrated. The chapter further illustrates the consequences of air–drying which is often part of the soil pretreatment when batch experiments are carried out. In chapter 3 different batch techniques are used

to investigate sorption nonideality. It is tested if data obtained by use of the investigated techniques can be described with the same set of kinetic sorption parameters. Finally, three batch data sets from the literature that showed unexplained sorption phenomena are reinvestigated by means of a kinetic model. In chapter 4 a set of batch and column data published by Maraqa et al. (1998) is reinvestigated. Maraqa et al. (1998) found that the data sets disagree with regard to the sorption parameters estimated with each technique. In this chapter I try to reconcile this apparent disagreement by a rigorous investigation using the kinetic two-stage model. Chapter 5 synthesizes the previous chapters and gives an outlook on future experimental and modeling strategies to investigate sorption kinetics and irreversible sorption.

Chapter 2

Effect of Air–Drying on Sorption Kinetics of the Herbicide Chlortoluron in Soil

Abstract

Batch techniques were utilized to investigate sorption kinetics of chlortoluron in two field-moist soils, a silt loam and a loamy sand, containing 1.1 and 0.7 % organic C. To investigate effects of soil pretreatment, a part of both soil samples was initially air-dried. Initially sorption-desorption isotherms were measured using field-moist soils. Both isotherms exhibited pronounced hysteresis. The fit of a nonlinear kinetic two-stage sorption model to the data suggests that hysteresis was caused by nonattainment of equilibrium within the 24 h agitation periods. This hypothesis is supported by the fact that the estimated kinetic parameters were well suited to predict rate studies in both soils. The prediction of sorption-desorption isotherms measured using air-dried soils failed. Compared to the predicted data, sorption in air-dried soil was increased while desorption hysteresis was less pronounced. Further, experiments indicated that changes of soil organic matter (SOM) caused by air-drying were responsible for this effect. Measuring 24 h partitioning coefficients using the air-dried soils, rewetted to field-moisture for varying periods of time, revealed that in the course of 80 h (silt loam) and 500 h (loamy sand) after rewetting, the sorption properties of the air-dried soils were again equal to those of the respective field-moist soils.

Introduction

Sorption of nonionic organic chemicals in soil increases dramatically, when the water content drops below a critical value (Hance, 1977; Rutherford and Chiou, 1992). This sorption behavior is mainly caused by added sorption to mineral surfaces as a consequence of the decreasing competitive sorption of water (Rao et al., 1989; Pennell et al., 1992). A second but less important effect is the change in polarity of SOM caused by dehydration. At low water contents the polarity of SOM decreases, so that sorption of nonionic organic chemicals is enhanced (Rutherford and Chiou, 1992). Information on the reversibility of these changes upon rehydration is limited. Burchill et al. (1981) and Boesten (1986) indicated that rehydration of SOM is a slow process with equilibration times of days or even weeks. As a consequence, the use of air-dried instead of field-moist soil may affect sorption measurements when both equilibrium and nonequilibrium sorption are studied within periods of several days. At present, it is often assumed that results of batch slurries or column studies with nonionic organic chemicals are unaffected by the initial moisture status of the soil. Air-dried soil was used for sorption studies by Clay et al. (1988) and Poletika et al. (1995). Other authors propose that air-dried soil is equilibrated with CaCl_2 -solution for 12 to 24 h prior to sorption experiments (OECD (Organisation for Economic Cooperation and Development), 1997; Moreau and Mouvet, 1997). In some cases, field-moist soil was used (Boesten, 1986; Pignatello and Huang, 1991; Reddy et al., 1995). Except of Boesten (1986) who reported an increase in sorption of cyanazine (2-[4-chloro-6-(ethylamino)-*s*-triazine-2yl]amino-2-methylpropionitrile) when initially air-dried soil was used in a 24 h batch experiment, none of the cited studies investigated if the soil water content at the start of the experiment had an influence on sorption.

Nonequilibrium sorption is often studied in batch experiments by monitoring the decrease of solute concentration with time. However, sorption-desorption experiments can be used for the same purpose (Streck et al., 1995). Sorption-desorption isotherms of organic chemicals often exhibit hysteresis (van Genuchten et al., 1974; Clay et al., 1988). Several explanations have been proposed for this behavior, such as biodegradation (Koskinen et al., 1979) or sorption to dissolved or colloidal particles (Karickhoff and Brown, 1978; Gschwend and Wu, 1985). However, there is evidence that the observed hysteresis is caused by nonat-

tainment of sorption equilibrium within the time period of the experiment (Selim et al., 1976; Karickhoff and Morris, 1985; Brusseau and Rao, 1989a). Sorption of organic chemicals is partly a fast process within minutes or hours, and partly a slower process with a solute uptake over days or even months (Brusseau and Rao, 1989b; Weber and Huang, 1996). An extensive review on the possible mechanisms causing slow sorption of organic chemicals is given in Pignatello and Xing (1996).

The purpose of this paper is to investigate the relationship between nonequilibrium sorption and hysteresis quantitatively by applying the kinetic two-stage model of Streck et al. (1995). I will further examine changes in sorbent properties caused by drying initially moist soil and their effects on sorption-desorption isotherms and sorption kinetics. For this study a pre- and postemergence herbicide chlortoluron (3-(3-chlor-p-tolyl)-1,1-dimethylurea), and two soils, a silt loam and a loamy sand, were selected.

Materials and Methods

Materials

All experiments were carried out with analytical chlortoluron standards (purity 99% (HPLC)) by Riedel de Haen (Seelze, Germany). The water solubility of chlortoluron at 20 °C is 70 mg L⁻¹. Soil samples were taken from the plow layer (0–30 cm) of two fields near Braunschweig, Germany. The soils at the two sites are a silt loam (Typic Hapludalf) and a loamy sand (Aquic Haplumbrept). They will be denoted as Loess and Sand, respectively. The main soil properties are given in Table 2.1. The organic C content was determined by dry combustion at 1360 °C after treating both soils with HCL (10%) at 60 °C for 90 minutes to destroy carbonates. Evolving CO₂ was measured coulometrically (Coulomat 701, Strhleim, Dsseldorf Germany). To check for residual chlortoluron, methanol extractions were performed with both soils as described in Zander et al. (1999). Residual chlortoluron was not detected. Soil material was passed through a 2 mm sieve and homogenized. One half of each sample was directly frozen at -15 °C while the other half was air-dried and then frozen. Preliminary sorption studies with fresh and frozen field-moist soil did not indicate any change in sorption proper-

ties. For some experiments, rehydrated soil samples were prepared by adding distilled water to air-dried soil until field-moisture was achieved. The samples were stored at 20 °C for three weeks and finally frozen at -15 °C.

Batch experiments

To obtain final chlortoluron concentrations of 0.2, 0.4, 0.6, 1.1, and 2.0 mg L⁻¹, sorption solutions were prepared by adding appropriate amounts of a 100 mg L⁻¹ acetone stock solution to volumetric flasks. Acetone was allowed to evaporate at room temperature by a constant flow of air. The flasks were subsequently filled to volume with 0.01 M CaCl₂. To completely dissolve the herbicide the flasks were put on a reciprocating shaker for 24 h at 30 rotations per minute (rpm). All concentrations were checked by subjecting the sorption solutions to the same extraction and measurement procedures as the experimental samples. All experiments were prepared in 50 mL Teflon® centrifuge tubes (Nalgene, Rochester, N. Y.).

For the sorption-desorption experiments and rate studies a 20 mL aliquot of chlortoluron solution was added to 10 g of soil. While sorption-desorption exper-

Table 2.1: Some properties of the investigated soils

Soil	pH [†]	Organic C [‡] content	Particle-size distribution [§]			Dominant clay [¶] mineralogy	Water content
			Clay	Silt	Sand		
		% by mass	_____ % by mass _____				% by mass (dry base)
Sand	5.5	1.1	9	11.3	79.7	M(50), K(35)**	10.5
Loess	7.2	0.7	18.3	71.0	10.7	M(65), K(20)	23.5

[†] In 0.01 M CaCl₂

[‡] Determined by dry combustion; see Materials and Methods section

[§] Pipet method (Gee and Bauder, 1986)

[¶] based on relative X-ray diffraction peak intensities: M, mica (illite), K, kaolinite

^{||} Determined gravimetrically by drying at 105 °C for 24 h

** in % of clay fraction

iments were prepared with field-moist, rehydrated and air-dried soil, rate studies were limited to field-moist (Sand and Loess) and air-dried soil (only Sand). When field-moist or rehydrated soil was used, final solution to soil ratios were 2.315 mL g^{-1} for the Sand, and 2.704 mL g^{-1} for the Loess. With air-dried soil, the final corresponding ratios were 2.030 mL g^{-1} for the Sand, and 2.077 mL g^{-1} for the Loess. Sorption-desorption experiments at smaller solution to soil ratios were prepared by adding a 20 mL aliquot of chlortoluron sorption solution to 20 g of field-moist soil. In this case, final solution to soil ratios were 1.212 mL g^{-1} for the Sand, and 1.471 mL g^{-1} for the Loess. The water contents of all samples were measured gravimetrically (105°C).

For the sorption-desorption experiments the soil suspensions were put on a reciprocating shaker (30 rpm) for 24 h at 20°C . Subsequently, they were centrifuged for 20 min at 20°C with 4500 *g*. A 10 mL aliquot of the supernatant was removed and stored in a glass tube at 4°C for further measurement. To measure desorption of chlortoluron, 10 mL of a replacement solution, containing 0.01 M CaCl_2 , was added to each tube. The sample was then shaken for another 24 h. This procedure was repeated another four times to obtain a total of 5 desorption measurements. Rate studies were measured at three initial concentrations (0.2, 0.6, and 2.0 mg L^{-1}). Measurements were carried out as described above. Solute concentration was determined after time periods varying between 11 and 275 h. Sorbed concentrations were calculated from measured solution concentrations by difference, taking into account the loss of solute mass resulting from the removal of solution. Blanks without soil did not indicate sorption to the Teflon[®] tubes. To quantify variation caused by soil handling and solution replacement one sorption-desorption isotherm was measured in 5 replicates. The coefficient of variation for solute concentrations was less than 3%. Single measurements were therefore considered sufficient for all sorption-desorption isotherms. The time for complete rehydration of the soils was investigated by storing the air-dried soils at their respective field-moisture (see Table 2.1) for various periods of time. The rewetted soils were sampled after 0, 24, 48, 72, 170, 220, and 506 h. At each time 24 h-partitioning coefficients were measured at three concentrations (0.2, 0.6, and 2.0 mg L^{-1}). The measured partitioning coefficients were divided by the 24 h-partitioning coefficients found for the same concentration in the respective field-moist soils. This ratio was then averaged for the three concentrations and plotted as a function of rehydration time. The experimental solution to soil ratios

were 2.315 mL g^{-1} (Sand) and 2.704 mL g^{-1} (Loess) for the field-moist as well as for the rewetted soil samples.

Variation of pH was monitored in parallel experiments prepared as described above but without chlortoluron. The coefficient of variation determined for the different experimental setups was 1.4% for the Loess and 1.8% for the Sand. An effect of pH on experimental results can therefore be excluded. The experiments were further used to monitor dissolved organic carbon (DOC) in the solutions. Measurements were carried out with an organic carbon analyser (TOCOR 4, MAIHAK Ag, Hamburg, Germany).

Chemical analysis

Experimental solutions were extracted with 300 mg C_{18} solid phase extraction (SPE) cartridges (Mallinckrodt Baker, Phillipsburg, N. J.). The cartridges were preconditioned once with 3 mL of methanol and twice with 3 mL of distilled water. After application of the sample volume (10 mL), the cartridges were vacuum-dried for 60 min. Chlortoluron was eluted 3 times with 400 μL methanol into 2 mL flasks. The flasks were filled to volume with distilled water. The samples were then transferred to autosampler vials. To avoid systematic errors and to obtain the true standard deviation of the extraction procedure, calibration was carried out daily. After preparing the calibration solutions in the same way as the sorption solutions two standard curves, ranging from 0.1 mg L^{-1} to 1.1 mg L^{-1} and 1.0 mg L^{-1} to 6.0 mg L^{-1} , were prepared. The calibration solutions were subjected to the same extraction procedure as the samples and used for external calibration. Quantification limit for chlortoluron was 0.05 mg L^{-1} . Considering the fivefold increase in solute concentration caused by SPE the quantification limit in the samples was 0.01 mg L^{-1} . Measurements were carried out with high performance liquid chromatography (HPLC; System Gold, Beckmann, San Ramon, Ca.) consisting of a 126 solvent module, a 502 autosampler module with rheodyne 7010 injection valve (sample loop 100 μL) and a 166 UV/VIS-detector module. It was equipped with both pre- and main column (8 x 3 mm and 125 x 2 mm) containing Nucleosil 100 C_{18} -material (particle size 5 μm). All runs were done isocratically at 0.3 mL min^{-1}

with a mobile methanol/water phase ratio of 47/53. UV–detection wavelength was 248 nm.

Extraction efficiency with SPE was checked by dividing the slope of the calibration curve subjected to the complete extraction procedure by the slope of the calibration curve of chlortoluron in a 47/53 methanol/water–mixture. The mean extraction efficiency was 98%. To check if substances endogeneous to soil solution had any effect on the extraction efficiency of chlortoluron, 80 μL of a 50 mg L^{-1} internal diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) standard were added to the aliquots of the calibration solutions and to the samples before applying them to the cartridges. Diuron, a substituted urea, behaves similarly to chlortoluron during the extraction procedure. The quotient of the mean area of diuron found in the calibration solutions and the mean area of diuron found in the samples was always between 98 and 102%. Effects on extraction efficiency due to substances endogeneous to soil solution could therefore be excluded.

Model

Kinetic sorption parameters of the soils were estimated using the nonlinear two–stage one–rate model of Streck et al. (1995). The model is based on the assumption that slow sorption is caused by intraorganic matter diffusion. Lacking information on particle size and geometry of the sorbent, the mathematical description of the diffusion process is simplified by assuming that the sorbent can be subdivided into two sorbent regions. The sorbate concentrations in the two regions, S_1 and S_2 , are defined per sorbent mass in region 1 and 2, respectively (mg kg^{-1}). In region 1, sorption is fast compared to the duration of the experiment so that equilibrium can be assumed:

$$S_1 = kC^m \quad (2.1)$$

In contrast, sorption in region 2 is rate–limited:

$$(1 - f) \frac{\partial S_2}{\partial t} = \alpha(S_1 - S_2) \quad (2.2)$$

C is the concentration of dissolved chemical while k denotes the Freundlich coefficient ($\text{mg}^{1-m} \text{L}^m \text{kg}^{-1}$), m the Freundlich exponent, α the sorption rate coefficient (d^{-1}) and f the fraction of region 1 sites (kg kg^{-1}). Brusseau et al. (1991a) demon-

strated that equation 2.2 can be related to diffusion in polymers by expressing α in terms of polymer diffusivity of the sorbate. The total concentration of the sorbed solute (S) is given by

$$S = fS_1 + (1 - f)S_2 \quad (2.3)$$

while the total concentration of solute C_t in a given volume, here the batch container, is given by

$$C_t = \theta C + \rho S \quad (2.4)$$

where ρ and θ denote mass of soil and volume of water in the container, respectively. At equilibrium, the model predicts the same concentration in both fractions:

$$S_1 = S_2 = kC^m \quad (t \rightarrow \infty) \quad (2.5)$$

Assuming negligible decay, the mass balance in a batch system within one sorption or desorption step is

$$\frac{dC_t}{dt} = 0 \quad (2.6)$$

By combining equations (2.1)–(2.6), the two–stage one–rate model can be written as

$$(\rho f m k C^{m-1} + \theta) \frac{\partial C}{\partial t} = \frac{\alpha}{(1 - f)} [C_t - \theta C - \rho k C^m] \quad (2.7)$$

For each sorption or desorption step, the initial condition $C_0 = C(0)$ is derived by solving

$$C_t = \theta C_0 + \rho f k C_0^m + \rho(1 - f)S_{20} \quad (2.8)$$

where $S_{20} = S_2(0)$ (the concentration in region 2 at the beginning of each step) is zero for the sorption step while for every desorption step it is taken from the last step. Equation (2.8) was solved for C_0 using the Newton algorithm. Equation (2.7) was solved numerically by the Burlisch–Stoer method (Press et al., 1992) in all cases. Concentrations were logtransformed for all parameter estimations as a multiplicative error model was assumed (Streck et al., 1995). The model was fitted to measured data using the Levenberg–Marquardt algorithm (Press et al., 1992).

Sorbed phase concentrations are often defined per unit mass of the total sorbent, S_{m1} and S_{m2} (e. g. Brusseau and Rao, 1989b). They are related to the sorbed phase concentrations defined per sorbent mass within each region, S_1 and S_2 , by:

$$S_{m1} = fS_1 \quad S_{m2} = (1 - f)S_2 \quad (2.9)$$

Our model is equivalent to the two-site model of Brusseau et al. (1991a) if the Freundlich exponent, m , is equal to one, so that S is a linear function of C . Our rate coefficient α may be related to their rate coefficient k_2 by $\alpha = (1 - f)k_2$. Brusseau and Rao (1989b) were the first to interpret a two-site model in terms of intraorganic matter diffusion. Brusseau et al. (1991a) presented a quantitative treatment of this interpretation.

Results and Discussion

Hysteresis and Sorption Nonequilibrium

Figure 2.1 (upper panel) illustrates the sorption progress with time in a simulated sorption–desorption experiment, calculated by the two-stage, one-rate model. The solute concentration in the solution added to the soil was set to 1.0 mg L^{-1} .

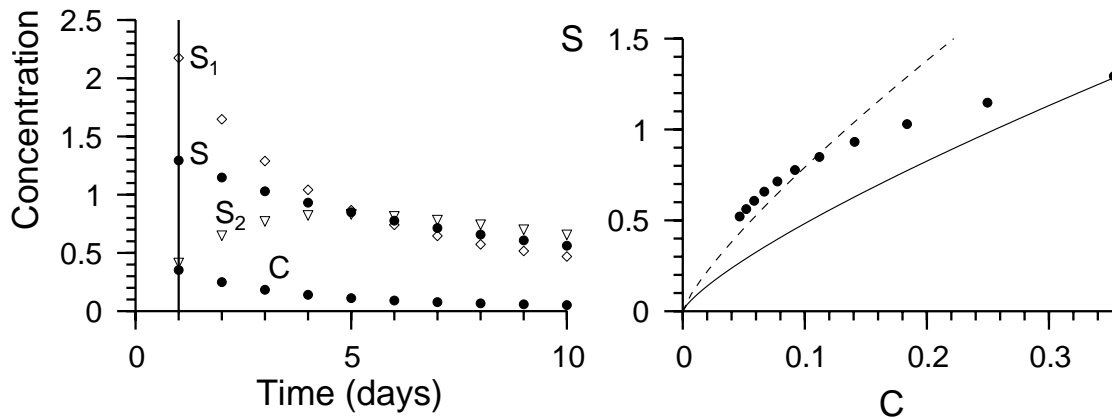


Figure 2.1: Dissolved (C in mg L^{-1}) and sorbed concentrations (S , S_1 , S_2 in mg kg^{-1}) as a function of time in a typical sorption–desorption experiment simulated with the nonlinear two-stage model (top). The vertical line in the top panel marks the end of the 24 h sorption step and the beginning of the first desorption step which is repeated every 24 h. The symbols mark the concentrations at the time of measurement at the end of each (de)sorption step (according to the experimental protocol). The bottom panel shows the corresponding sorption–desorption isotherm. The solid line in the bottom panel denotes the 24 h-sorption isotherm while the dashed line indicates true equilibrium, $S = kC^m$. Parameters used are $\alpha = 0.1 \text{ d}^{-1}$, $k = 5.0 \text{ mg}^{1-m} \text{ L}^m \text{ kg}^{-1}$, $f = 0.5$ and $m = 0.8$. Solution to soil ratio is 2 mL g^{-1} . In each desorption step half of the solution is replaced (modified after Streck et al. (1995)).

After one day sorption is interrupted and desorption induced by replacing half of the solution volume every 24 h. In the top panel the dissolved concentration C (mg L^{-1}), the total sorbed concentration S (mg kg^{-1}) and the domain concentrations S_1 and S_2 (mg kg^{-1}) for the sorption step as well as the desorption steps are plotted as a function of time. While C and S are directly measurable the domain concentrations S_1 and S_2 shown in the upper panel of Figure 2.1 cannot be individually measured. After the 24 h sorption period the dissolved concentration C has dropped to a value of about 0.35 mg L^{-1} due to sorption in the regions 1 and 2. The total sorbed concentration is about 1.3 mg kg^{-1} while the sorbed concentrations in the regions 1 and 2 are 2.2 mg kg^{-1} and 0.4 mg kg^{-1} , respectively. The higher sorbed phase concentration in region 1 as compared to region 2 indicates that the system has not yet reached equilibrium.

In the desorption part of the experiment C decreases as part of the solution is repeatedly replaced. With C , S_1 decreases as by equation (2.1) both concentrations are always in equilibrium. The sorbed concentration S_2 , however, still rises as the mass transfer from region 1 to region 2 continues ($S_2 < S_1$). After about five days the flux between region 1 and region 2 reverses ($S_2 > S_1$) and the sorbed phase concentrations in both regions decrease. When S and C are plotted as sorption–desorption isotherm the isotherm appears to be hysteretic as illustrated in the lower panel of Figure 2.1.

Conversely, hysteretic sorption–desorption isotherms may be used to estimate kinetic sorption parameters. Figure 2.2 demonstrates the good fit of the two–stage, one–rate model to measured chlortoluron sorption–desorption isotherms of both soils. In Table 2.2, the estimated sorption parameters together with the respective regression statistics are given. According to t ratios and correlation matrices, the fit is statistically sound. Table 2.2 shows that the Freundlich coefficient k is higher for the Sand than for the Loess. This is in agreement with the higher organic C content of the Sand. The fraction f of region 1 sites is about 0.4 for both soils. This is similar to values found by Brusseau et al. (1991) who evaluated sorption kinetics of diuron in a sandy soil. Interpreting the Freundlich coefficient as the partitioning coefficient at $C=1 \text{ mg L}^{-1}$ (Loess: 3.72 L kg^{-1} ; Sand: 5.48 L kg^{-1}) yields K_{OC} -values of 498 L kg^{-1} for the Sand and 531 L kg^{-1} for the Loess. These values are very similar indicating that SOM is the main sorbent

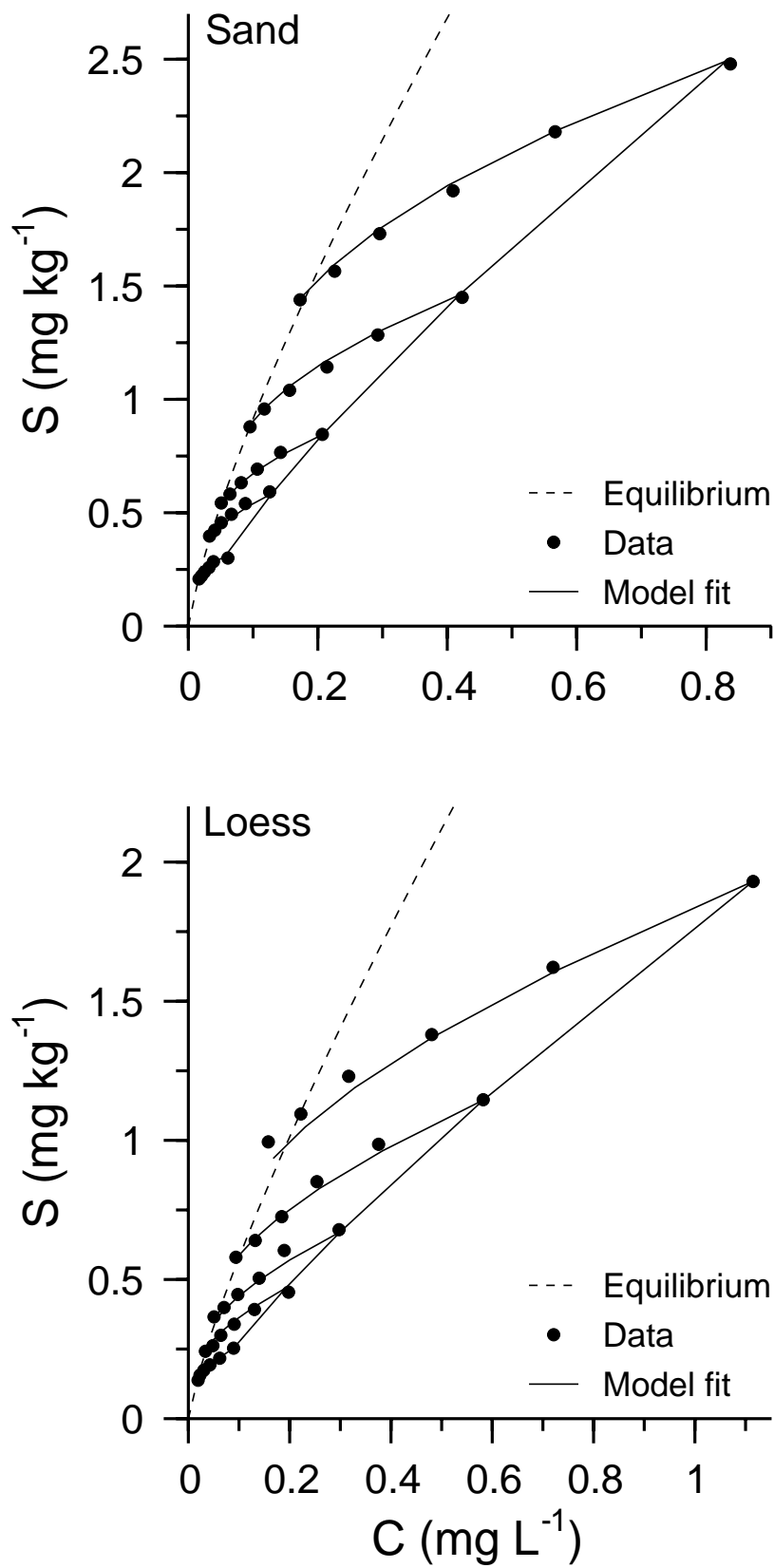


Figure 2.2: Model fit to measured chlortoluron sorption-desorption isotherms of field-moist soils. Equilibrium line is $S = kC^m$.

Table 2.2: Results of parameter estimation for the field–moist soils.

Soil	Sum of Squares	Parameter	Estimate	Approximate Standard Error	<i>t</i> Ratio	Correlation Matrix Entries			
						α^\dagger	f	k^\ddagger	m
Sand	3.95E-3	α	0.085	0.010	8.30	1.000			
		f	0.443	0.015	30.46	0.548	1.000		
		k	5.479	0.316	17.32	-0.724	-0.873	1.000	
		m	0.780	0.012	65.10	0.015	-0.599	0.639	1.000
Loess	5.03E-3	α	0.070	0.013	5.26	1.000			
		f	0.408	0.029	13.88	0.700	1.000		
		k	3.720	0.414	8.98	-0.731	-0.963	1.000	
		m	0.805	0.024	33.75	0.084	-0.555	0.575	1.000

 $^\dagger \text{d}^{-1}$ $^\ddagger \text{mg}^{1-m} \text{L}^m \text{kg}^{-1}$

in both soils. Sorption to clay seems to be negligible. The similar fraction of region 1 may be interpreted in terms of a similar size of the rate–limited sorption domain in the sorbent of both soils. The pairs of estimated parameters k and $\alpha/(1 - f)$ are close to the LFER (linear free energy relationship) line for type II chemicals established by Brusseau and Rao (1989a). However, Brusseau and Rao (1989a) assumed linear sorption while sorption of chlortoluron is nonlinear in this case.

The parameters estimated from the sorption–desorption experiments for field–moist soil were used to predict chlortoluron sorption behavior in rate studies. The results are shown in Figure 2.3. The excellent agreement with measured data further confirms the ability of the model to describe the sorption behavior of chlortoluron under different experimental conditions. Three conclusions may be drawn from this observation.

First, it is unlikely that hysteresis in Figure 2.2 is caused by different equilibration times at specific sorption sites in the ad– and desorption phase of the experiment rather than by intraorganic matter diffusion. Any difference in the ad–

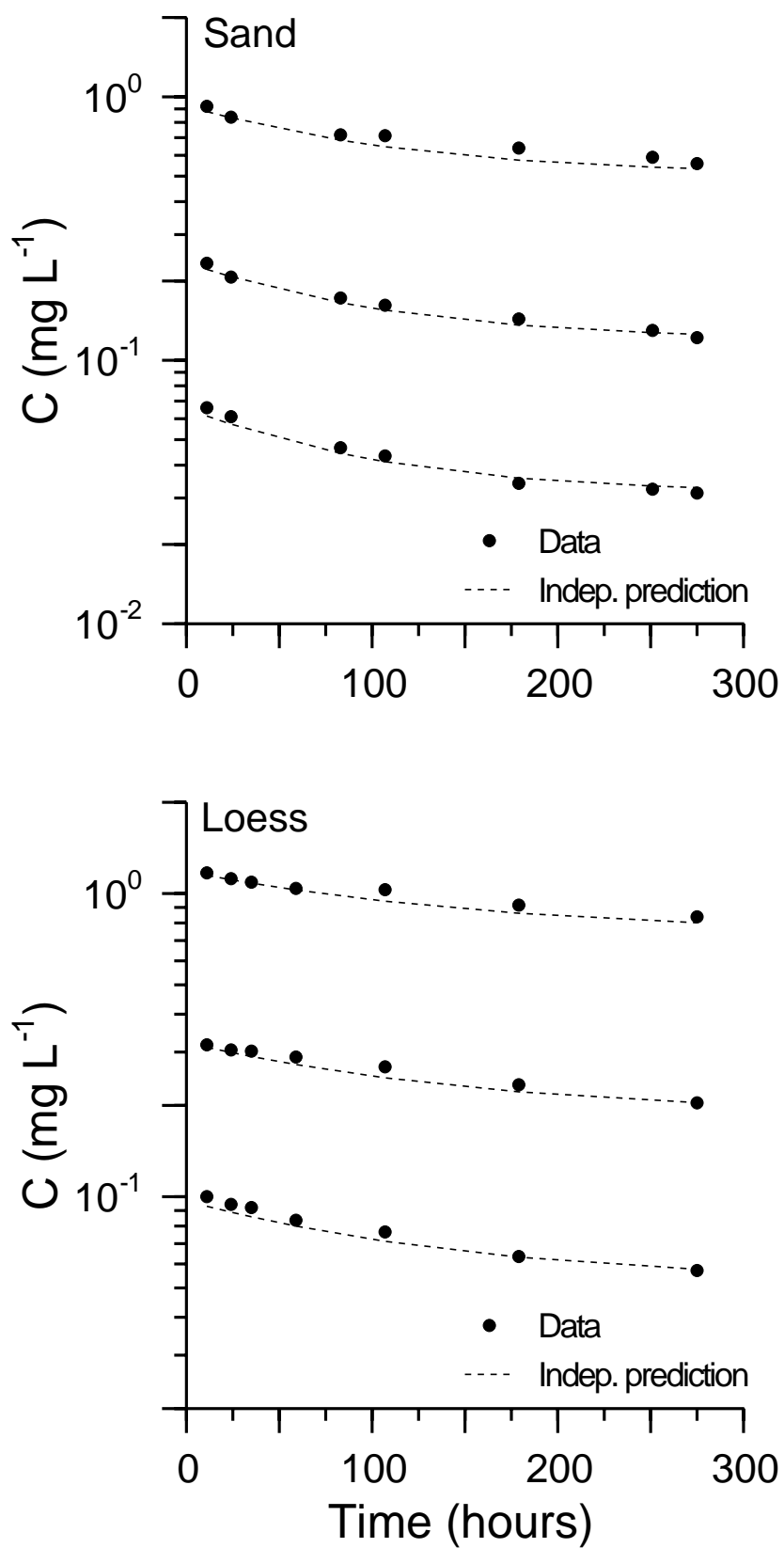


Figure 2.3: Measured and independently predicted chlortoluron rate studies for the field-moist soils. Initial chlortoluron concentrations were 0.2, 0.6 and 2.0 mg L^{-1} .

or desorption equilibration times would have affected the estimated sorption parameters of the mass transfer model making the successful prediction of the rate studies in Figure 2.3 very unlikely.

Second, the experimental results indicate that the amount of DOM (dissolved organic matter)–bound chlortoluron is negligible in our experiments. In a sorption–desorption experiment, DOM is repeatedly removed from the system while in a rate study it is not. If a significant fraction of chlortoluron were bound to DOM, both experimental systems could certainly not be described with the same model (which neglects DOM) using the same set of parameters. Further, it was shown by Chiou (1989) that the fraction of solute bound to DOM is negligible compared to the fraction in soil or the dissolved fraction for solutes with $\log K_{OM} < 3$ and a DOM concentration in solution that is less than 100 mg L^{-1} . Assuming an average carbon content of 58% for DOM in agricultural soils (Scheffer and Schachtschabel, 1992) the $\log K_{OM}$ of chlortoluron is about 2.9, while the DOM concentrations were on average 25 mg L^{-1} for all experimental solutions. So, both conditions were met.

Third, our results negate an effect of repeated centrifugation, caused by a partially irreversible compaction of the sorbent which may decrease the rate of desorption (Bowman and Sans, 1985b). While in a sorption–desorption experiment the sample is repeatedly centrifuged, in a rate study the sample is only centrifuged once. The independent prediction of the latter experiment should fail if an effect of repeated centrifugation were present.

Sorbent properties and soil moisture

To check if sorbent properties are affected by soil moisture, sorption–desorption experiments were performed with initially air-dried soil. Figure 2.4 compares the resulting isotherms with isotherms independently predicted by the two-stage one-rate model based on the estimated kinetic sorption parameters of Table 2.2. The agreement between measured and independently predicted data is poor. Solute uptake of the air-dried soils is higher than predicted by the model. The difference is smaller for Loess than for Sand. The desorption branches of measured and predicted isotherms appear to converge with each desorption step, indicating that hysteresis is less pronounced for the air-dried soils.

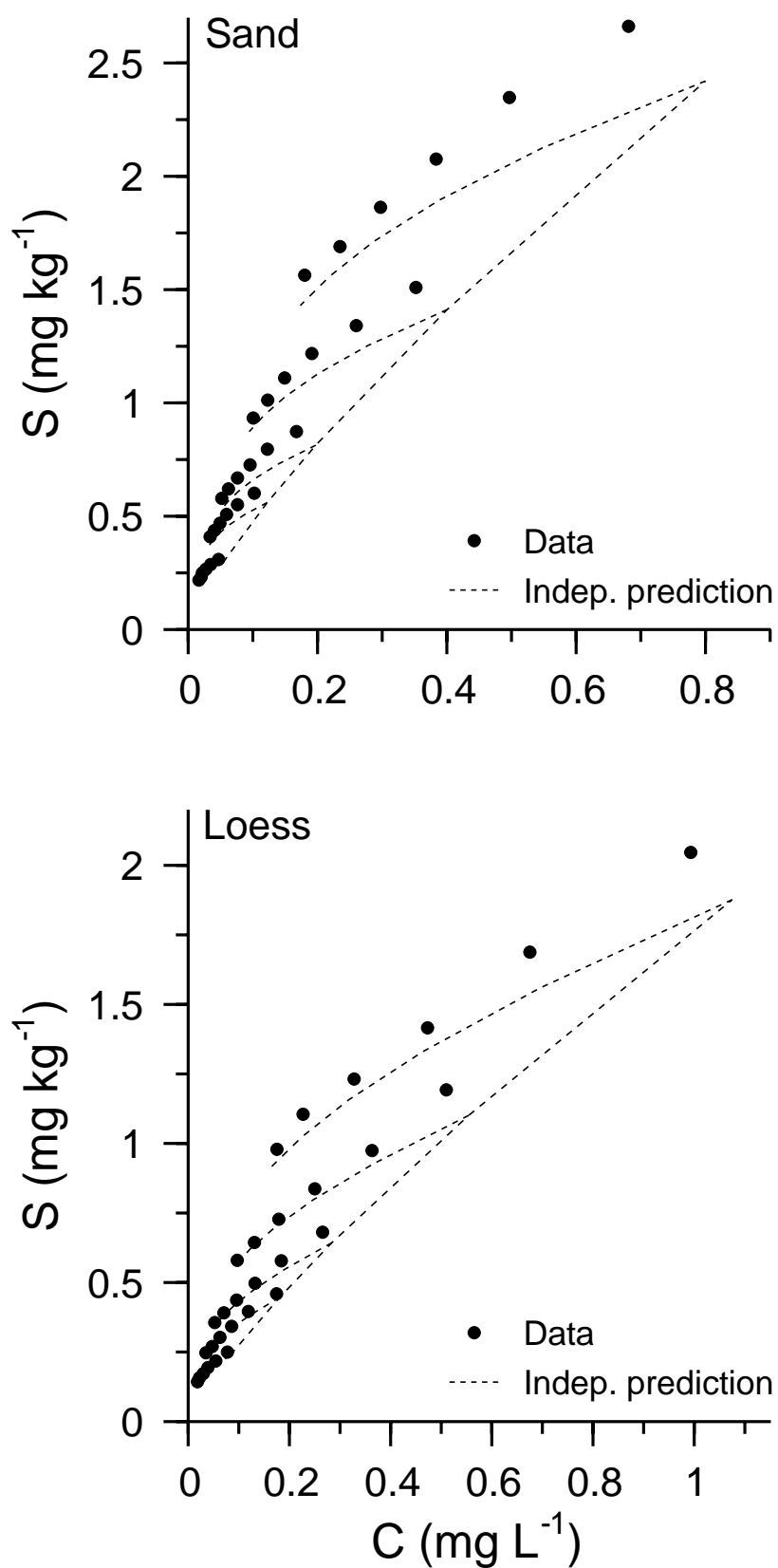


Figure 2.4: Measured chlortoluron sorption-desorption isotherms on air-dried soils. The independently predicted isotherms were calculated using the sorption parameters in Table 2.2.

Since there is a difference in the solution to soil ratio for the experiments with field-moist and air-dried soil (2.315 vs. 2.030 mL g⁻¹ for the Sand and 2.704 vs. 2.077 mL g⁻¹ for the Loess) I checked the impact of solution to soil ratio by measuring sorption-desorption isotherms of the field-moist soils at solution to soil ratios of 1.212 mL g⁻¹ (Sand) and 1.471 mL g⁻¹ (Loess). The measured and the independently predicted isotherms obtained by solving equation (2.7) using the sorption parameters estimated at higher solution to soil ratios (Table 2.2) show good agreement (Figure 2.5). Since the solution to soil ratios of the two experiments with field-moist soils enclose the solution to soil ratios of the sorption-desorption experiments with air-dried soils, I conclude that the observed difference between air-dried and field-moist soil demonstrated in Figure 2.4 is not due to differences in solution to soil ratios.

Since soil samples were taken from the plow layer, a large fraction of the soil had been subject to the natural cycles of drying and moistening. The observed change in sorption due to drying should therefore be reversible, presumed that the time to moisten the sample is sufficient. The comparison of the rate study using field-moist Sand already presented in the top panel of Figure 2.3 with a rate study using air-dried Sand supports this assumption. Figure 2.6 shows the partitioning coefficient k' ($k' = S/C$) as a function of time calculated for both experiments. While there is a large difference between field-moist and air-dried Sand after 11 h, the difference decreases until it almost vanishes after 275 h indicating that the observed changes are reversible.

When air-dried soil is to be used in sorption-desorption experiments, it is important to know which rehydration period has to be selected. Figure 2.7 presents the results of an experiment conducted to determine the rehydration time. The figure shows the ratio R of the partitioning coefficient (determined after 24 h) for (rewetted) air-dried and field-moist soil as a function of rehydration time. For air-dried (rehydration time equal to zero) Sand and Loess R is 1.32 and 1.14, respectively. Complete rehydration takes about 500 h for the Sand, but only about 80 h for the Loess.

Unfortunately, the necessary rehydration time is in the range of a typical sorption-desorption experiment. From this, it follows that two processes are effective in such an experiment when air-dried soil is used. The first process is kinetic sorption which leads to sorption-desorption hysteresis as demonstrated in Figure

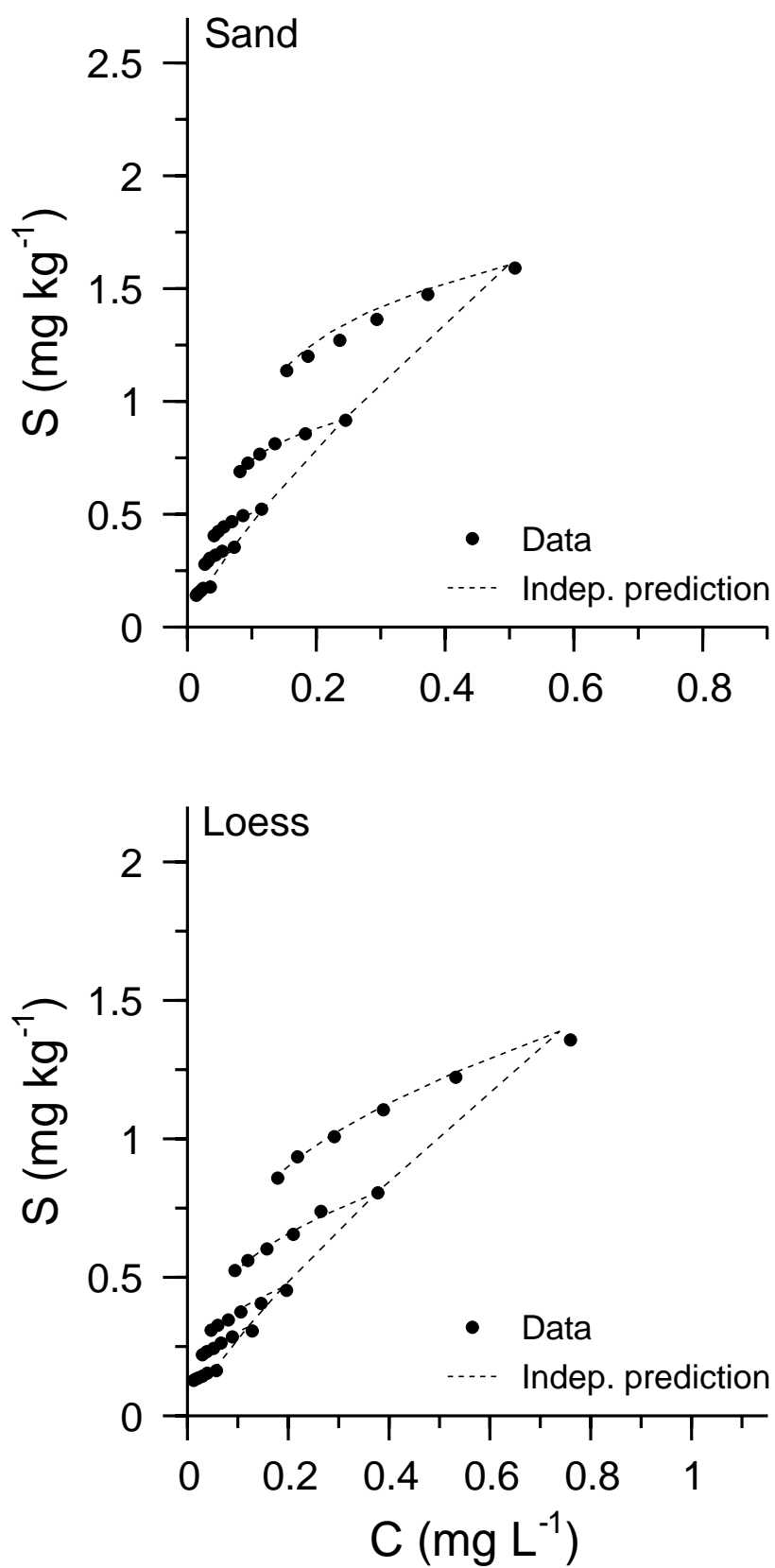


Figure 2.5: Measured and independently predicted chlortoluron sorption-desorption isotherms on field-moist soils at solution to soil ratios of 1.212 mL g^{-1} (Sand) and 1.471 mL g^{-1} (Loess).

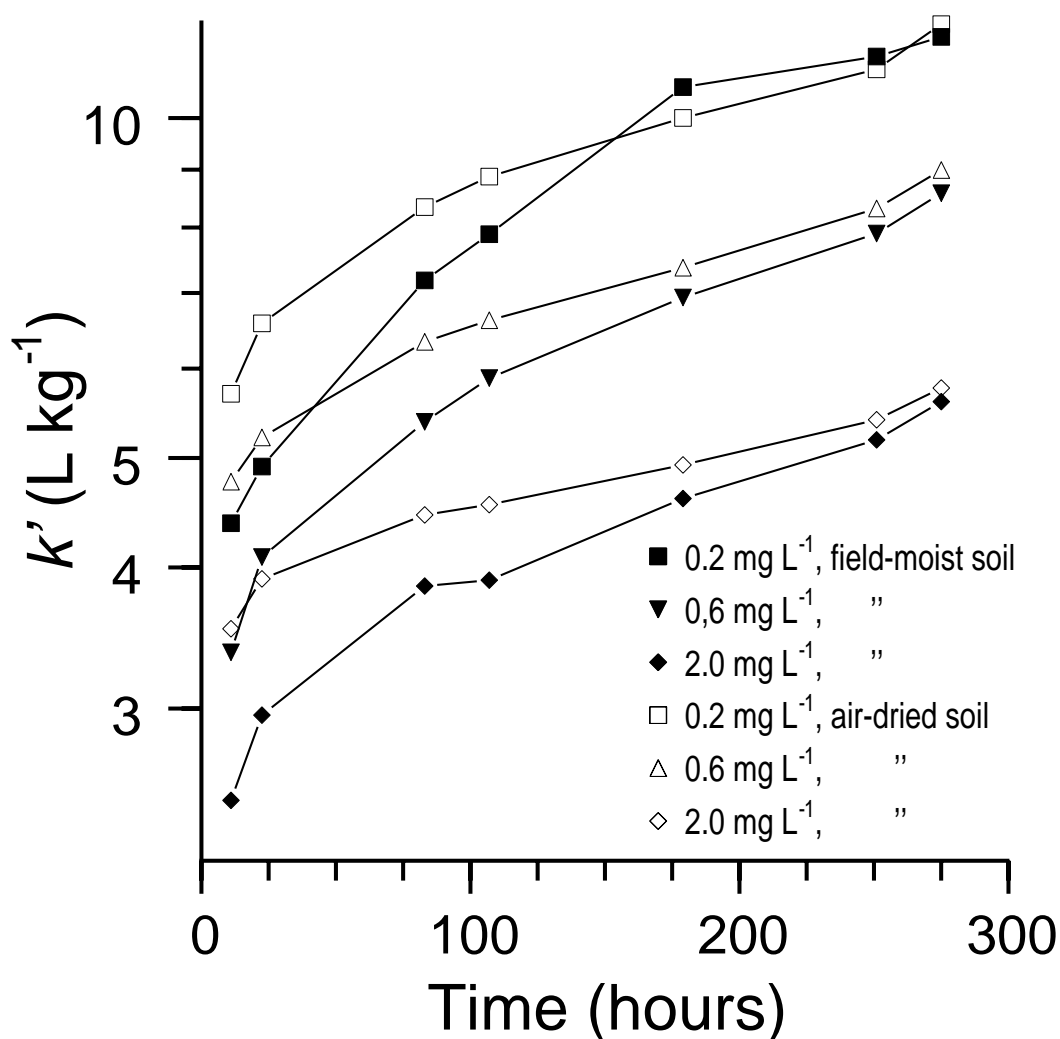


Figure 2.6: Partitioning coefficient k' of chlortoluron in field-moist and air-dried Sand at three concentrations as a function of sorption time.

2.1. The second process is the slow reversal of sorbent property changes caused by air-drying. These changes lead to more solute uptake in the sorption step, while the process of rehydration increases the release of solute with time, so that the desorption branches of air-dried soil slowly approach those of the field-moist soil. This explains the observed deviation between measured and predicted data in Figure 2.4. I further determined chlortoluron sorption-desorption isotherms of the rehydrated soils. Figure 2.8 demonstrates that these isotherms are well predicted by the model using parameters of Table 2.2. Hence, I may conclude that changes of sorption properties due to drying are completely reversible.

Although the sorption-desorption isotherms measured with air-dried soil are influenced by rehydration, it was possible to fit the two-stage model to these

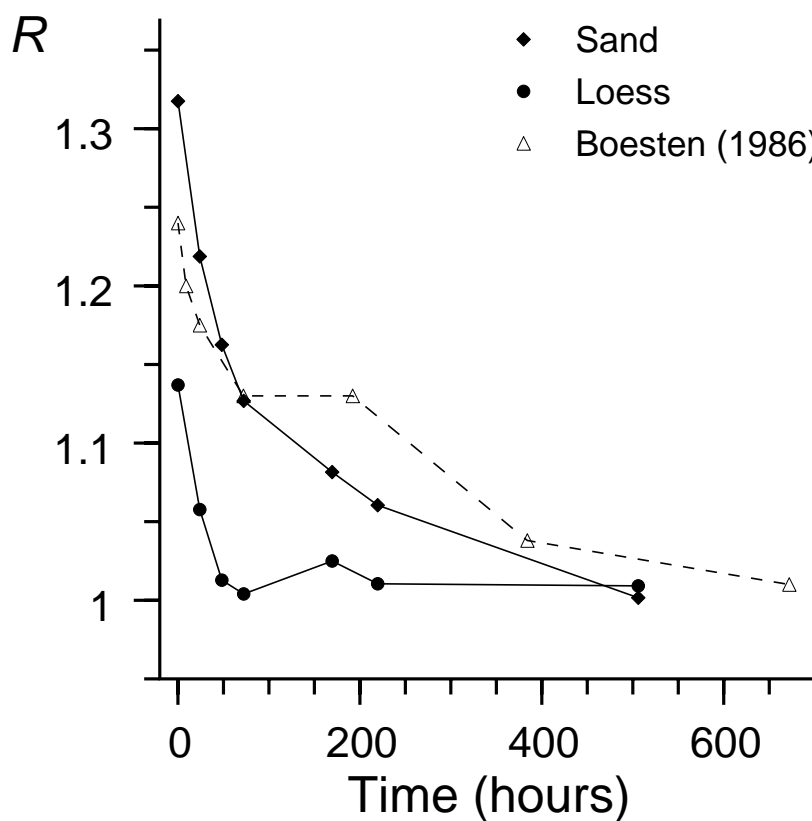


Figure 2.7: Ratio R of the 24 h partitioning coefficients determined in (rewetted) air-dried and field-moist soils. R is plotted against the time of rehydration. Results of Boesten (1986) found in a similar experiment with cyanazine on a loamy sand are also shown.

isotherms with good agreement (results not shown). To allow a better comparison to earlier results the fraction f of region 1 sites was fixed to the values shown in Table 2.2 during the fitting procedure. In comparison to the parameters given in Table 2.2, k increased while α decreased. The change of m was only slight (Sand: $k = 7.399$, $\alpha = 0.047$, $m = 0.786$, $f = 0.443$; Loess: $k = 4.350$, $\alpha = 0.051$, $m = 0.809$, $f = 0.408$). The results show that if air-dried soil is used k and α can be considerably overestimated or underestimated, respectively. The interpretation of both parameters in terms of intraorganic matter diffusion is not possible. As rehydration and diffusion occur on a similar time scale the diffusion coefficient is not constant with time but a function of rehydration time (e.g. water concentration within the sorbent). This phenomenon, which is known as anomalous diffusion in polymer science (Crank, 1975; Vieth, 1991) renders the meaning of the parameters k and α doubtful. Accounting for anomalous diffusion would require a more complex model than the simple mass transfer model

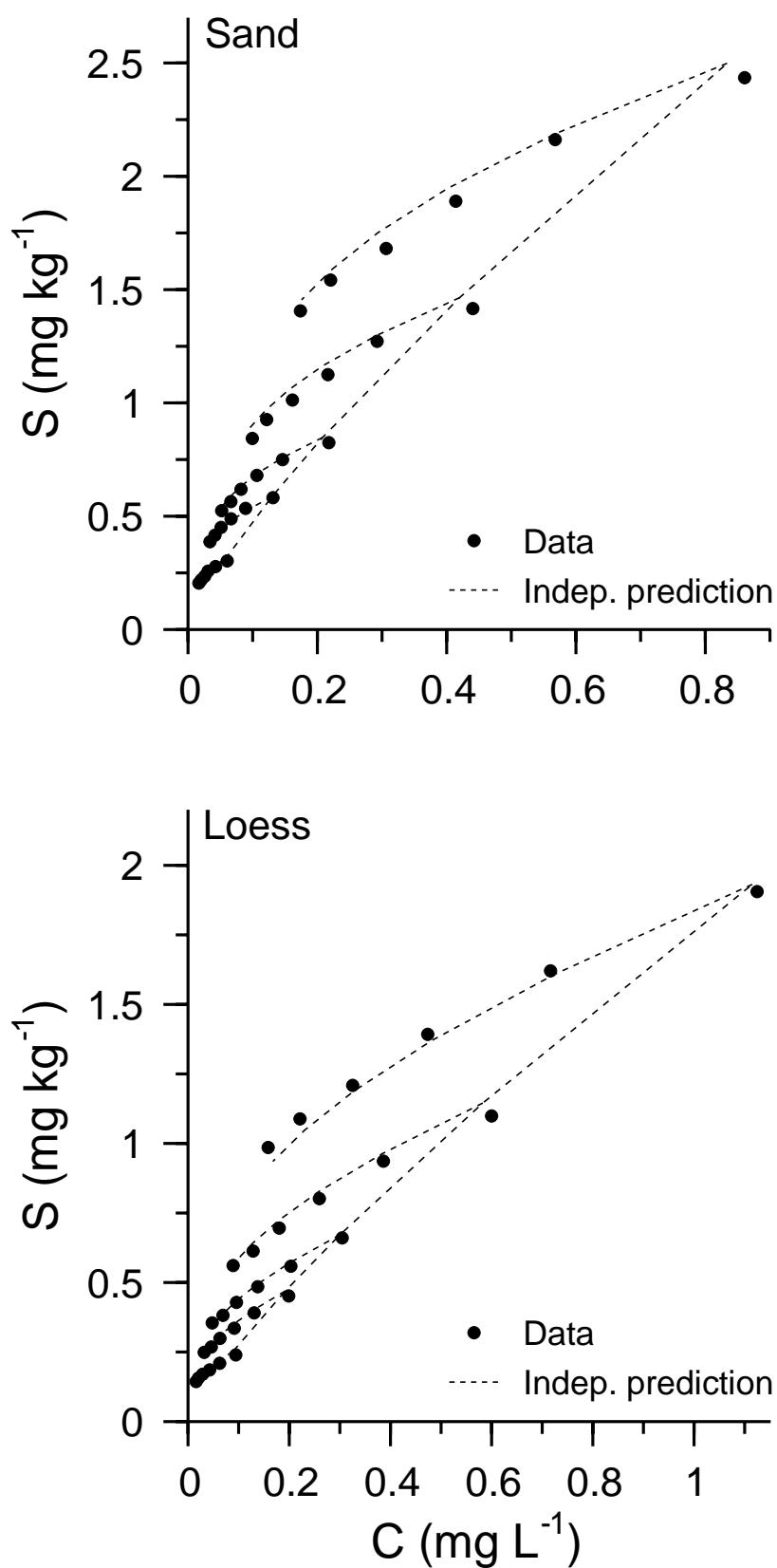


Figure 2.8: Measured chlortoluron sorption–desorption isotherms on rehydrated soils. The independently predicted isotherms were calculated with sorption parameters given in Table 2.2.

Our observations are in accordance with ideas of Burchill et al. (1981) and Mingelgrin and Gerstl (1993). These authors stated that humic structures rehydrate only with difficulty. When dried, the polar groups may associate through conformations in which they are preferentially oriented towards the interior. Hydrophobic portions are oriented to the outside of the polymer interacting through van der Waals attractive forces. Upon rehydration, this structure cannot change readily. Burchill et al. (1981) concluded that hydrophobic and non-polar molecules will readily bind to the exposed surfaces of dried humic substances in soil leading to an increase in sorption as compared to field-moist soil.

Rehydration times similar to those observed here were also found by Lyon and Rhodes (1993). Rehydrating dried peat with water these authors reported that swelling equilibrium (e.g. complete rehydration) was attained only after several weeks. Envisioning SOM as a polymer with rubbery and glassy domains (Leboeuf and Weber, 1997) I can relate my findings to the results of Kabra et al. (1991). These authors demonstrated that the swelling kinetics in a glassy polymer are a function of cross-linking inside the polymer. By increasing cross-linking in a hydrogel they increased the time to reach swelling equilibrium from 6 hours to 2 days. For sorption of cyanazine to a loamy sand, Boesten (1986) found the ratio R of the 24 h partitioning coefficients to be 1.24 for air-dried vs. field-moist soil and a rehydration time of about 3 weeks when the dry soil had been stored at the water content of the respective field-moist condition (see Figure 2.7). The process of rehydration may provide an alternative explanation of the results of Chen and Wagenet (1997) who reported a decrease in retardation of atrazine (2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine) when comparing column experiments with a similar mean travel time before and after γ -irradiation. They attributed this to sorbent property changes caused by γ -irradiation. However, the column was initially filled with air-dried soil. After carrying out the breakthrough experiment, the moist column was transported to another lab for γ -irradiation. A second breakthrough experiment was then carried out with the sterilized column. When fitting a two-site model to the measured data Chen and Wagenet (1997) reported a change of k from 1.07 mL g^{-1} to 1.81 mL g^{-1} and a change of α from 5.52 d^{-1} to 2.32 d^{-1} (recalculated from their sorption characteristic time T_s) when the irradiated column (their experiment Ic) is compared with the nonirradiated column (their experiment Ia). The increase of k and the decrease of α is similar to the change in sorption parameters I observed when field-moist and air-dried soil were compared. Since the soil in the irradiated case had time to rehydrate dur-

ing transport and sterilization, one may argue that the observed change in solute retardation was caused in fact simply by rehydration instead of irradiation.

Conclusions

Our results demonstrate clearly that the use of air–dried soil in sorption–desorption experiments affects sorption behavior of organic chemicals. Herbicide uptake is increased in the sorption step while the observed desorption hysteresis is less pronounced. Sorption parameters estimated with a kinetic model showed a considerable deviation from those estimated from experiments with field–moist soil. The effect is most probably caused by a change of the molecular structure of SOM that is slowly reversed upon rehydration. Slow rehydration kinetics of SOM, if present, will also be important when equilibration time of a solute is measured in a rate study prepared with air–dried soil. Increase of sorption due to kinetic solute uptake and decrease of sorption due to slow rehydration of SOM may compensate changes in solute concentrations over part of the experiment, pretending that equilibrium is achieved. In column experiments, the use of air–dried soil may overestimate solute retardation as compared to field–moist soil. When air–dried soil is used for batch or column studies, soil material should be completely rehydrated before the start of the experiment. From the results of this study and the work of Boesten (1986) rehydrating soil for about 2 to 3 weeks may be considered sufficient. The equilibration time of 12 h recommended by OECD (Organisation for Economic Cooperation and Development) (1997) is too short for complete rehydration of soil. Investigations of a larger variety of soils could clarify if slow rehydration is a frequent phenomenon and if 3 weeks can in general be considered sufficient for rehydration.

Chapter 3

Nonsingular Behavior of Organic Chemicals in Sorption–Desorption Experiments – the Role of Slow Sorption Kinetics

Abstract The sorption–desorption behavior of chlortoluron in two soils – a silt loam and a loamy sand – was investigated using three different batch techniques. The first technique is the classic decant–refill method where part of the supernatant is replaced by solute–free solution. The second technique is similar; however, part of the supernatant is replaced by solute containing solution instead. In the third technique desorption is induced by successive dilution of the supernatant with time. Nonsingular sorption of chlortoluron was observed independent of the method. I fitted a kinetic two–stage model to the data of the first technique to estimate sorption rate parameters. With this set of parameters, the model predicted the data measured with the second and third technique well. The agreement indicates that nonsingularity phenomena observed by means of the different techniques may be explained by slow sorption kinetics, probably caused by intraorganic matter diffusion. The ability of the model to describe nonsingular sorption–desorption data was further tested on data sets from the literature where nonsingularity remained unexplained or was explained by other causes than slow solute uptake. The different phenomena observed in each study could be readily explained by the two–stage model indicating the importance of slow sorption kinetics in all experiments.

Introduction

Sorption kinetics of nonpolar or weakly polar hydrophobic organic chemicals in soil–water systems involve time periods ranging from days to weeks, month or even years (Ball and Roberts, 1991). For soils that are not well aggregated and contain a moderate to high amount of soil organic matter (SOM) slow sorption kinetics of nonpolar or weakly polar hydrophobic organic chemicals have been increasingly linked to slow uptake by SOM. Slow sorption has been related to an activated hole–filling (or emptying) process in a condensed domain of SOM (Xing and Pignatello, 1997) or to a slow diffusive penetration of this domain (Brusseau et al., 1991a; Weber and Huang, 1996). In this study, I will focus on the latter, the so–called intraorganic matter diffusion (e. g. Brusseau et al., 1991a), which is symmetrical (assuming Fickian diffusion) with respect to the kinetics of sorption and desorption. There is an ongoing debate on whether the microporous mineral matrix or SOM is the main cause for slow sorption kinetics of hydrophobic organic chemicals in soils or sediments (Pignatello and Xing, 1996). However, the very weak interaction of hydrophobic chemicals with mineral constituents of soil in presence of water and the relative abundance of SOM in the soils considered above renders intraparticle diffusion within the mineral matrix an unlikely cause. The mineral matrix may, however, play an indirect role by encapsulating SOM thereby hindering the access of solute (Luthy et al., 1997).

The current idea of the physical structure of SOM is that of a polymer mesh consisting of a rubbery domain which is flexible due to relatively weak forces between the structural units and a glassy domain which is more condensed and rigid (Pignatello, 1998). In the rubbery domain sorption will be fast compared to that in the glassy domain. This explains the common observation that hydrophobic organic chemicals interact with SOM in two distinct sorption stages – a fast and a slow one. Changes in the solution–phase concentration during the slow stage can be very small over long periods. Due to analytical errors these changes may be difficult to identify. As a consequence, in many routine sorption–desorption experiments an agitation time of about 24 h was considered sufficient to establish sorption equilibrium within the sorption step. However, an increase in the equilibration time beyond 24 h, has been found to increase sorption of hydrophobic organic chemicals from 30% to as much as 10–fold (Pignatello and Xing, 1996). Considering these findings, nonsingular or hysteretic sorption behavior observed

in many sorption–desorption experiments may be artificial (Huang et al., 1998). The terms nonsingular or hysteretic sorption refer to deviations from the initial solute partitioning line in the successive steps of such an experiment. In the following I will use the term nonsingular sorption to describe this phenomenon.

Especially the common interpretation that nonsingularity of sorption–desorption isotherms is due to irreversible binding or entrapment of the investigated chemical should be reconsidered. The true assessment of nonsingularity requires that the experimental system is at true equilibrium before desorption is induced. In case this condition is not met a rigorous examination with regards to slow sorption kinetics is a prerequisite before nonsingular data should be interpreted regarding desorptive restrictions due to irreversible binding or entrapment. This can be accomplished by applying a diffusion model or a first order rate model (in case the particle geometry is unknown) to data. In our view, only the failure of such an approach makes it suitable to speculate on other causes for nonsingularity.

By now, successful modeling of nonsingular sorption–desorption data by means of nonequilibrium models assuming reversible sorption has been accomplished by Miller and Pedit (1992), Ma and Selim (1994), Streck et al. (1995), and Altfelder et al. (1999). While the last three authors demonstrated that nonsingularity can be described by means of a two–stage sorption model, Miller and Pedit (1992) modeled nonsingular sorption–desorption isotherms using a reactive surface–diffusion model. Selim et al. (1976) as well as Davidson et al. (1980) demonstrated that nonsingular sorption–desorption data can be readily simulated by means of a two–stage sorption rate model.

In this study, sorption–desorption behavior of chortoluron in two soils – a silt loam and a loamy sand – is investigated using three different batch techniques. The techniques are (1) the method of consecutive desorption, first described by Swanson and Dutt (1973), and Davidson and McDougal (1973) (2) the method of repeated addition, first described by Bowman (1979), and (3) a modification of the method of dilution desorption first described by Rao et al. (1978). While the first two methods are classic decant–refill methods where part of the supernatant is replaced by solute–free (1) or solute–containing (2) solution, desorption

in the last method is induced by diluting the supernatant in each desorption step. The nonsingular sorption–desorption data measured with the method of consecutive desorption will be used to estimate kinetic parameters by means of a two–stage kinetic sorption model. Using this set of kinetic parameters I will show that an independent prediction of data measured with methods (2) and (3) is possible. This indicates that the different sorption phenomena observed with the different techniques can be explained by slow sorption kinetics. The ability of the two–stage model to predict sorption–desorption data was further tested on three data sets obtained by different authors who applied one of the methods described above (Bowman, 1979; Koskinen et al., 1979; Bowman and Sans, 1985b). From the many data sets published I chose these sets because the authors either compared results obtained by two different experimental techniques or varied the experimental protocol of one technique to gain insight into sorption–desorption mechanisms. Additionally all studies have been cited to underline the influence of experimental techniques on sorption–desorption behavior (Koskinen and Harper, 1990; Barriuso et al., 1992; Huang et al., 1998). I will show that the phenomena observed by the different authors can be explained by nonequilibrium sorption indicating that slow sorption kinetics must be considered before an interpretation regarding desorption restrictions is suitable.

Materials and Methods

Materials

I used two topsoils (0–30 cm) – a silt loam (Typic Hapludalf) and a loamy sand (Aquic Haplumbrept) – taken from the plow horizon of two fields near Braunschweig, Germany. The soils will be denoted as Loess and Sand, respectively. The Loess contains 18.3 % clay, 71 % silt, 0.7 % organic C and has a pH of 7.2; the Sand contains 9 % clay, 11.3 % silt, 1.1 % organic C and has a pH of 5.5. The pHs were determined in soil slurries with 0.01 M CaCl_2 at a solution to soil ratio of 2.5 mL g⁻¹. Soils were passed through a 2 mm sieve and stored at -15 °C. Experiments were carried out with analytical chlortoluron (3–(3–chlor–p–tolyl)–1,1–dimethylurea) standards (purity 99% (HPLC)) by Riedel de Haen (Seelze, Germany). Water solubility of chlortoluron is 70 mg L⁻¹ (at 20°C).

Pesticide-grade methanol and acetone were obtained from Mallinckrodt Baker (Phillipsburg, N. J.). CaCl_2 was obtained from Fluka Chemicals (Buchs, Switzerland).

Batch experiments

All batch experiments were conducted at 20 °C with either field-moist or rehydrated soil (Altfelder et al., 1999). For the experiments, starting solutions with final chlortoluron concentrations of 0.2, 0.4, 0.6, 1.1, and 2.0 mg L⁻¹ were prepared in 0.01 M CaCl_2 . 50 mL Teflon[®] centrifuge tubes were used in all experiments (Nalgene, Rochester, N. Y.). Blanks showed no sign of chlortoluron sorption to Teflon[®]. Preliminary to all experiments the water content of the soil was measured gravimetrically after drying at 105 °C. Three different experimental protocols to investigate chlortoluron sorption behavior are described below.

Method of consecutive desorption

The sorption step in the method of consecutive desorption (MCD) was carried out by adding 20 mL of the above-mentioned chlortoluron starting solutions to 10 g of moist soil. For each of the five concentration levels one sample was prepared. The final solution volume and soil mass in the batch container were 21.9 mL and 8.1 g for the Loess or 20.95 mL and 9.05 g for the Sand. The soil suspensions were shaken for 24 hours on a reciprocating shaker (30 rpm). Subsequently, they were centrifuged for 20 min at 4500 g. A 10 mL aliquot of the supernatant was removed and stored in a glass tube at 4 °C until analysis. For the first desorption step this aliquot was replaced by 10 mL of 0.01 M CaCl_2 solution free of chlortoluron and the samples shaken for another 24 hours. Again, a 10 mL aliquot of the supernatant was removed and stored until analysis. This cycle was repeated four more times to obtain a total of five desorption measurements.

Method of repeated addition

The experimental protocol of the method of repeated addition (MRA) was the same as that of the MCD except that the 10 mL aliquot removed in each step was replaced by the respective chlortoluron starting solution initially added to each sample. As in the MCD, this cycle was repeated five times. A total of six successive sorption measurements (instead of one sorption measurement and five desorption measurements) were therefore obtained for each sample.

Method of dilution desorption

In the method of dilution desorption (MDD), 5 mL of the above-mentioned chlortoluron starting solutions was added to 5 g of moist soil. For each of the five concentration levels four samples were prepared. The oven-dried equivalents of soil and the solution volume in the batch containers were 4.05 g and 5.95 mL for the Loess or 4.53 g and 5.47 mL for the Sand. The soil suspensions were shaken for 24 hours on a reciprocating shaker (30 rpm). One sample of each initial concentration was subsequently centrifuged for 20 min at 4500 *g* and a 3.5 mL aliquot of the supernatant was removed and stored in a glass tube at 4°C until analysis. Desorption was induced in the three remaining samples by diluting them with 5 mL of 0.01 M CaCl₂ thereby increasing the total solution volume to 10.95 mL (Loess) or 10.47 mL (Sand). The samples were shaken for another 24 hours. Again one sample of each concentration was centrifuged. This time a 8 mL aliquot of the sample was removed and stored until analysis. This procedure was repeated two more times with dilution volumes of 10 mL and 20 mL in the respective third and fourth desorption step. The aliquots removed for analysis were 15 mL in the third and 20 mL in the fourth step. The experiments conducted using the MDD were carried out in duplicate.

Chemical and data analysis

Aliquots were extracted with 300 mg C₁₈ solid phase extraction (SPE) cartridges (Mallinckrodt Baker, Phillipsburg, N. J.). After vacuum-drying, the cartridges were eluted with methanol into 2 mL flasks and filled to volume with distilled water. Measurements were carried out with high performance liquid chromatography

(HPLC; System Gold, Beckmann, San Ramon, Ca.). Details of the chemical analysis are given in Altfelder et al. (1999). After solution concentrations were determined, the sorbed concentrations of each method were calculated by difference, accounting for the method-dependent loss or increase of mass due to removal and addition of solution.

Model

All experiments were analyzed using a nonlinear two-stage model. In the model the sorbent is assumed to consist of two domains. The mass transfer between both regions is driven by the difference in domain concentrations, thereby approximating diffusion-controlled sorption. For the relationship between the compartment approach and diffusion see Brusseau et al. (1991a). In domain 1, sorption is fast compared to the duration of the experiment so that equilibrium can be assumed:

$$S_1 = kC^m \quad (3.1)$$

In contrast, sorption in domain 2 is rate-limited:

$$(1 - f) \frac{\partial S_2}{\partial t} = \alpha(S_1 - S_2) \quad (3.2)$$

C is the concentration of dissolved chemical (mg L^{-1}), while S_1 and S_2 are the concentrations of the sorbed chemical in region 1 and 2 (mg kg^{-1}). The parameter k denotes the Freundlich distribution coefficient ($\text{mg}^{1-m} \text{L}^m \text{kg}^{-1}$), m the Freundlich exponent, α the sorption rate coefficient (day^{-1}) and f is the fraction of the equilibrium domain. The concentration of sorbed solute (S) is given by $S = fS_1 + (1 - f)S_2$. For $t = \infty$, all sorbed concentrations are identical (e. g. $S = S_1 = S_2$).

The total concentration of solute C_t in the slurry, is given by $C_t = \theta C + \rho S$ where ρ denotes the mass of soil and θ the volume of water in the batch container. Assuming negligible decay, the mass balance in a batch system within one sorption or desorption step is $dC_t/dt = 0$. The equation describing kinetic sorption within a batch system can then be written as (Altfelder et al., 1999)

$$(\rho f m k C^{m-1} + \theta) \frac{\partial C}{\partial t} = \frac{\alpha}{(1 - f)} [C_t - \theta C - \rho k C^m], \quad (3.3)$$

subject to the initial condition $C_0 = C(0)$. Equation (3.3) was solved numerically by Bulirsch–Stoer integration (Press et al., 1992) in all cases. Before fitting the

model to measured data all concentrations were logtransformed (Streck et al., 1995). Parameter estimation was achieved by applying the Levenberg–Marquardt algorithm (Press et al., 1992).

For the MCD the sorption step is carried out by adding a fixed amount of herbicide solution (θ) to a fixed amount of soil (ρ). The samples were then shaken for the time interval Δt . After removal of a solution fraction ω this fraction is replaced by the same amount of herbicide-free solution and the sample is shaken again for an interval of Δt . The removal and replacement of solution may be repeated N times yielding a desorption isotherm with N desorption points. Mathematically this procedure may be expressed as (cf. Streck et al., 1995)

$$C^{\eta=0}(t) = F(\Delta t; C_t^{\eta=0}, C_t^{\eta=0}/(\theta + \rho f k C_0^{m-1})) \quad (4a)$$

$$C^\eta(t) = F(\Delta t; C_t^{\eta-1} - \omega \theta C^{\eta-1}, \\ ((1 - \omega)\theta C^{\eta-1} + \rho f k (C^{\eta-1})^m)/(\theta + \rho f k C_0^{m-1})) \quad (4b)$$

$$\eta = 0, 1, \dots, N \quad (4c)$$

where $F(\Delta t; C_t; C_0)$ denotes the solution of (3.3), $\eta = 0$ the sorption step, and η the η th of N desorption steps. For the MRA Equation (4b) changes to

$$C^\eta(t) = F(\Delta t; C_t^{\eta-1} - \omega \theta C^{\eta-1} + \omega \theta C_{inp}, \\ ((1 - \omega)\theta C^{\eta-1} + \omega \theta C_{inp} + \rho f k (C^{\eta-1})^m)/(\theta + \rho f k C_0^{m-1})) \quad (5)$$

with C_{inp} being the solution concentration added in each step. For the MDD Equation (4b) changes to

$$C^\eta(t) = F(\Delta t; C_t, \\ ((\theta^{\eta-1} + \theta_a^\eta)C^{\eta-1} + \rho f k (C^{\eta-1})^m)/((\theta^{\eta-1} + \theta_a^\eta) + \rho f k C_0^{m-1})) \quad (6)$$

Here the total concentration C_t remains the same throughout the experiment. $\theta^{\eta-1}$ denotes the solution volume from the last step while θ_a^η is the volume added in the n^{th} step. In case sorption is nonlinear ($m \neq 1$) the initial concentration C_0 for all methods was calculated by means of the Newton algorithm.

Results and Discussion

Chlortoluron sorption–desorption isotherms determined by the MCD in both soils are nonsingular (Figure 3.1). Parameters estimated by fitting the nonlinear two-stage model to the measured data are given in Table 3.1. The low standard errors in addition to the good agreement between measured and modeled data in Figure 3.1 indicate that the set of data is adequately described by the model. Further evidence that slow sorption kinetics are the likely cause for chlortoluron nonsingularity in the two soils examined can be found in Altfelder et al. (1999). Consequently, it should be possible to predict chlortoluron sorption behaviour independent of the experimental technique used in a batch study. Of course, it is a prerequisite that the experimental technique has no influence on the sorption of chlortoluron, otherwise the independent model prediction will fail and experimental effects on sorption may be identified.

The first experimental technique examined is the MRA. In contrast to the MCD, desorption is not induced in this experimental technique. The experimental results in Figure 3.2 also show nonsingular sorption. Assuming that equilibrium is not reached within the 24 h agitation period, the effect can be readily explained. After the first 24 h part of the mass in the batch container is removed, but more mass is added as the replacement solution has the same chlortoluron concentration as the starting solutions. After another 24 h one part of the solute had been in contact with the soil for 48 h the other for 24 h. As a result the isotherms appear to be nonsingular since sorption after 48 h is increased due to the continuing solute uptake by soil when compared to sorption after 24 h. The good agreement between the model prediction using the parameter estimates independently derived (Table 3.1) and the measured data supports this explanation (Figure 3.2).

Table 3.1: Parameter estimates of the two-stage model and associated standard errors (SE) for the method of consecutive desorption (MCD).

Soil	α^\dagger	SE	f	SE	k^\ddagger	SE	m	SE
Sand	0.085	0.010	0.443	0.015	5.479	0.316	0.780	0.012
Loess	0.070	0.013	0.408	0.029	3.720	0.414	0.805	0.024

$^\dagger \text{d}^{-1}$

$^\ddagger \text{mg}^{1-m} \text{L}^m \text{kg}^{-1}$

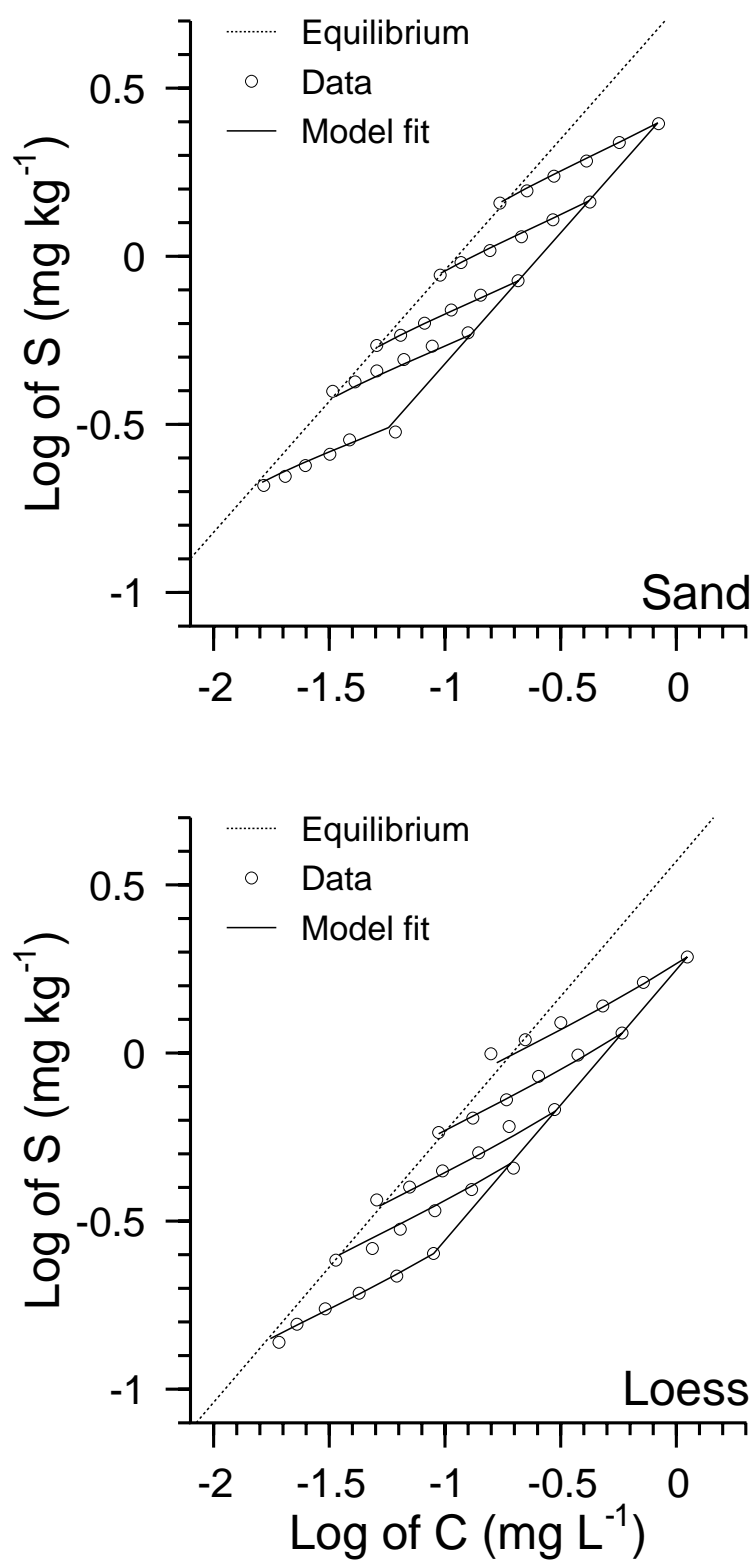


Figure 3.1: Sorption–desorption isotherms of chlortoluron measured with the method of consecutive desorption (MCD) for the Loess and Sand. The solid lines are fitted using the two–stage model. The dashed line indicates sorption equilibrium.

The second experimental technique examined is the MDD. A strength of this method compared to the MCD and the MRA is the lack of centrifugation between the ad- and desorption steps. Further, each desorption point is measured on an individual sample – error propagation causing apparent nonsingularity as possible with the MCD is impossible. However the MDD also has an experimental weakness: During the experiment the solution to soil ratio increases from 1.47 to 10.11 mL g⁻¹ for the Loess and from 1.21 to 8.93 mL g⁻¹ for the Sand. Depending on the value of the Freundlich coefficient the number of possible desorption steps is limited as the inaccuracy in the calculated sorbed concentration in the solid phase and consequently of the sorption parameters increases with increasing solution to soil ratio. According to McDonald and Evangelou (1997) the optimal solution to soil ratio can be calculated from the Freundlich equilibrium coefficient by $k/1.2$. For the Freundlich equilibrium coefficient of chlortoluron in Sand ($k = 5.5 \text{ mg}^{1-m} \text{ L}^m \text{ kg}^{-1}$) the optimal solution to soil ratio would be 4.6 mL g⁻¹. When estimating the optimal solution to soil ratio for the apparent Freundlich coefficient after 24 hours ($k'_{24} = 2.8 \text{ mg}^{1-m} \text{ L}^m \text{ kg}^{-1}$) this ratio is even less at 2.4 mL g⁻¹. The optimal solution to soil ratio for the Loess is even smaller as sorption of chlortoluron is less pronounced. A continued increase of the solution volume to induce further desorption is therefore critical when calculating the sorbed concentration via mass balance.

MDD isotherms are presented in Figure 3.3. Both isotherms exhibit a pronounced nonsingularity similar to that found with the MCD. Measured and predicted data (using the parameter set of Table 3.1) in Figure 3.3 show good agreement. As the MDD lacks the repeated centrifugation and resuspension procedure of the MCD and MRA, the procedure can be excluded as a cause for nonsingular sorption observed with the MCD and MRA. This is further evidence, that slow sorption kinetics are responsible for nonsingular sorption of chlortoluron.

In Figure 3.4 the data of all three methods are compiled for the Sand. While the increase in deviation from the 24 hr isotherm with each successive desorption step is similar for the MCD and the MDD, the increase appears to be less pronounced with each successive sorption step for the MRA. The sorption points of the MRA and the MCD are almost identical. However, the sorption points of the MDD are shifted along the 24 h sorption isotherm to lower concentrations because the initial solution to soil ratio is different.

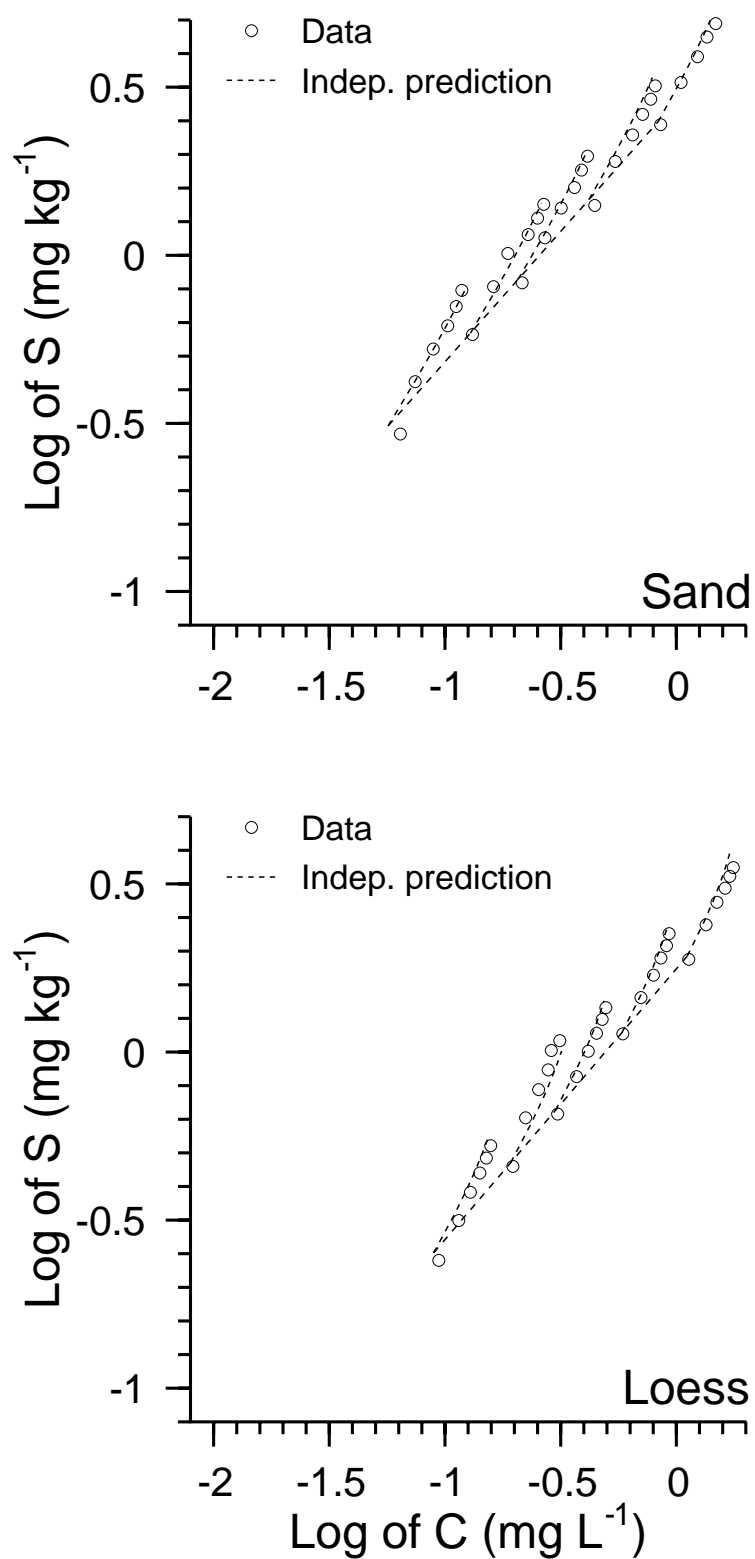


Figure 3.2: Chlortoluron isotherms determined with the method of repeated addition (MRA). The predicted isotherms were calculated with the parameter sets given in Table 3.1.

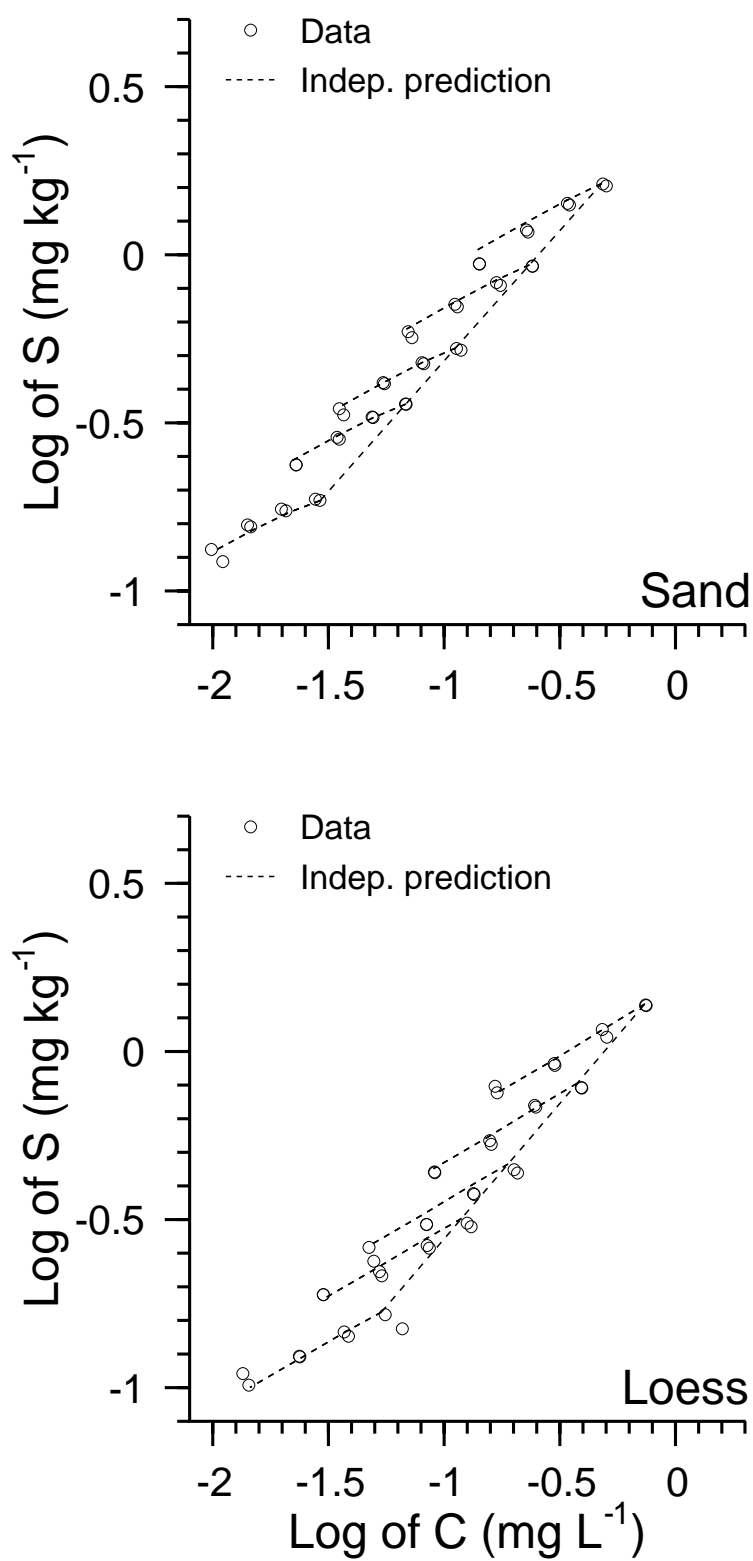


Figure 3.3: Sorption–desorption isotherms of chlortoluron measured with the method of dilution desorption (MDD). The predicted isotherms were obtained with the parameter sets given in Table 3.1.

Figure 3.5 illustrates the time dependence of the Freundlich coefficient k' for the three methods. In addition, I present data from a rate study (Altfelder et al., 1999). Model predictions using the parameter set of Table 3.1 are also included. All Freundlich coefficients k' are normalized to the Freundlich coefficient after 24 hours (k'_{24}). Since during a rate study, neither the mass of solute nor the solution volume or the sorbent mass change, the change in k' can be fully attributed to slow sorption kinetics. The rate study can therefore be taken as a reference for other methods. In the MRA, the increase of k' with time is slower than in a rate study. This effect is caused by the addition of solute every 24 h. The contact time of the solute to soil depends on the time of addition to the batch tube. The overall contact time is therefore lower after 48 h, 72 h, 96 h etc. compared to a rate study where all of the solute mass is added at $t = 0$. This leaves less time for equilibration with the solid phase shifting k' to lower values. The magnitude of shift is determined by the amount of solute added, compared to the amount already in the batch container. The more solute relative to the mass already in the container is added the smaller will be the increase in k' after each step.

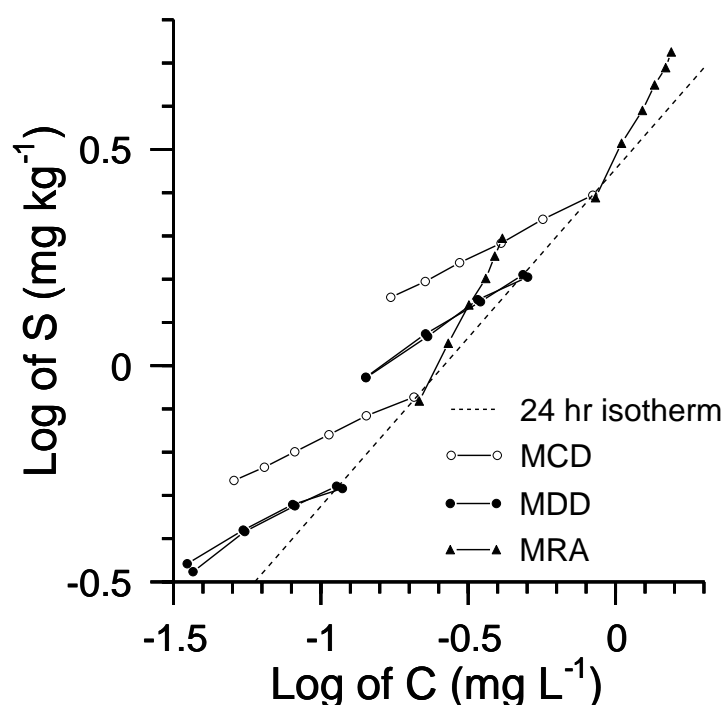


Figure 3.4: Chlortoluron isotherms obtained by the methods of consecutive desorption (MCD), dilution desorption (MDD), and repeated addition (MRA) in Sand at two initial concentrations (0.6 and 2.0 mg L⁻¹).

Compared to the rate study, the repeated removal of solute in the MCD leads to higher concentrations in the sorbed phase (relative to the respective solution concentration) after each desorption step because desorption equilibrium is not reached within the steps. This effect shifts the measured k' to higher values after each desorption step compared to the value of k' in a rate study after the same period of time. The same effect appears in the MDD where the decrease of solute concentration is achieved by approximately doubling the solution volume in each step. The increase of k' is about the same with the MCD and MDD in the first and second desorption step. In the third step, the model predicts a slightly stronger increase in k' for the MDD. The increase is not reflected by the data. However, the data is subject to a higher error as the solution to soil ratio has reached about 10 mL g^{-1} in this step, which increases the uncertainty in the estimated k' .

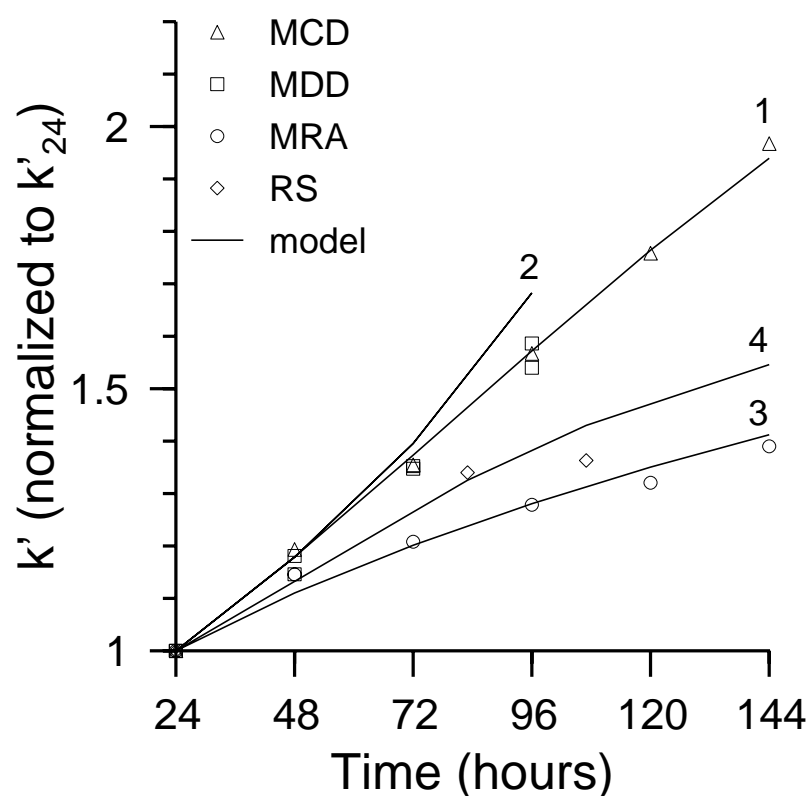


Figure 3.5: Modeled and measured apparent Freundlich coefficient k' as a function of time for the methods of consecutive desorption (MCD), dilution desorption (MDD), and repeated addition (MRA) in Sand. Additionally data of a rate study (RS) with chlortoluron in Sand (Altfelder et al., 1999) are presented. The numbers on the modeled curves denote the simulated methods (MCD=1, MDD=2, MRA=3, RS=4).

The position of a desorption point in a data plot using the MCD is a function of the mass of solute removed in each desorption step. In the MDD the desorption pathway is governed by the amount of dilution volume in each desorption step. While the cause for desorption is the same, desorption isotherms are difficult to compare as a repeated dilution may have a different effect compared to a repeated removal of solute. The similarity in the desorption isotherms observed here may be explained by the fact that half of the solution volume was removed in one method while solution volume was doubled in the other causing a similar effect. Simulated experiments using the two-stage model and different replacement or dilution volumes for both methods in Figure 3.6 demonstrate the dependence of desorption nonsingularity on the amount of replacement or dilution volume in case of slow sorption kinetics. Increasing the replacement or dilution volume leads to a decreasing desorption nonsingularity in both methods.

Evaluation of literature data

To illustrate that the ability of the kinetic two-stage model to describe the various phenomena associated with the different experimental techniques is not limited to sorption of chlortoluron, the model was applied to several published sets of data. Each experiment will be described briefly. I will further discuss each authors interpretation of his findings, with regard to our results.

Data set 1

Bowman (1979) studied the sorption of parathion (*O,O*-diethyl *O-p*-nitrophenylphosphorothioate) in Bondhead sandy loam. First, they used the MRA (six solute removals) and then induced desorption with the MCD (three solute removals). Bowman (1979) stated that the sorption isotherm produced by the MRA was very similar to that produced by the standard 24 h batch method at varying initial concentrations. In contrast, the desorption isotherm produced by the MCD was nonsingular. The data of Bowman (1979) is presented in Figure 3.7. Additionally the 24 h Freundlich isotherm obtained by Bowman and Sans (1985a) for the same

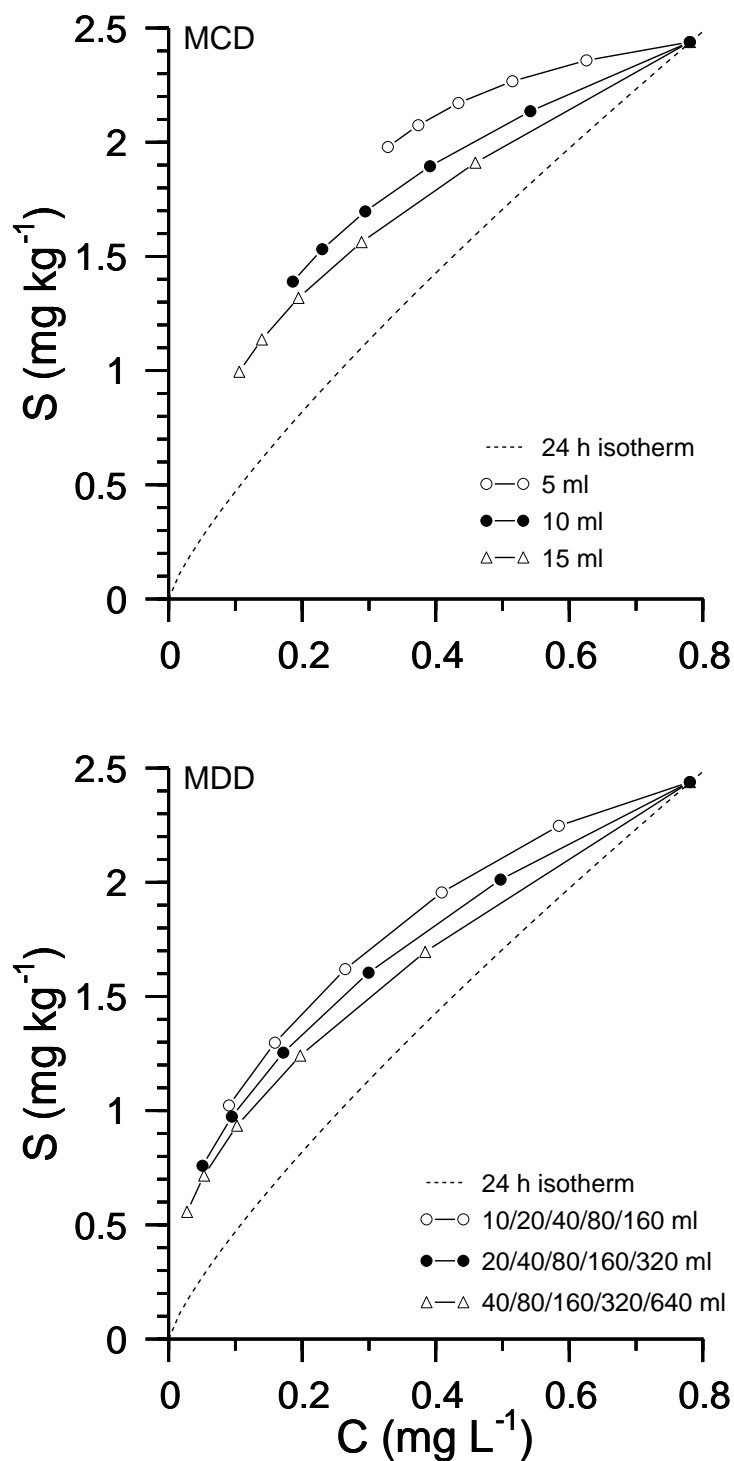


Figure 3.6: MCD isotherms simulated with varying replacement volumes (upper panel, see legend). The lower panel shows sorption–desorption MDD isotherms simulated with varying dilution volumes in each desorption step (see legend). The initial solution volume and soil mass were 20 mL and 10 g for all simulations. The sorption parameters were $\alpha = 0.1 \text{ d}^{-1}$, $k = 5.0 \text{ mg}^{1-m} \text{ L}^m \text{ kg}^{-1}$, $f = 0.5$ and $m = 0.8$.

solute and soil at the same solution to soil ratio (30 mL g^{-1}) is shown in Figure 3.7. It can be seen that the sorption isotherm determined with the MRA follows the 24 h sorption isotherm for the first three sorption steps as stated by Bowman (1979). In the next four steps, however, the data starts to deviate from the 24 h isotherm showing sorption nonsingularity similar to that shown in Figure 3.2. In the three desorption steps measured with the method of consecutive desorption the nonsingularity is also present.

The fit of the two-stage model to the data of Bowman (1979) together with the equilibrium isotherm estimated by the model is also shown in Figure 3.7. For the fit m , was fixed to the value of the 24 h isotherm given by Bowman and Sans (1985a). The estimated sorption parameters are given in Table 3.2. The data is described adequately by the model, indicating that a kinetic sorption is the cause for the nonsingularity.

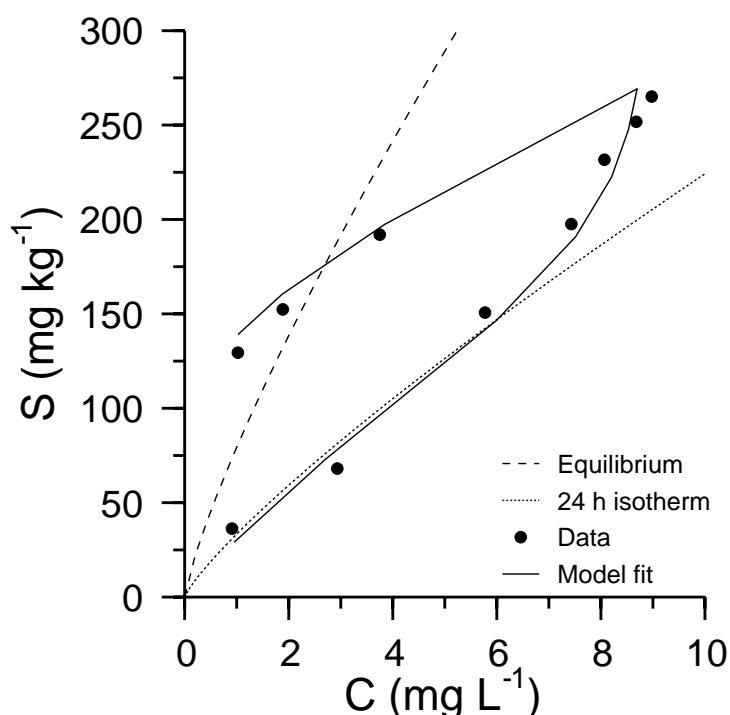


Figure 3.7: Parathion isotherm data scanned from Figure 1 in Bowman (1979). Also shown are the model fit of the two-stage model as well as the calculated sorption equilibrium. The 24 h isotherm was calculated with the Freundlich parameters of parathion in the same soil (Bowman and Sans, 1985a).

Why does the system follow the 24 h sorption isotherm during the first two desorption steps although the complete data set is obviously influenced by nonequilibrium sorption? The reason is that Bowman (1979) increased the concentration of the replacement solutions in the first two steps, but kept it constant during the following four steps. At the start of the experiment Bowman (1979) added 30 mL of a 1.92 mg L^{-1} parathion solution to 1 g of soil, introducing a total of $57.6 \text{ } \mu\text{g}$ into the batch reactor. After the sorption step about $22.7 \text{ } \mu\text{g}$ (40 %) of this mass was removed in a 25 mL aliquot. By replacing this aliquot with a solution containing 4.8 mg L^{-1} of parathion $120 \text{ } \mu\text{g}$ of parathion were added to the system. 23 % of the total mass in the tube was now “old” parathion which had been in contact with the soil for 24 h, while 77 % had just been added. Even if a kinetic sorption prevails the partitioning of parathion after agitating for another 24 h should therefore be similar to that after the first 24 h as most of the parathion had only been in contact with the soil for 24 instead of 48 h. The same effect holds for the next step as a parathion solution with a concentration of 9.6 mg L^{-1} was added. In the following steps the solution concentration in the aliquots used for replacement remained at 9.6 mg L^{-1} so the fraction of parathion new to the system becomes smaller compared to the mass already in the system. The continuing sorption of parathion already in the system for varying periods of time now dominates solute partitioning leading to the nonsingularity observed in Figure 3.7 after the third replacement step. Comparing the ratio between the mass

Table 3.2: Parameter estimates of the two-stage model for the literature data. The estimates for the last data set were obtained by (a) keeping $m = 0.85$ as determined by Koskinen et al. (1979) and (b) fitting m .

author		α^{\dagger}	f	k^{\ddagger}	m
Bowman (1979)		0.051	0.304	85.25	0.83
Bowman and Sans (1985b)		0.034	0.418	85.45	0.83
Koskinen (1979)	(a)	0.023	0.325	16.74	0.85
	(b)	0.034	0.268	11.03	1.13

$\dagger \text{ d}^{-1}$

$\ddagger \text{ mg}^{1-m} \text{ L}^m \text{ kg}^{-1}$ (Bowman, 1979, Bowman and Sans, 1985b)

or $\mu\text{mol}^{1-m} \text{ L}^m \text{ kg}^{-1}$ (Koskinen et al., 1979)

already in the batch and that new to the system for this data and the data shown in the upper panel of Figure 3.2 (where nonsingularity of chlortoluron is already visible after the first replacement) reveals that the latter ratio is much larger at 60:40 compared to 23:77 after the first solution replacement. Our point is further strengthened by the observation of Bowman and Sans (1985a) that agitating the sample for 48 instead of 24 h lead to an increase in sorption of parathion by Bondhead sandy loam.

Data set 2

Bowman and Sans (1985b) investigated the effect of centrifugation and resuspension on desorption nonsingularity of parathion in Bondhead loamy sand by comparing data measured with the MCD to data measured with the MDD. Their MDD is different to ours in that dilution to varying volumes is carried out immediately after the sorption step. The study has been cited by numerous authors (Brusseau and Rao, 1989b; Koskinen and Harper, 1990; Ma and Selim, 1996; Huang et al., 1998) to underline the influence of experimental techniques on desorption nonsingularity. The data are presented in Figure 3.8. From the figure it is obvious that desorption nonsingularity for the MDD is less pronounced than for the MCD. Similar findings for various chemicals and soils were made by Rao et al. (1978). Rao et al. (1978) and Bowman and Sans (1985b) concluded that the centrifugation/resuspension steps in the MCD might be responsible for the observed increase in nonsingularity. Bowman and Sans (1985b) proposed that a partially irreversible compaction of the sorbent by centrifugal forces greatly increased the time required for desorption processes to reestablish equilibrium thereby increasing nonsingularity.

Figure 3.8 demonstrates that the parameters (Table 3.2) obtained by fitting the two-stage model to data measured with the MCD can be used to predict data measured with the MDD. Hence, the difference between the MCD and the MDD can be fully explained by kinetic sorption. The equilibrium isotherm estimated by the model as well as the 24 h isotherm given by Bowman and Sans (1985b) are also shown. For the model fit, m was taken from Bowman and Sans (1985b). Note that the sorption parameters estimated for parathion sorption in Bondhead sandy loam (Table 3.2) using the data of Bowman (1979) and Bow-

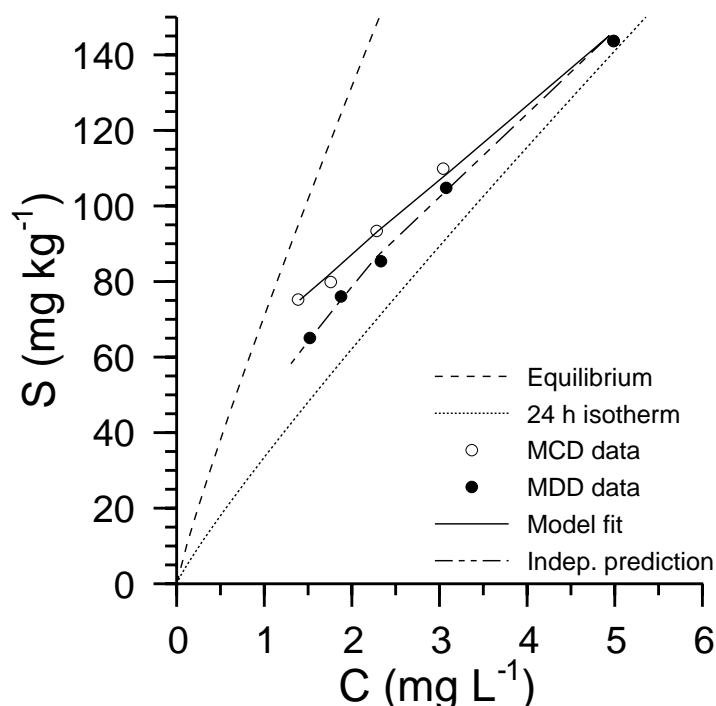


Figure 3.8: Parathion isotherm data of the method of consecutive desorption (MCD) and the method of dilution desorption (MDD) scanned from Figure 1 in Bowman and Sans (1985b). Also shown are the model fit of the two-stage model to the data measured with the MCD and sorption equilibrium. The estimated kinetic sorption parameters (Table 3.2) were then used to predict data measured with the MDD. The 24 h isotherm was taken from Bowman and Sans (1985a).

man and Sans (1985b) are very similar despite the considerable difference in concentration range and experimental technique of both studies.

Why does the nonsingularity differ when the MCD and the MDD are compared? This is in contrast to our finding that nonsingularity is similar for both methods (Figure 3.4). I already showed in Figure 3.6 that desorption nonsingularity depends on the details of the experimental protocol, which renders the comparison of the two methods, at least without a model, difficult. The reason here is that Bowman and Sans (1985b) carried out the dilution steps immediately after the 24 h sorption step. The experiment was therefore completed within 48 h while the sorption–desorption procedure for the MCD lasted 120 h. Recall that in our MDD samples would have been successively diluted, so the experiment would have lasted 120 h as well. In case nonsingularity is caused by kinetic sorption, the desorption points of their MDD will lie on the partitioning isotherm corresponding to a sorption–desorption time of 48 h. As a consequence nonsin-

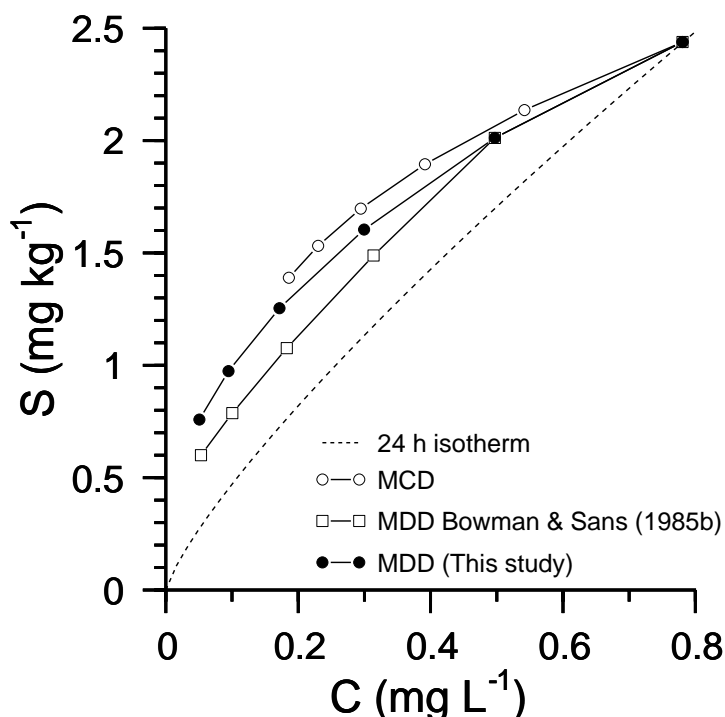


Figure 3.9: Simulated sorption-desorption isotherms for the method of consecutive desorption (MCD), the method of dilution desorption (MDD) as described in Bowman and Sans (1985b), and the method of dilution desorption (MDD) presented in this study. The kinetic parameters were the same as in Figure 3.6.

gularity is less pronounced than for the method of consecutive desorption where the sorption-desorption steps correspond to periods ranging from 24 to 120 h.

In Figure 3.9 simulated isotherms (initial concentration: 2.0 mg L^{-1}) for the MCD and the MDD variant used by Bowman and Sans (1985b) together with our MDD variant used here are presented. The initial solution to soil ratio is 2 mL g^{-1} for all cases. In the MCD half the solution is replaced in each step. For the MDD the solution volume is either doubled directly (Bowman and Sans, 1985b) or in an incremental fashion (our protocol) for each successive desorption point. The final solution volumes are therefore the same for both variants of the method after each desorption step. The figure shows that with kinetic sorption the comparison of the different desorption isotherms does not allow meaningful conclusions without the support of a model. While nonsingularity is strongest

with the MCD it is lowest with the MDD variant described in Bowman and Sans (1985b). To our best knowledge, all studies except ours in which the MCD and MDD were compared (Rao et al., 1978; Singh et al., 1989; Rocio Estrella et al., 1993) used the MDD described in Bowman and Sans (1985b).

Data set 3

Koskinen et al. (1979) reported an interesting effect when applying the MCD to study desorption of 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) by Palouse silt loam. While the sorption period was kept constant at 24 h, nonsingularity was found to increase when the desorption periods were extended from 3 to 48 h. Koskinen et al. (1979) stated that the trend observed contradicts nonattainment of equilibrium during desorption. They therefore ruled out that nonequilibrium is a major cause for the observed nonsingularity. Instead, they proposed that some other effect overshadowed the possible effect of nonattainment of equilibrium. The data together with the 24 h isotherm given by Koskinen et al. (1979) are plotted in Figure 3.10. The desorption periods corresponding with each desorption isotherm are also given. For the desorption isotherm with the shortest equilibration time of 3 h, the seventh desorption step was extended to 16 h.

Despite considerable scattering, the data is adequately described by the kinetic two-stage model (Figure 3.10). The estimated equilibrium isotherm is presented as well. For the fit the parameter m was fixed to 0.83 as determined by Koskinen et al. (1979) for the 24 h sorption isotherm. Fitting m instead of keeping m fixed yielded slightly better results, however the estimated m is greater than one and thus quite different from the value observed by Koskinen et al. (1979). The estimated sorption parameters are shown in Table 3.2. The model is even capable to describe the increase in nonsingularity when extending the desorption time from 3 to 16 h. The increased nonsingularity with increasing equilibration times may be explained by the continuing sorption to kinetic sites during the desorption procedure. Altfelder et al. (1999) have shown that during the first desorption steps the concentration in region 2 of the sorbent may still rise. From this it follows that longer equilibration times in the desorption steps will lead to increasing concentration in the sorbed phase and consequently to an increase in nonsingularity. An increase in atrazine (6-chloro-*N*-ethyl-*N'*-(1-

methylethyl)-1,3,5-triazine-2,4-diamine) nonsingularity with increasing equilibration times during the desorption phase of the experiment was also successfully modeled by Ma and Selim (1994). The findings of Koskinen et al. (1979) should therefore be interpreted rather as evidence for and not against kinetic sorption.

When testing for sorption nonequilibrium with the MCD both the sorption and desorption period should be increased with time. When doing so the resulting isotherm should eventually become singular in case nonsingularity is caused by slow sorption kinetics.

The lower part of Figure 3.11 shows simulated data for the MCD at an initial concentration of 0.6 mg L^{-1} . Equilibration times in the sorption and desorption step vary from 3 to 240 h. At 240 h, the sorption-desorption isotherm is

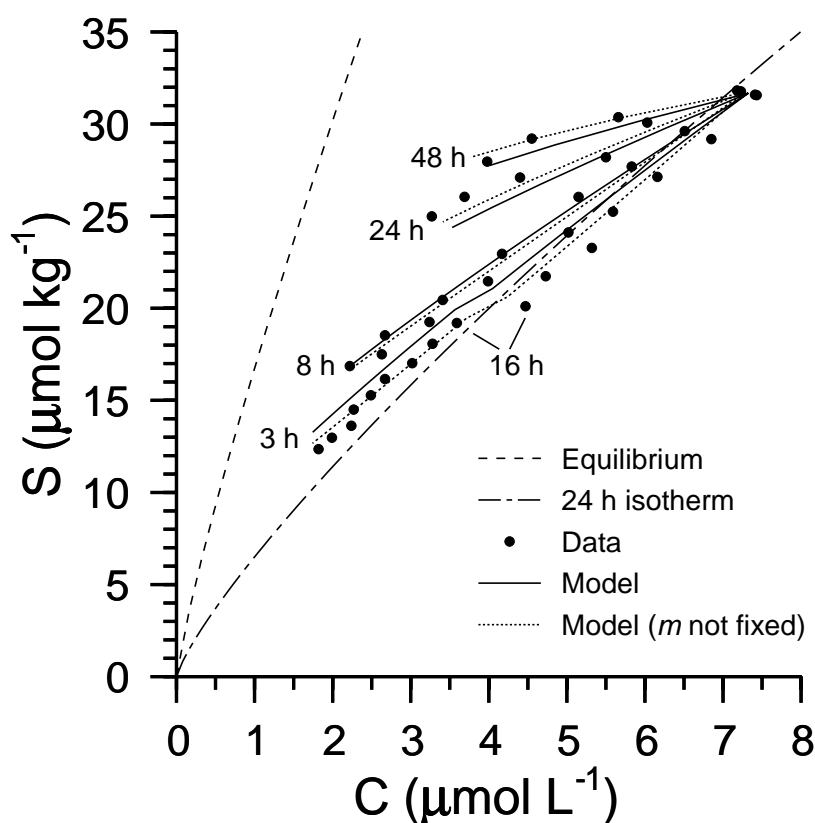


Figure 3.10: 2,4,5-T sorption-desorption isotherm data scanned from Figure 4 in Koskinen et al. (1979). Also shown are model fits of the two-stage model as well as sorption equilibrium. Model fits were obtained by (a) fixing m to the value given in Koskinen et al. (1979) and (b) fitting m . The 24 h isotherm was calculated with the Freundlich parameters given in Koskinen et al. (1979).

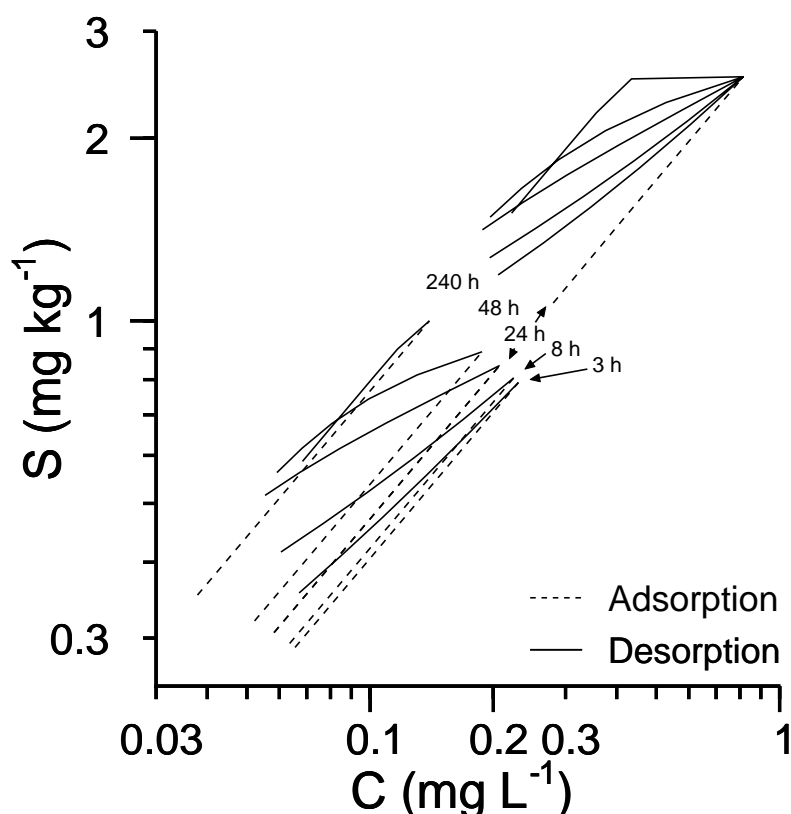


Figure 3.11: Simulated sorption–desorption isotherms for the method of consecutive dilution (MCD) at two initial concentrations (0.6 and 2.0 mg L^{-1}). The isotherms at the lower concentration were simulated by varying both sorption and desorption times from 3 to 240 h. The isotherms at the higher concentration were simulated by keeping the sorption period constant at 24 h and varying the desorption steps from 3 to 240 h. The kinetic parameters were the same as in Figure 3.6.

nearly singular as equilibrium is almost reached. Singular sorption–desorption isotherms of phenanthrene for geologically young soils and sediments were reported by Huang and Weber (1997) and Weber et al. (1998) when allowing equilibration times of 576 and 336 h during sorption and desorption, respectively. In case only desorption times are increased as described by Koskinen et al. (1979) while sorption time is held constant at 24 h, nonsingularity will increase until all desorption points lie on the mutual equilibrium isotherm. This procedure is simulated in the upper part of Figure 3.11 for an initial concentration of 2 mg L^{-1} . The Figure illustrates the increase in nonsingularity with increasing length of the desorption period. For a desorption period of 240 h the desorption curve bends sharply after the first desorption step and then starts to follow the equilibrium isotherm in the remaining steps as equilibrium is reached within each step.

Conclusions

Chlortoluron sorption–desorption data as well as literature data on sorption–desorption of several organic chemicals were examined using a kinetic model. All data sets showed nonsingular sorption behavior. This behavior could be readily explained by slow sorption kinetics even for the literature data sets where nonsingularity was explained by a variety of other causes before. Especially the fact that the applied two–stage model is symmetrical concerning the sorption and desorption rate of a solute illustrates the difficulties associated with the interpretation of nonsingular sorption data with regard to desorption restrictions. While sorption–desorption nonsingularity is probably not always caused by slow sorption kinetics awareness must be increased that data should be carefully tested to exclude kinetic effects. Verifying that sorption equilibrium is reached during sorption by means of a rate study may be difficult due to experimental limitations in detecting very small concentration changes during slow solute uptake. Using a model to estimate kinetic parameters on one set of data and then testing the model in a predictive mode for another set of data may be more precise in the identification of true nonsingularities. Only if kinetic effects can be excluded it is reasonable to speculate on other causes. The application of a kinetic model should therefore become a routine procedure in future investigations of nonsingular sorption–desorption data.

Chapter 4

Nonequilibrium Sorption of Organic Chemicals – Compatibility of Batch and Column Techniques

Abstract This study resolves an apparent inconsistency between the dimethylphthalate (DMP) batch and column data reported by Maraqa et al. (1998). These authors found that retardation coefficients obtained by fitting a linear two-stage model to column data were about 50 % smaller than those calculated from the distribution coefficient of a 14-day isotherm. In this study, a linear and a nonlinear two-stage model were fitted simultaneously to the 3- and 14-day isotherms as well as to the sorption rate study reported by Maraqa et al. (1998). With the estimated set of rate parameters and the dispersion coefficient obtained from a tritium tracer experiment, the transport model was able to predict the column data adequately. It is demonstrated that the differences in the retardation coefficients observed by Maraqa et al. (1998) result from the experimental difficulties in detecting the tailing of nonequilibrium breakthrough curves. While it has been known that lack of tail data leads to an underestimation of R from moment analysis, the same problem seems to affect curve fitting as complete tail data is crucial in estimating R as well as sorption rate parameters.

Introduction

Organic contaminants are introduced into the subsurface through diffuse sources such as regionally applied agrochemicals as well as point sources including accidental spills, hazardous waste sites or landfills. Development of remedial actions to deal with these contaminants requires understanding the physical, chemical, and biological processes affecting their mobility. Among these processes, sorption is believed to be a very important mechanism that dramatically influences their environmental fate. At the laboratory-scale, batch or packed column experimental techniques are commonly employed to gain insight into sorption behavior of organic chemicals. Results obtained from the laboratory are then utilized to predict actual transport in the field. Batch and column results have been found to agree in some cases (e. g. Lee et al., 1988; MacIntyre et al., 1991; Gaber et al., 1992). However, a disagreement of the results has been found in others (e. g. Bilkert and Rao, 1985; MacIntyre and Stauffer, 1988; Piatt et al., 1996). Disagreement has been attributed to different causes such as loss of sorbent from the column, variations in column flow, immobile water in the column (MacIntyre et al., 1991), mixing differences between the two methods (Schweich et al., 1983), reduction in soil particle spacing in the column compared to batch systems (Celorie et al., 1989), different soil/water ratios (Karickhoff and Morris, 1985), and the possibility of soil abrasion in batch experiments (Boesten, 1986). An often neglected cause, however, is the failure to reach sorption equilibrium within the experimental time scale. This can have serious implications on the interpretation of data obtained by both techniques.

With many nonionic organic chemicals, sorption equilibrium is not reached within the experimental period for typical batch or column experiments (Streck et al., 1995). If sorption equilibrium is falsely assumed, erroneous "equilibrium" constants that are lower than the true equilibrium values will be estimated (Brusseu et al., 1991). A direct estimation of the equilibrium constant is difficult as equilibration may take several weeks, months, or possibly years (Ball and Roberts, 1991). To overcome this problem inverse modeling can be used to estimate sorption rate and equilibrium parameters from column or batch data.

In batch experiments, slow sorption rates result in continuously decreasing solute concentrations even after the typical time span of the experiment. In the column experiments, slow sorption or desorption rates lead to pronounced tailing

of the breakthrough curves. For the case of a pulse input, the column experiment is terminated when the quantification limit of the target chemical is reached. Breakthrough curves may lack much of the tail data although most of the solute has actually been recovered. Sorption parameters estimated by inverse modeling of batch and column data are therefore subject not only to random errors but also to errors caused by the necessity to use a truncated set of data that are specific to the experimental technique employed.

Most studies that found deviating sorption parameter values between batch and column experiments are limited to comparisons of parameter sets obtained from each experimental technique (MacIntyre and Stauffer, 1988; Lion et al., 1990; Piatt et al., 1996). However, as batch and column techniques differ considerably, the errors in estimated sorption parameters that are associated with slow sorption rates may be negligible in one system while being quite large in the other. This can be tested by the independent prediction of data obtained with one experimental technique using sorption parameters obtained by fitting a sorption rate model to the respective other set of data. Only if both procedures fail is it conclusive that causes other than slow sorption rates are responsible for the observed discrepancy between the two techniques.

The column and batch data reinvestigated in this study were presented by Maraqa et al. (1998) who studied the sorption and transport of DMP in two soils. They found that batch data could not be predicted with sorption rate parameters estimated from column data. Retardation coefficients determined from column experiments were 50 % smaller than those determined from batch experiments. By additional experiments they could exclude experimental causes given frequently to explain differences in batch and column data. The reason for the observed discrepancy remained unclear. In this study, I will resolve this discrepancy by showing that DMP transport in the soil columns can be described adequately with parameters estimated from batch experiments.

Methods

I limit the description of the isotherm studies, the sorption rate studies and the column experiments to the main features of each experiment. More details are given in Maraqa et al. (1997, 1998). The soils had been collected from the A and B horizons of Oakville sand (mixed mesic Typic Udipsamment) located in North Star, MI. The organic carbon contents of the A and B horizons were 2.25 % and 0.7 %, respectively. The soils were air dried and ground to pass through a 0.85 mm sieve. Experimental solutions were prepared by dissolving DMP in 0.005 *M* CaCl₂ containing 0.05 % sodium azide to avoid biodegradation. Chemical analysis of DMP was carried out using high-performance liquid chromatography (HPLC) with UV detection.

Batch experiments

Batch experiments included a 14-day rate study and a 3- and 14- day sorption isotherm measured for each soil. In all experiments the soil to solution ratio was $\approx 1:1.5 \text{ g mL}^{-1}$. The rate study was carried out at an initial concentration of $\approx 20 \text{ mg L}^{-1}$. For the isotherms, the initial concentration varied from $\approx 5 \text{ mg L}^{-1}$ to $\approx 140 \text{ mg L}^{-1}$. The experiments were carried out in 25 mL Corex[®] centrifuge tubes with Teflon[®]-lined screw caps. The tubes were tumbled end over end for the desired period of time and then centrifuged at 1250 *g* for 30 min. Aqueous samples were collected with glass syringes and analyzed for DMP. The amount sorbed by the soil was determined by difference. Blanks were prepared to verify that sorption to the tubes and caps could be excluded.

Column experiments

The soils used in the saturated-flow column experiments were packed into glass columns (5.45 cm i.d.) of 30.2 cm length with Teflon[®] plates on each end. A pulse input of approximately two pore volumes of a 30 mg L⁻¹ DMP solution was injected into the columns with three different velocities. The columns were then eluted at the originally applied flow rates with a DMP-free 0.005 *M* CaCl₂-azide solution. Effluent samples were collected with glass syringes attached to

the outlet of the column. No evidence of DMP sorption was detected when a miscible–displacement experiment was conducted on a column packed with glass beads.

Modeling

Model description

Sorption of DMP in the two soils was investigated with a two–stage model. Models of this type are frequently used to describe nonequilibrium sorption of organic chemicals and have often been found to work best when describing slow sorption rates (Pignatello, 1989). I assume slow sorption to be caused by a diffusive uptake of solute into soil organic matter. This process is simplified by assuming that solute is transferred into two serially arranged regions within the sorbent one of which is in direct contact with the surrounding solution. The sorbate concentrations in these two regions, S_1 and S_2 (mg kg^{-1}), are defined per unit sorbent mass in region 1 and 2, respectively. The difference in concentration between the two regions is considered the driving force for sorption and desorption processes, with the rate assumed proportional to the respective concentration difference. In region 1, sorption is fast relative to the duration of the experiment so that equilibrium can be assumed:

$$S_1 = kC^m \quad (1)$$

In contrast, sorption in region 2 is assumed to be rate–limited:

$$(1 - f) \frac{\partial S_2}{\partial t} = \alpha(kC^m - S_2) \quad (2)$$

where C is the concentration of dissolved chemical (mg L^{-1}), the parameters k ($\text{mg}^{1-m} \text{L}^m \text{kg}^{-1}$) and m denote the Freundlich equilibrium parameters, α is the sorption rate coefficient (d^{-1}), f is the fraction of region 1 sites, and t is time (d). The total concentration of the sorbed solute S (mg kg^{-1}), is given by

$$S = fS_1 + (1 - f)S_2 \quad (3)$$

At equilibrium, the model predicts the same concentration in both fractions of the solid phase:

$$S = S_1 = S_2 = kC^m \quad (t \rightarrow \infty) \quad (4)$$

S_1 and S_2 can be related to the sorbed-phase concentrations defined per unit mass of the total sorbent (e. g. Brusseau and Rao, 1989b) by $S_{t1} = fS_1$ and $S_{t2} = (1 - f)S_2$. Equation (2) may then be rewritten:

$$\frac{\partial S_{t2}}{\partial t} = k_2((1 - f)kC^m - S_{t2}) \quad (5)$$

With $m = 1$, the governing equations reduce to the linear two-site model used by Maraqa et al. (1998). In this case, the coefficient k is commonly denoted k_D . The rate coefficient k_2 is related to α by $k_2 = \alpha/(1 - f)$.

Parameter Estimation on Batch Data

The 3- and 14-day isotherms, as well as the 14-day rate-study may be combined to one rate study with samples shaken for various periods of time at different concentrations. Due to the inclusion of isotherm data, the set is biased concerning information on solute partitioning after 3 and 14 days while for sorption times before and between these times information is only available from the rate study. Assuming negligible decay, the total concentration

$$C_t = \theta C + \rho S \quad (6)$$

in a closed batch reactor remains constant ($dC_t/dt = 0$). Here, ρ is the bulk density and θ is the volumetric water content. The sorption rate equation can then be written as

$$(\rho f m k C^{m-1} + \theta) \frac{\partial C}{\partial t} = \frac{\alpha}{(1 - f)} [C_t - \theta C - \rho k C^m] \quad (7)$$

In a rate study with a sorbent initially free of solute, Equation (7) is subject to the initial condition $C(0) = C_0$ which is derived by solving

$$C_t = \theta C_0 + \rho f k C_0^m \quad (8)$$

The nonlinear form of Equation (8) was solved for C_0 using the Newton algorithm. Equation (7) was numerically solved by the Bulirsch–Stoer method (Press et al., 1989) in all cases. S_1 can then be derived using Equation (1). Following this S_2 can be calculated via mass balance. The model was fitted to measured data using the Levenberg–Marquardt algorithm (Press et al., 1989) and assuming a multiplicative error model (Streck et al., 1995).

Modeling of Column Data

Assuming convective–dispersive solute transport in a homogeneous soil column with constant water content and flux, negligible decay, and slow two–stage sorption the governing transport equation may be written as

$$\left(1 + \frac{\rho}{\theta} f k_m C^{m-1}\right) \frac{\partial C}{\partial t} + \frac{\rho}{\theta} (1 - f) \frac{\partial S_2}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + v \frac{\partial C}{\partial z} \quad (9)$$

where z denotes depth (positive downward), D is the dispersion coefficient ($\text{cm}^2 \text{d}^{-1}$), and v the average pore water velocity (cm d^{-1}). Equation (9) is coupled with the sorption rate equation (2) through $\partial S_2 / \partial t$. The following initial and boundary conditions were assumed (pulse input):

$$C(z, 0) = 0 \quad (10)$$

and

$$J_w C(0, t) - D \theta \left. \frac{\partial C(z, t)}{\partial z} \right|_{z=0+} = \begin{cases} J_w C_i & : 0 < t < t_i \\ 0 & : \text{otherwise} \end{cases} \quad (11)$$

Equation (9) was solved numerically using a fully implicit finite difference scheme in combination with the Newton–Raphson algorithm. Transport and sorption equations were coupled by iteration. For the linear case ($m = 1$), the numerical solution was tested against a semi–analytical solution (see Streck et al. (1995) for details of this procedure) before the DMP column experiments were modeled.

Results and Discussion

Combined plots of the 3– and 14–day isotherms of DMP in Oakville A and Oakville B soils, together with the data from the rate studies, are shown in Figure 4.1. In addition the figure shows simulation results obtained by fitting the linear and nonlinear form of the two–stage model to the data. The simulation results for Oakville A soil presented in the upper panel were estimated by fitting both models simultaneously to all data. For the Oakville B soil, however, the rate study in the lower panel of Figure 4.1 is not consistent with the isotherm data. The last point of the rate study which corresponds to a sorption period of 14 days does not coincide with the 14–day isotherm, although the time dependent partitioning should be the same at similar equilibration times. The same holds true for the rest of the rate

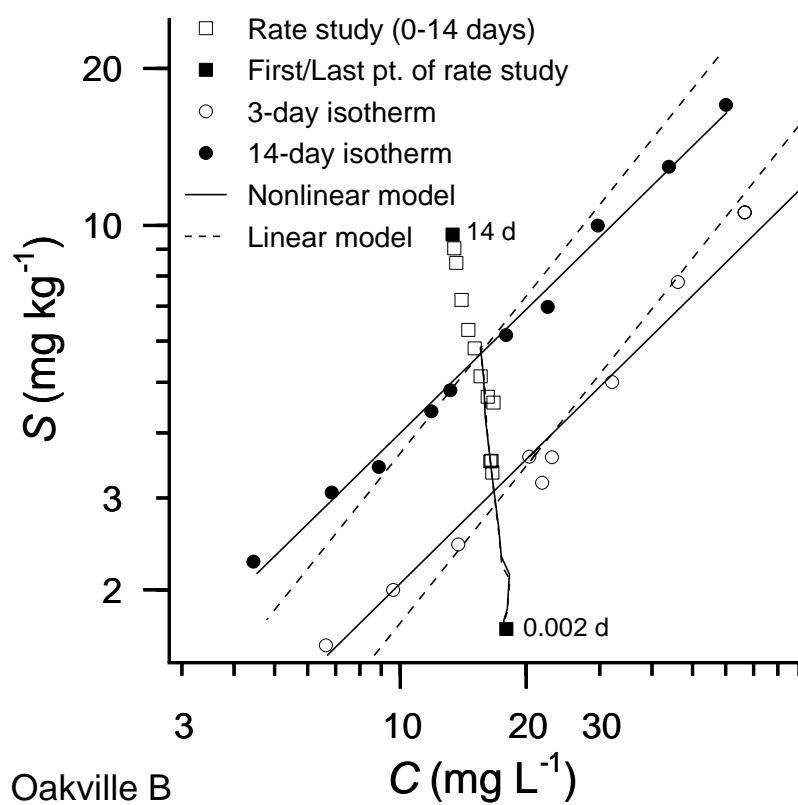
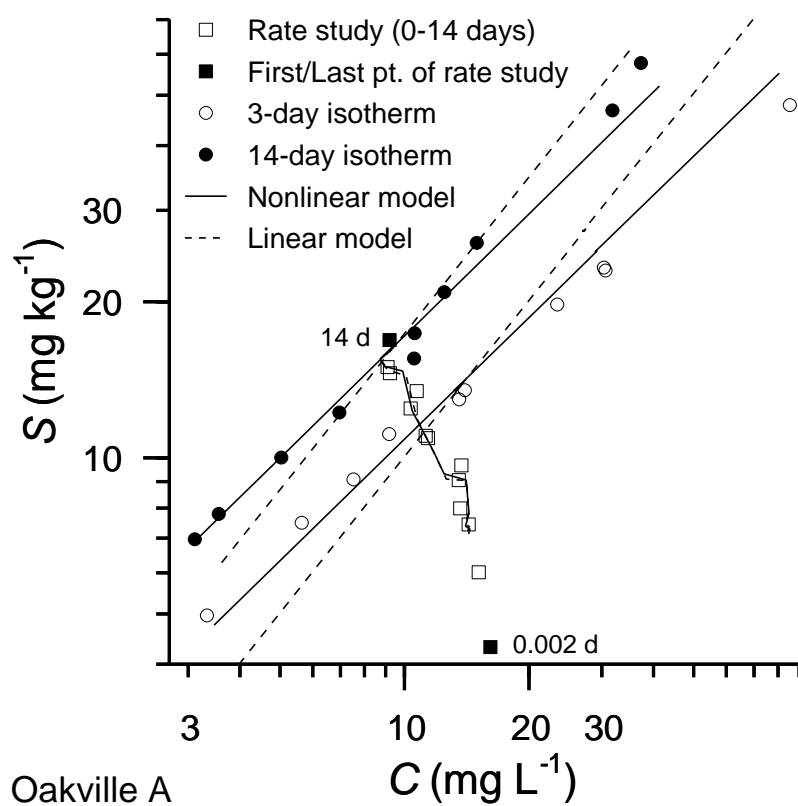


Figure 4.1: Measured and simulated batch data for DMP on Oakville A and B soils. Simulations were carried out with the linear and nonlinear two-stage model.

study starting with the second data point corresponding to a sorption period of 0.5 h. Despite shorter equilibration times sorption is enhanced as compared to sorption after 3 and 14 days in the isotherm study. I therefore limited the model fit to the isotherm data and the first data point of the rate study. The corresponding simulation results (including a simulation of the rate study with this set of parameters) are shown in the lower panel of Figure 4.1. Sorption rate parameters of the linear and nonlinear models are listed for both soils in Table 4.1. The fit was slightly improved by using the nonlinear form of the model. Note that fluctuations of the rate study simulations are caused by variations in the experimental soil to solution ratio as well as differences in initial concentrations. k and k_D listed in Table 4.1 are 17 to 71 % higher than the respective values calculated by Maraqa et al. (1998) for the 14-day isotherms. This indicates that after 14 days sorption equilibrium is not reached in either soil.

Sorption parameters, derived from independent batch experiments, were utilized to predict transport of DMP through Oakville A and B soil columns under the three flow conditions reported by Maraqa et al. (1998). For each experiment, the hydrodynamic dispersion coefficient (D) had been estimated from a tracer experiment with tritium (Maraqa, 1995; Maraqa et al., 1997) which was concurrently injected with DMP into the soil columns. The input concentration C_0 , the flow velocity v and the bulk density ρ of each column were either set or measured experimentally. I emphasize that none of the necessary transport parameters was

Table 4.1: Sorption rate parameters estimated from the batch experiments assuming a multiplicative error model. The approximate standard error (SE) of each parameter is also listed.

Soil	Linear model							
	α	SE	f	SE	k_D	SE		
	(d ⁻¹)				(L kg ⁻¹)			
Oakville A	0.102	0.029	0.279	0.040	1.819	0.128		
Oakville B	0.054	0.075	0.182	0.058	0.519	0.337		
	Nonlinear model							
	α	SE	f	SE	k	SE	m	SE
					(mg ^{1-m} L ^{m} kg ⁻¹)			
Oakville A	0.123	0.019	0.305	0.027	2.893	0.191	0.785	0.027
Oakville B	0.078	0.029	0.221	0.025	0.780	0.095	0.792	0.020

obtained by fitting the model to DMP breakthrough data. Predicted and experimental results for Oakville A and B soils are shown for in Figures 4.2 and 4.3, respectively.

Using the 14-day distribution coefficients presented by Maraqa et al. (1998) breakthrough curves based on the local equilibrium assumption (LEA, Valocchi, 1985) are also presented. As evident from the rate study, as well as the difference between the 3- and 14-day isotherms, (Figure 4.1) the LEA is not justified. The nonlinear model predicted the measured breakthrough best, however, the linear model is only slightly less successful in data prediction. Better results were obtained for Oakville B soil. The model was least successful in describing breakthrough data with Oakville A soil at the lowest velocity.

In the case of linear sorption the retardation coefficient R is defined as

$$R = 1 + \frac{\rho k_D}{\theta} \quad (12)$$

Maraqa et al. (1998) estimated R for each column experiment using three different methods: (a) moment analysis, (b) fitting a linear two-site model using the CXTFIT program (Parker and van Genuchten, 1984) to breakthrough data and (c) calculation using the distribution coefficient estimated from the 14-day isotherms. It can be seen from Table 4.2 that R increases in the same order. While the difference between R determined by moment analysis and curve fitting is small there is a large difference between both values and that determined by means of the 14-day distribution coefficient. Although the retardation coefficients determined by fitting the linear two-stage model to batch data (this study) are even larger than those estimated by Maraqa et al. (1998) from the 14-day isotherms our values are able to predict the column data adequately. Underestimation of R determined from the column experiments compared to R determined from batch data was nearly independent of the time-scale of the column experiment. As the time-scale of the rate study and the slowest column experiment is similar (14 days), the batch technique seems to be preferable for the determination of R in both soils.

It has been shown, through this work, that a single set of sorption-related transport parameters (i. e. k_D , f and α) can be used to satisfactorily describe transport of DMP through sandy soil columns independent of pore-water velocity. Compare this to what has been reported by Maraqa et al. (1998) regarding the dependence of R (or k_D) on average pore-water velocity of DMP on

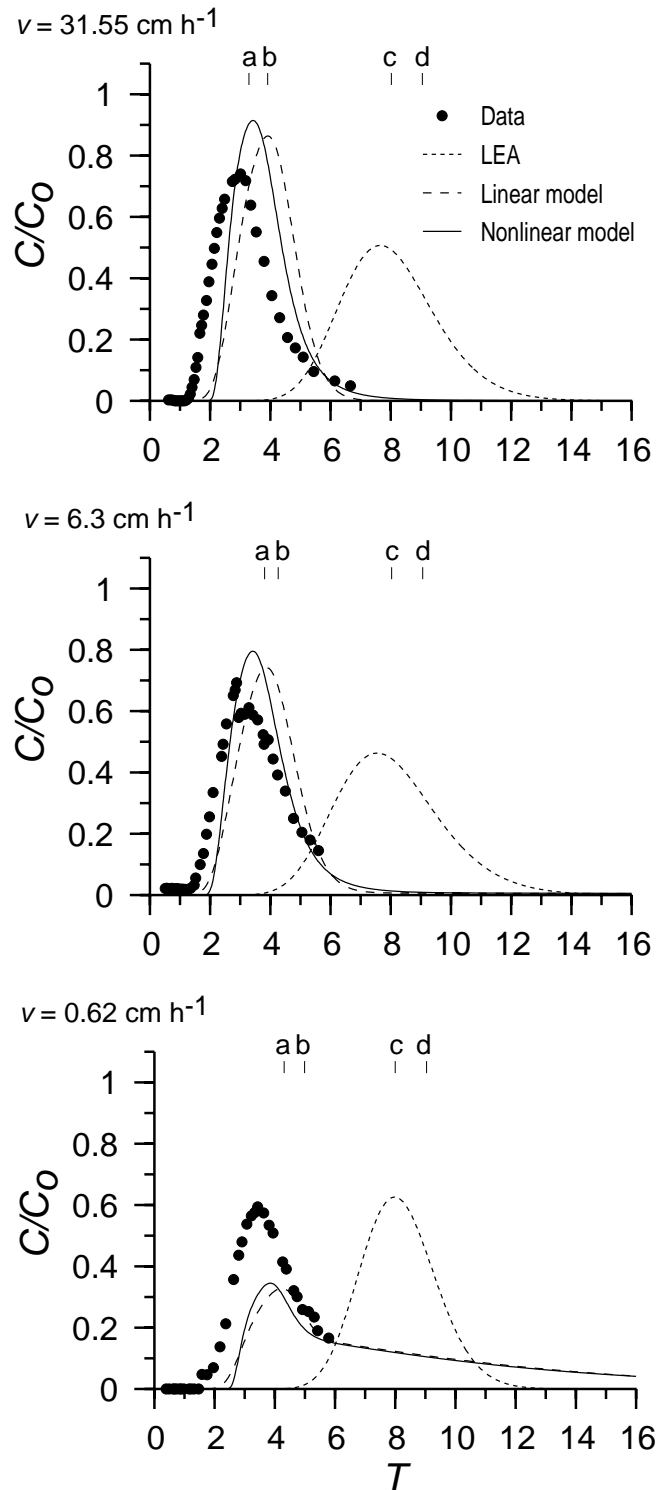


Figure 4.2: Measured and simulated breakthrough curves of DMP column experiments with Oakville A soil. The simulated breakthrough curves were estimated using the parameter set given in Table 4.1. The LEA breakthrough curves were calculated with the 14-day distribution coefficient given by Maraqa et al. (1998). The letters in each figure denote first moments $E[T]$ calculated from (a) the measured curve, (b) fitting CXTFIT to measured data, (c) the 14-day distribution coefficient (all given by Maraqa et al. (1998)) and (d) the parameters of the linear two-stage model estimated from the batch data (this work).

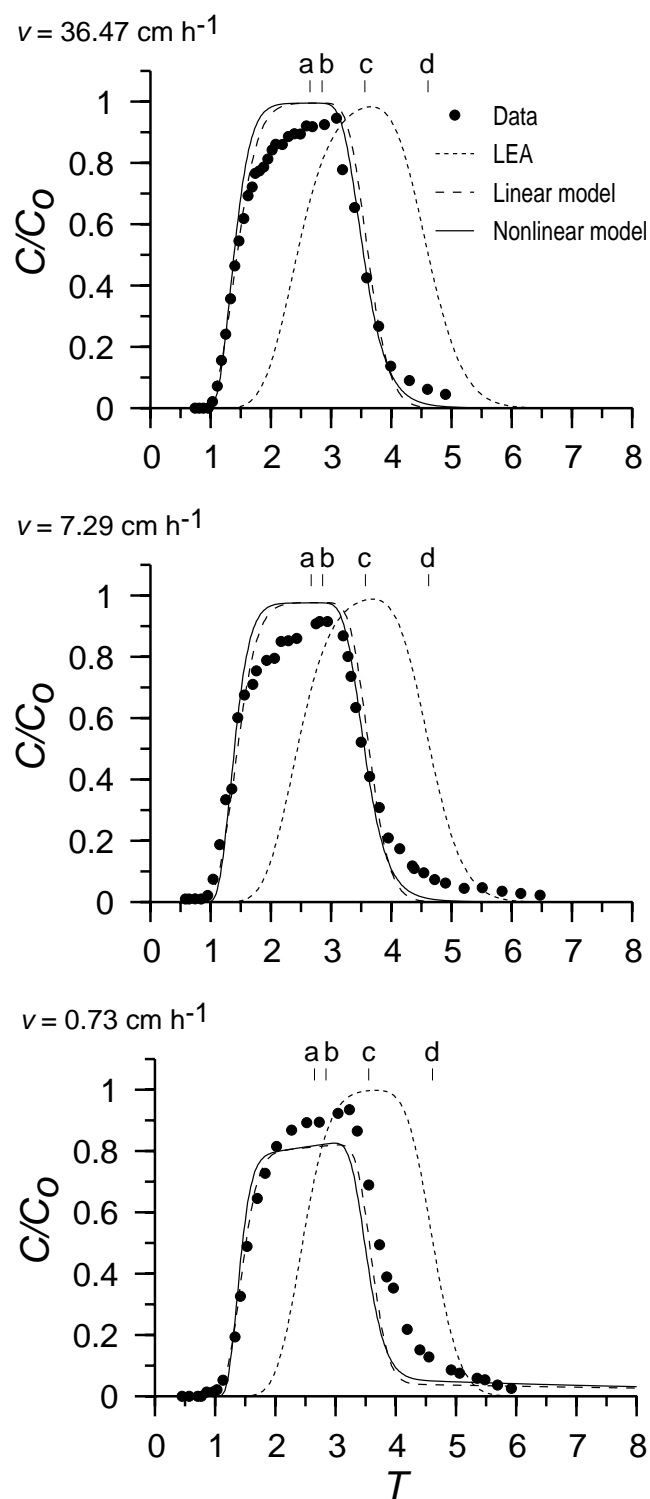


Figure 4.3: Measured and simulated breakthrough curves of DMP column experiments with Oakville B soil. For further information see caption of Figure 4.2.

Oakville A soil. Also, several investigators including Maraqa et al. (1999) and Brusseau (1992) reported a functional relationship between mass-transfer coefficient and average pore–water velocity. With these unexpected results, modelers of subsurface contaminant transport are faced with a real challenge in transferring laboratory–determined parameters to field scenarios.

Differences in our retardation factors and those reported by Maraqa et al. (1998) become particularly marked if the first moments $E[T]$ of the breakthrough curves are compared. For linear sorption and a pulse input of duration T_0 , the first moment $E[T]$ was defined as (Maraqa et al., 1998)

$$E[T] = R + \frac{T_0}{2} \quad (13)$$

where T is the dimensionless time given by $T = vt/L$, with L being the column length. The first moments $E[T]$ are denoted by letters in Figures 4.2 and 4.3, and were estimated from the respective retardation coefficients given in Table 4.2. While the first moment and the peak maximum of the corresponding breakthrough curve agree closely for cases (a), (b) and (c) there is a large shift of the first moment of the breakthrough curve simulated with the rate parameters (d) obtained independently from batch experiments (The breakthrough curves obtained

Table 4.2: List of batch and column determined retardation coefficients for DMP sorption on Oakville A and B soils together with experimental and simulated percent recovery rates based on the linear model

Experiment					% Recovery	
	R_{moment}	$R_{\text{curve fit}}$	$R_{14 \text{ day iso.}}$	$R_{\text{batch fit}}$	(Measured)	(Simulated)
A1 ($v=31.55 \text{ cm h}^{-1}$)	2.32	2.95	7.04	8.07	88.2	97.1
A2 ($v=6.3 \text{ cm h}^{-1}$)	2.83	3.28	7.04	8.07	90.3	83.7
A3 ($v=0.62 \text{ cm h}^{-1}$)	3.35	4.03	7.04	8.07	82.0	39.4
B1 ($v=36.47 \text{ cm h}^{-1}$)	1.50	1.85	2.47	3.52	94.7	99.5
B2 ($v=7.29 \text{ cm h}^{-1}$)	1.51	1.70	2.47	3.52	98.1	97.8
B3 ($v=0.73 \text{ cm h}^{-1}$)	1.71	1.73	2.47	3.52	99.5	86.2
First moment in Figures 4.2 and 4.3 denoted by:	a	b	c	d		

by CXTFIT (case b) are not shown in Figures 4.2 and 4.3, however, they nearly coincide with the measured data). Since the first moment of a breakthrough curve is independent of kinetic limitations (Valocchi, 1985; Streck and Piehler, 1998) the simulated curve in case (d) is accompanied by extensive tailing to account for the large shift between $E[T]$ and peak maximum.

Experimentally it would be very difficult to identify this tailing in the breakthrough curves of DMP on Oakville A and B soils since the measurement has to be terminated when the quantification limit of the solute is reached. Table 4.2 shows the simulated mass recovery calculated for the experimental duration of each measured breakthrough curve. The simulated mass recovery varies between 83.7 and 99.5 % with the exception of the low velocity experiment (A3 in Table 4.2) where the simulated recovery is only 39.4 %. The experimental recovery for the measured curves varies between 82.0 and 99.5 % (Table 4.2). With the exception of experiment A3, the simulated and experimental recoveries are reasonably close. While most of the solute has leached from the columns, low concentration tailing can continue for extended periods of time. The extrapolation of data to account for the effect of tailing (Maraqa et al., 1998) would be difficult and subject to high uncertainty. Small experimental errors in the recovered solute will lead to larger errors in the calculation of the small solute mass which remains in the column and is needed for extrapolation. Any parameter estimation by moment analysis of data, e. g. the independent estimation of R which is often practiced to reduce the number of fitted parameters when applying a kinetic transport model, is then impossible (Lee et al., 1991; Brusseau, 1992; Piatt and Brusseau, 1998). Maraqa et al. (1998) noted that tailing of breakthrough curves limits moment analysis of data. Furthermore, these limitations are also very likely to apply to parameter estimation by inverse modeling. It can therefore be concluded that there are severe practical limitations to estimating rate parameters using column experiments in the case of slow to very slow sorption.

To further illustrate these problems, Figure 4.4 shows the effect of pore water velocity on breakthrough curves for a given set of sorption rate parameters. The figure shows simulated breakthrough curves at six different flow velocities v using the parameter set describing linear sorption on Oakville B soil (Table 4.1). For

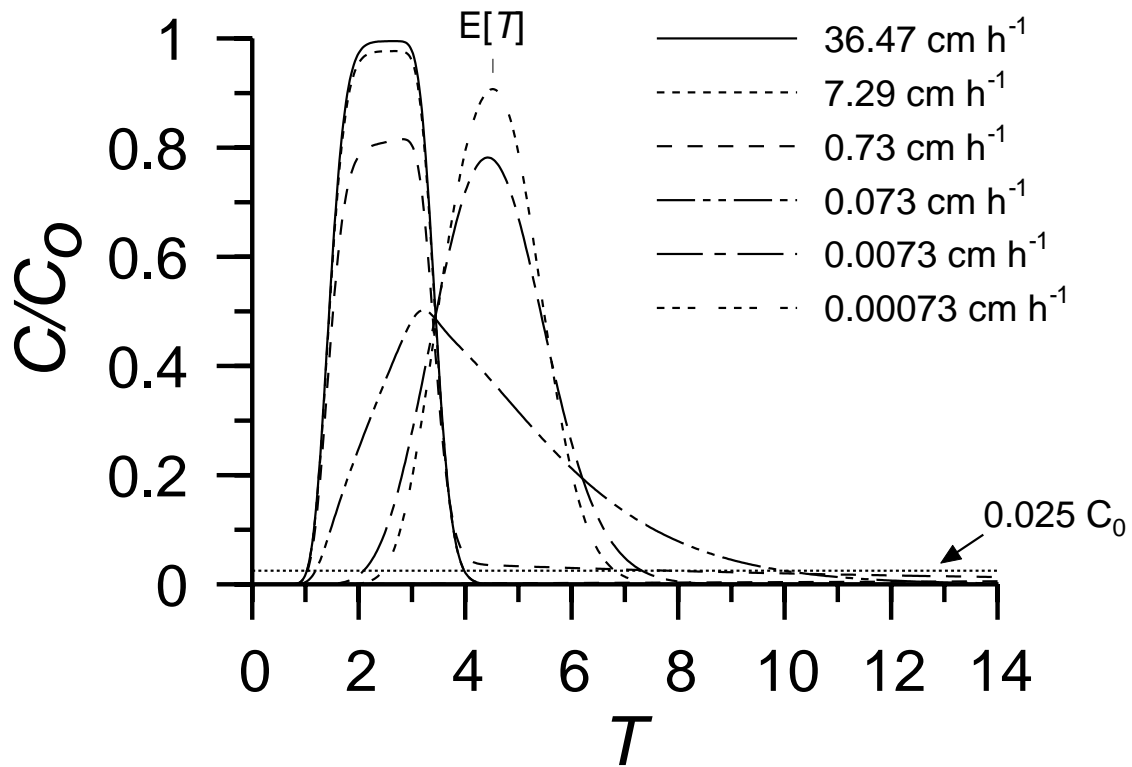


Figure 4.4: Simulated DMP breakthrough curves at six different flow velocities using sorption rate parameters estimated for Oakville B soil. The quantification limit used to calculate recovery in Table 4.3 is also shown. The experimental conditions chosen for the three highest flow velocities are the same as those of the experiments B1, B2 and B3 (figure modified after Selim et al. (1976)).

all simulations, I assumed a constant Peclet number ($P = vL/D$) of 80 and a pulse input of 2 pore volumes. The conditions chosen for the first three simulated curves were the same as those of the column experiments with Oakville B soil. When plotted against dimensionless time (Figure 4.4), the first moments of all curves, $E[T]$, coincide regardless of pore water velocity. At the three highest pore water velocities the location of the peak is mainly determined by the equilibrium sorption sites. The rate-limited sites play only a minor role in the leaching of the main mass of solute. However, leaching of solute desorbed from the rate-limited sites continues for a long time at low concentrations, thus producing the deviation between peak maximum and first moment. While for the two highest velocities Figure 4.4 does not resolve tailing, extreme tailing is visible for the breakthrough curve at 0.73 cm h^{-1} . At a pore water velocity of 0.073 cm h^{-1} sorption nonequilibrium has the largest influence on breakthrough curve shape. At the lowest

Table 4.3: Characteristics of the simulated breakthrough curves in Figure 4.4. $\text{VAR}(T)$, ω , and ϵ denote variance, Damkhler number, and percentage fraction of variance due to kinetic sorption, respectively.

v (cm h ⁻¹)	36.47	7.29	0.73	0.073	0.0073	0.00073
approximate duration of the experiment	12 h	2.4 d	24 d	8 mo	6.5 yr	65 yr
$\text{VAR}[T]$	1798.96	361.44	38.27	5.91	2.67	2.35
ω	0.0047	0.0235	0.2345	2.3454	23.454	234.54
ϵ	77185	15548	1557	155.7	15.57	1.56
% recovery assuming a quanti- fication limit of 0.025 C_0	99.4	97.6	87.7	98.0	99.5	99.6

velocities the solute approaches local equilibrium conditions even at the nonequilibrium sites.

Experimentally velocities of 0.073 cm h⁻¹ or lower are rather impractical from the experimenter's point of view. With a velocity of 0.073 cm h⁻¹ the experiment would have lasted about 8 months (see Table 4.3) using a 30.2-cm column. Experimental velocities of column studies with nonionic organic chemicals are most often one to three orders of magnitudes higher (MacIntyre and Stauffer, 1988; Lee et al., 1991; Brusseau et al., 1991a; Piatt et al., 1996). Lower flow velocities were used in the experiments of Gaber et al. (1992) (0.17 cm h⁻¹) and Larsen et al. (1992) (0.11 cm h⁻¹). Interestingly, these authors found agreement between retardation coefficients derived from batch experiments with those from column experiments. In contrast, MacIntyre and Stauffer (1988) and Piatt et al. (1996) who used pore water velocities of 2.23 to 28.5 cm h⁻¹ and of 27 cm h⁻¹, respectively, found increased retardation coefficients in batch studies, in agreement with the observations of Maraqa et al. (1998) discussed here. This may be attributed to the difficulties in the identification of tailing.

The importance of tailing can be further evaluated by comparing the variances of the breakthrough curves. For the linear two-stage model the variance of a breakthrough curve corresponding to a pulse input of duration $T = T_0$ can be

written as (cf. Valocchi, 1985, and Streck et al., 1995)

$$\text{VAR}[T] = \frac{2R^2}{P} + \frac{2(1 - \beta)^2 R^2}{\omega} + \frac{T_0^2}{2} \quad (14)$$

where

$$\beta = (\theta + f\rho k_D)/(\theta + \rho k_D) \quad (15)$$

$$\omega = \alpha(R - 1)\frac{L}{v} \quad (16)$$

The term $1 - \beta$, characterizes the amount of solute bound to kinetic sites normalized to the total amount of solute in the solid and liquid phase at equilibrium. The Damkhler number ω represents the ratio of the residence time of a sorptive solute (minus residence time of a tracer) to reaction time. The variances and Damkhler numbers of the simulated breakthrough curves in Figure 4.4 are listed in Table 4.3. For the experiment with the highest pore water velocity, the variance is about 800 times larger than for the lowest flow velocity. Only in the experiment at the lowest velocity the Damkhler number is > 100 and, according to Brusseau et al. (1991), LEA would be justified. Relying on ω when deciding which model to use may however not be sufficient. The parameter ω does not account for the relative significance of rate-limited sorption under various experimental conditions. A better criterion is the percentage ratio of variance due to kinetic sorption to variance to equilibrium sorption and length of pulse input (Valocchi, 1985):

$$\epsilon = \frac{2(1 - \beta)^2 R^2 / \omega}{\frac{2R^2}{P} + \frac{T_0^2}{2}} \cdot 100 \quad (17)$$

The values of ϵ are listed in Table 4.3. Setting the critical value to 10%, only the experiment at the lowest flow velocity may be modeled with LEA. Although this agrees with the results found for a critical Damkhler number of 100, Equation (17) shows that ϵ is not only a function of ω but also of the pulselength and the Peclet number P . Equation (17) can be rearranged to yield:

$$\omega\epsilon = \frac{100}{\frac{1}{(1 - \beta)^2 P} + \left(\frac{T_0}{2(1 - \beta)R}\right)^2} \quad (18)$$

Note that $\omega\epsilon$ is equal to the Damkhler number for $\epsilon = 1$. The product $\omega\epsilon$ is plotted as a function of pulselength and P in Figure 4.5. The figure reveals that there is no critical value of ω which, if exceeded, justifies the use of a LEA model. Especially

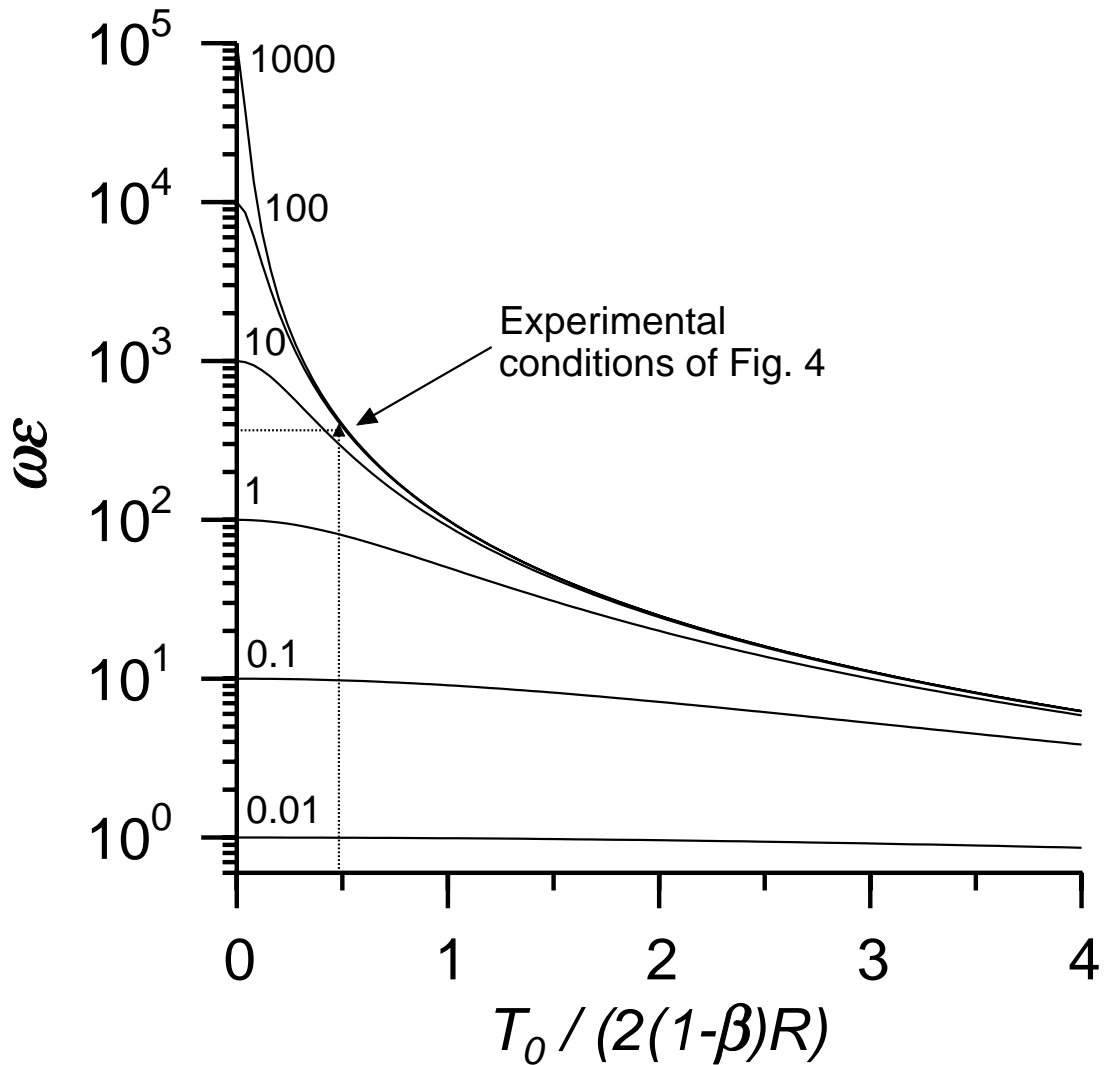


Figure 4.5: Dependence of the product $\omega\epsilon$ on pulse length and Peclet number. ω denotes the Damkhler number while ϵ is the percentage fraction of variance due to kinetic sorption. Numbers on curves indicate values of $(1 - \beta)^2 P$.

at high P 's and low pulse input length, large values of ω are required in order to ensure that the percentage of variance due to kinetic sorption remains small.

In addition Table 4.3 shows the simulated recoveries of each experiment assuming a quantification limit of $0.025 C_0$. The recovery at the highest and lowest flow velocity is almost the same although the high velocity experiment exhibits extreme tailing. The lowest recovery was calculated for the experiment at an intermediate velocity of 0.73 cm h^{-1} where tailing is associated with rather high concentration, so that a large fraction of the total mass is leached during tailing. However, according to the variance tailing in this experiment is less extreme than

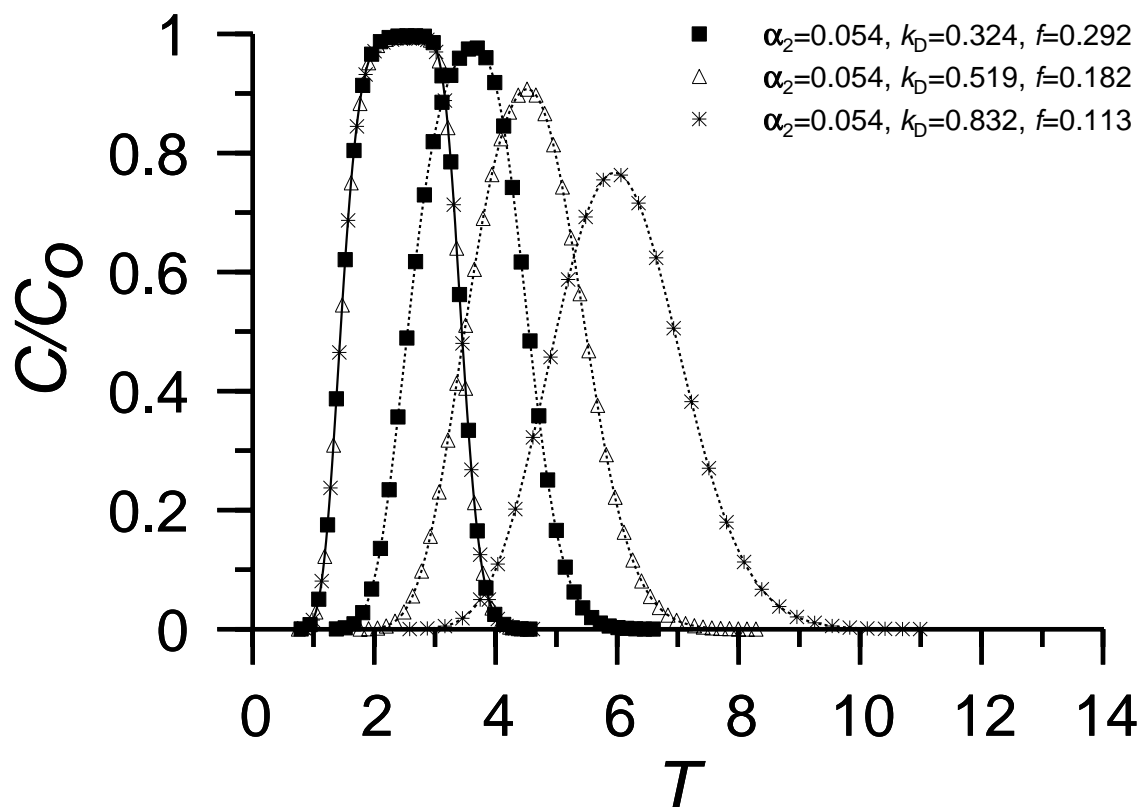


Figure 4.6: Simulated breakthrough curves calculated for three sets of linear sorption rate parameters at two pore water velocities. Solid lines represent curves at a pore water velocity of 36.47 cm h^{-1} while the dotted lines represent curves at $0.00073 \text{ cm h}^{-1}$. The second set of parameters is identical to that given for DMP sorption to Oakville B soil in Table 4.1. The first and last set of parameters were obtained by varying f while keeping the product $f k_D$ constant.

in the experiment with the highest flow velocity. The assumed quantification limit of $0.025 C_0$ is plotted in Figure 4.4 to indicate the tails unaccounted for. In the light of these results, the assumption that a high recovery at a given quantification limit is an indicator for the lack of tailing (Lion et al., 1990; Maraqa et al., 1998), is erroneous.

Figure 4.6 demonstrates that the difficulties associated with estimating first and second moment from data exhibiting extreme tailing also apply when parameter identification is attempted by fitting a kinetic model to such data. The figure demonstrates simulated experiments at two flow velocities, 36.47 and $0.00073 \text{ cm h}^{-1}$. The experimental conditions are identical to the breakthrough curves at highest and lowest velocity in Figure 4.4. The second parameter set given in the legend is identical to that estimated with the linear model on Oakville B soil batch data. The two other sets were produced by varying f while $f k_D$ was kept con-

stant. This results in the sorption capacity of equilibrium sites remaining constant, the capacity of rate-limited sites is decreased for the first set and increased for the last set. Since the equilibrium sites dictate the shape of breakthrough curves at high flow velocities the curves almost coincide, despite the fact that their variances range from 306 to 2550. In contrast, at the low flow velocity, the curves are very different due to the influence of rate-limited sites.

Finding a unique solution by fitting a kinetic model to experimental breakthrough data at the high flow velocity is unlikely. This problem was also pointed out by Toride et al. (1995) who recommended that, at minimum, the distribution coefficient k_D should be determined independently. However, this approach is impractical as in the case of slow sorption rates, equilibrium is not reached within a practical time period for batch experiments. An alternative approach would be to independently estimate all sorption parameters by inverse modeling of a batch rate experiment, as demonstrated above. This strategy has been applied previously by Streck et al. (1995) who successfully predicted simazine transport in a lysimeter experiment with rate parameters obtained from a batch study.

Conclusions

Differences in retardation coefficients determined by batch- and column experiments (Maraqa et al., 1998) could be related to the analytical difficulties in determining the extensive tailing of breakthrough curves. As demonstrated by simulations, the information on tailing is crucial when nonequilibrium sorption parameters are to be estimated by fitting a transport model to breakthrough curves. The lack of tail data in the column experiments led to an underestimation of R by up to 60 % as compared to the value obtained by fitting the two-stage model to batch data. Underestimation of R was nearly independent of the time-scale of the column experiment. As the time-scale of the slowest column experiment is similar to the time-scale of the sorption rate experiment (14 days), the batch technique seems to be preferable in the case studied. Although the identification of very slow sorption rates is possible with column techniques (Figure 4.4), these experiments have to be carefully designed, with flow velocities ranging over many orders of magnitude. This may though not be practicable. At similar time scales, batch techniques seem to be better suited for identifying slow sorption

kinetics as, with relatively high to intermediate flow velocities, the susceptibility of sorption rate parameter estimation to tailing is not paralleled by a similar effect in sorption rate studies.

Chapter 5

Synthesis

Synthesis

The preceding chapters have shown that unexplained phenomena associated with sorption of organic chemicals in soils may be explained by slow kinetics. The use of equilibrium models to describe and investigate measured data, still a common practice, must therefore be questioned in many cases. In this chapter I will put together the principal results of the previous chapters and then give an outlook on possible lines for future research.

Chapter 2 has shown that the wetting and drying dynamics of SOM have considerable influence on batch or column studies. The still common routine of air-drying soil before sorption experiments are carried out leads to incorrect results. The increased sorption of air-dried SOM and its slow rehydration is most probably caused by a rearrangement of the macromolecular segments in SOM during swelling and shrinking processes with changing water content. In view of the kinetic nature the use of equilibrium models such as linear, Langmuir or Freundlich isotherms to describe the sorption and desorption branches of hysteretic (or non-singular) isotherms is physically meaningless and purely descriptive. Sorption hysteresis is caused by the failure to reach sorption equilibrium within the sorption and desorption steps. Obtaining environmentally relevant sorption parameters from such data requires the investigation with a kinetic model. The easiness of applying equilibrium models can not be an argument for their validity in describing the underlying process.

Chapter 3 demonstrates that nonsingular isotherms obtained by different batch techniques can be described by a single set of sorption parameters. The ability of the two-stage model to describe previously unexplained nonsingularities is further demonstrated on three sets of literature data. All nonsingularities are successfully modeled, further verifying slow sorption. The results suggest that in many earlier studies the lack of a comprehensive sorption model to evaluate data has led to considerable confusion and much speculation on possible causes of sorption nonsingularity.

In Chapter 4 an apparent discrepancy between sorption parameters estimated by Maraqa et al. (1998) on a) batch- and b) column-data is resolved by applying the kinetic two-stage model to both sets of data. While a prediction of column data with sorption parameters obtained from a batch shows adequate agreement

the opposite strategy (e.g. predicting batch from column data) fails. The chapter illustrates that in case of slow to very slow sorption kinetics there are severe experimental limitations to column experiments. Such experiments are likely to exhibit extreme, nondetectable tailing at concentrations well below the detection limit. As the tail data are crucial for moment analysis (a common method in estimating retardation coefficients) and also when a model is fitted to column data, the applicability of column experiments for the investigation of slow sorption is limited. It is demonstrated that experimental flow velocities must vary over many orders of magnitude to allow the correct identification of slow sorption parameters. As this strategy includes very slow flow velocities (requiring experimental times of several month or years) it is rather impractical from the experimenters point of view.

It follows the results of this work, that the measurement and modeling of sorption/desorption isotherms to gain information on slow kinetics should become a routine procedure in future research on organic chemicals. Additionally, the comparison of independent model predictions with data obtained by other techniques opens up the chance to discriminate true from apparent restrictions during desorption of organic chemicals.

Being far from perfect, the two-stage model is able to describe sorption/desorption phenomena that were unexplained before. It is therefore clearly superior to the common evaluation of sorption/desorption data by equilibrium expressions. However, it is still a rather crude model for the real process and there is evidence that it is limited in its ability to describe longterm sorption processes. In this work the use of the model was limited to sorption data measured in the range of up to several weeks. It should be tested if longterm sorption over several month to several years can be identified from such data. Future research should focus on this issue, especially as it would be very useful to identify longterm behaviour from relatively short experiments which are much more practical. It is, however, likely that the model has to be extended or changed to achieve this goal.

Finally, column experiments of organic chemicals should always be accompanied by kinetic batch studies. Kinetic sorption parameters could then be obtained by fitting a kinetic model to both sets of data and tested in a predictive manner on the respective other set. By following this strategy experimental limitations concerning the investigation of kinetic behavior may be identified for each tech-

nique. Such a strategy has rarely been applied, but should also become a routine procedure in future studies.

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Data Tables

Soil mass (kg)	0.00908		
Water content (L)	0.00092		
Volume added(L)	0.02000		
Fraction of discarded solution	0.478		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20016	0.06107	0.30010
1. Des.		0.03868	0.28443
2. Des.		0.03181	0.25766
3. Des.		0.02491	0.23854
4. Des.		0.02041	0.22147
5. Des.		0.01648	0.20805
Ads.	0.40032	0.12572	0.59197
1. Des.		0.08809	0.54020
2. Des.		0.06646	0.49303
3. Des.		0.05076	0.45602
4. Des.		0.04086	0.42294
5. Des.		0.03273	0.39668
Ads.	0.60048	0.20695	0.84563
1. Des.		0.14259	0.76602
2. Des.		0.10648	0.69219
3. Des.		0.08156	0.63235
4. Des.		0.06434	0.58221
5. Des.		0.05072	0.54273
Ads.	1.10088	0.42315	1.44960
1. Des.		0.29273	1.28406
2. Des.		0.21415	1.14274
3. Des.		0.15646	1.03983
4. Des.		0.11735	0.95763
5. Des.		0.09533	0.87914
Ads.	2.00160	0.83737	2.47903
1. Des.		0.56677	2.18028
2. Des.		0.40888	1.91990
3. Des.		0.29568	1.73041
4. Des.		0.22601	1.56532
5. Des.		0.17270	1.43926

Table .1: Data of Figure 2.2 and 3.1 (upper panel).

Soil mass (kg)	0.00811		
Water content (L)	0.00189		
Volume added (L)	0.02000		
Fraction of discarded solution	0.457		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads	0.20032	0.08918	0.25333
1. Des.		0.06190	0.21699
2. Des.		0.04255	0.19291
3. Des.		0.03037	0.17332
4. Des.		0.02291	0.15599
5. Des.		0.01917	0.13784
Ads	0.40064	0.19771	0.45443
1. Des.		0.13041	0.39228
2. Des.		0.09045	0.33935
3. Des.		0.06405	0.29907
4. Des.		0.04852	0.26202
5. Des.		0.03374	0.24207
Ads	0.60096	0.29753	0.67902
1. Des.		0.18924	0.60445
2. Des.		0.13977	0.50463
3. Des.		0.09763	0.44602
4. Des.		0.07033	0.39931
5. Des.		0.05070	0.36557
Ads	1.10176	0.58214	1.14587
1. Des.		0.37543	0.98602
2. Des.		0.25372	0.85161
3. Des.		0.18438	0.72590
4. Des.		0.13196	0.64004
5. Des.		0.09389	0.58007
Ads	2.00320	1.11514	1.93032
1. Des.		0.72007	1.62168
2. Des.		0.48058	1.38021
3. Des.		0.31657	1.23032
4. Des.		0.22212	1.09490
5. Des.		0.15785	0.99449

Table .2: Data of Figure 2.2 and 3.1 (lower panel).

Soil mass (kg)	0.00904		
Water content (L)	0.00096		
Volume added(L)	0.02000		
Time (h)	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg L ⁻¹)
11	0.2	0.06607	0.28928
24		0.06107	0.30010
83		0.04657	0.33450
107		0.04334	0.34199
179		0.03412	0.36337
251		0.03240	0.36736
275		0.03134	0.36980
11	0.6	0.23357	0.78587
24		0.20695	0.84563
83		0.17238	0.92775
107		0.16179	0.95230
179		0.14343	0.99488
251		0.12987	1.02631
275		0.12182	1.04498
11	2	0.92057	2.29037
24		0.83737	2.47903
83		0.71717	2.76196
107		0.71173	2.77457
179		0.63918	2.94279
251		0.58942	3.05817
275		0.55818	3.13058

Table .3: Data of Figure 2.3 (upper panel).

Soil mass (kg)	0.00812		
Water content (L)	0.00188		
Volume added(L)	0.02000		
Time (h)	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg L ⁻¹)
11	0.19976	0.10010	0.22229
24		0.09431	0.23970
35		0.09211	0.24380
59		0.08358	0.26680
107		0.07650	0.28588
179		0.06345	0.32104
275		0.05714	0.33804
11	0.59928	0.31666	0.62277
24		0.30466	0.66031
35		0.30211	0.66198
59		0.28864	0.69825
107		0.26787	0.75423
179		0.23353	0.84673
275		0.20410	0.92605
11	1.99760	1.17179	1.76266
24		1.12476	1.90553
35		1.09190	1.97792
59		1.03810	2.12287
107		1.02904	2.14729
179		0.91604	2.45174
275		0.83755	2.66322

Table .4: Data of Figure 2.3 (lower panel).

Soil mass (kg)	0.00989		
Water content (L)	0.00011		
Volume added(L)	0.02000		
Fraction of discarded solution	0.497		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20016	0.04698	0.30912
1. Des.		0.03460	0.28680
2. Des.		0.02749	0.26627
3. Des.		0.02200	0.24964
4. Des.		0.02003	0.23142
5. Des.		0.01663	0.21809
Ads.	0.40032	0.10230	0.60130
1. Des.		0.07633	0.55068
2. Des.		0.05933	0.50808
3. Des.		0.04901	0.46908
4. Des.		0.04052	0.43680
5. Des.		0.03393	0.40923
Ads.	0.60048	0.16749	0.87341
1. Des.		0.12241	0.79573
2. Des.		0.09565	0.72640
3. Des.		0.07633	0.66899
4. Des.		0.06222	0.62053
5. Des.		0.05186	0.57868
Ads.	1.10088	0.35224	1.50946
1. Des.		0.25997	1.34096
2. Des.		0.19125	1.21785
3. Des.		0.14922	1.10998
4. Des.		0.12306	1.01232
5. Des.		0.10072	0.93335
Ads.	2.00160	0.68104	2.66198
1. Des.		0.49686	2.34793
2. Des.		0.38358	2.07596
3. Des.		0.29750	1.86321
4. Des.		0.23483	1.68988
5. Des.		0.18020	1.56356

Table .5: Data of Figure 2.4 (upper panel).

Soil mass (kg)	0.00975		
Water content (L)	0.00025		
Volume added (L)	0.02000		
Fraction of discarded solution	0.494		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20032	0.07753	0.24985
1. Des.		0.05463	0.21791
2. Des.		0.03904	0.19425
3. Des.		0.03009	0.17281
4. Des.		0.02248	0.15774
5. Des.		0.01834	0.14330
Ads.	0.40064	0.17457	0.45920
1. Des.		0.11880	0.39598
2. Des.		0.08590	0.34248
3. Des.		0.06269	0.30258
4. Des.		0.04744	0.26995
5. Des.		0.03497	0.24720
Ads.	0.60096	0.26577	0.68067
1. Des.		0.18397	0.57799
2. Des.		0.13215	0.49692
3. Des.		0.09576	0.43698
4. Des.		0.07069	0.39082
5. Des.		0.05255	0.35600
Ads.	1.09780	0.51012	1.19278
1. Des.		0.36334	0.97439
2. Des.		0.25018	0.83675
3. Des.		0.17914	0.72768
4. Des.		0.13096	0.64399
5. Des.		0.09706	0.58006
Ads.	2.00320	0.99307	2.04640
1. Des.		0.67528	1.68791
2. Des.		0.47290	1.41565
3. Des.		0.32794	1.23170
4. Des.		0.22701	1.10499
5. Des.		0.17550	0.97915

Table .6: Data of Figure 2.4 (lower panel).

Soil mass (kg)	0.01808		
Water content (L)	0.00192		
Volume added(L)	0.02000		
Fraction of discarded solution	0.456		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.19960	0.03554	0.17768
1. Des.		0.02432	0.17163
2. Des.		0.02122	0.16194
3. Des.		0.01802	0.15408
4. Des.		0.01524	0.14748
5. Des.		0.01372	0.14090
Ads.	0.39920	0.07264	0.35348
1. Des.		0.05400	0.33590
2. Des.		0.04362	0.31862
3. Des.		0.03468	0.30533
4. Des.		0.03134	0.29020
5. Des.		0.02694	0.27820
Ads.	0.59880	0.11512	0.52275
1. Des.		0.08624	0.49409
2. Des.		0.06910	0.46717
3. Des.		0.05650	0.44423
4. Des.		0.04782	0.42351
5. Des.		0.04132	0.40494
Ads.	1.09780	0.24558	0.91653
1. Des.		0.18310	0.85645
2. Des.		0.13590	0.81240
3. Des.		0.11212	0.76607
4. Des.		0.09384	0.72622
5. Des.		0.08166	0.68909
Ads.	1.99600	0.50854	1.59123
1. Des.		0.37312	1.47414
2. Des.		0.29414	1.36352
3. Des.		0.23650	1.27072
4. Des.		0.18718	1.19972
5. Des.		0.15416	1.13623

Table .7: Data of Figure 2.5 (upper panel).

Soil mass (kg)	0.01619		
Water content (L)	0.00381		
Volume added (L)	0.02000		
Fraction of discarded solution	0.420		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20032	0.05746	0.16294
1. Des.		0.03949	0.15387
2. Des.		0.03006	0.14335
3. Des.		0.02178	0.13696
4. Des.		0.01591	0.13214
5. Des.		0.01217	0.12782
Ads.	0.40064	0.12843	0.30600
1. Des.		0.08905	0.28459
2. Des.		0.06655	0.26268
3. Des.		0.05173	0.24337
4. Des.		0.03817	0.23135
5. Des.		0.02964	0.22032
Ads.	0.60096	0.19665	0.45312
1. Des.		0.14629	0.40572
2. Des.		0.10580	0.37490
3. Des.		0.08106	0.34594
4. Des.		0.06019	0.32656
5. Des.		0.04695	0.30885
Ads.	1.10176	0.37790	0.80517
1. Des.		0.26474	0.73816
2. Des.		0.21005	0.65508
3. Des.		0.15759	0.60249
4. Des.		0.11985	0.56066
5. Des.		0.09417	0.52439
Ads.	2.00320	0.75978	1.35709
1. Des.		0.53234	1.22228
2. Des.		0.38855	1.10493
3. Des.		0.29139	1.00782
4. Des.		0.21844	0.93512
5. Des.		0.17900	0.85821

Table .8: Data of Figure 2.5 (lower panel).

Soil condition		Field-moist	Air-dried
Soil mass (kg)		0.00904	0.00991
Water content (L)		0.00096	0.00009
Volume added(L)		0.02	0.02
Time (h)	C_0 (mg L ⁻¹)	k' (L kg ⁻¹)	k' (L kg ⁻¹)
11	0.2	4.38	5.70
24		4.91	6.58
83		7.18	8.34
107		7.89	8.87
179		10.65	10.00
251		11.34	11.05
275		11.80	12.11
11	0.6	3.36	4.76
24		4.09	5.21
83		5.38	6.34
107		5.89	6.62
179		6.94	7.37
251		7.90	8.32
275		8.58	9.00
11	2	2.49	3.53
24		2.96	3.91
83		3.85	4.45
107		3.90	4.55
179		4.60	4.93
251		5.19	5.41
275		5.61	5.77

Table .9: Data of Figure 2.6.

Soil Sorption time	Sand 24 h		
Soil condition:	Soil mass (kg)	Water content (L)	Volume added(L)
Air-dried	0.00989	0.00011	0.02
Rehydrated	0.00902	0.00098	0.02
Field-moist	0.00903	0.00097	0.02
	k' (L kg ⁻¹) at $C_0 = 0.2$ mg L ⁻¹	k' (L kg ⁻¹) at $C_0 = 0.6$ mg L ⁻¹	k' (L kg ⁻¹) at $C_0 = 2.0$ mg L ⁻¹
Air-dried soil	6.13	5.18	3.65
Soil rehydrated for (h):			
24	5.49	4.69	3.56
48.25	5.43	4.45	3.30
72.25	5.16	4.33	3.25
169.5	5.11	4.14	3.03
219.5	4.71	4.20	3.04
506	4.50	3.87	2.92
747.5	4.40	3.82	2.91
Field-moist soil	4.76	3.78	2.82
Soil Sorption time	Loess 24 h		
Soil condition:	Soil mass (kg)	Water content (L)	Volume added(L)
Air-dried	0.00975	0.00025	0.02
Rehydrated	0.00810	0.00190	0.02
Field-moist	0.00811	0.00189	0.02
	k' (L kg ⁻¹) at $C_0 = 0.2$ mg L ⁻¹	k' (L kg ⁻¹) at $C_0 = 0.6$ mg L ⁻¹	k' (L kg ⁻¹) at $C_0 = 2.0$ mg L ⁻¹
Air-dried soil	3.10	2.73	1.95
Soil rehydrated for (h):			
24	2.95	2.47	1.82
48.25	2.91	2.21	1.81
72.25	2.73	2.37	1.75
169.5	2.88	2.35	1.78
219.5	2.88	2.34	1.72
506	2.95	2.30	1.70
747.5	2.84	2.18	1.75
Field-moist soil	2.84	2.28	1.73

Table .10: Data used to calculate R in Figure 2.7 (see section: "Materials and Methods" in Chapter 2 for details).

Soil mass (kg)	0.00902		
Water content (L)	0.00098		
Volume added (L)	0.02000		
Fraction of discarded solution	0.477		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20016	0.06057	0.30286
1. Des.		0.04255	0.27762
2. Des.		0.03099	0.25732
3. Des.		0.02574	0.23519
4. Des.		0.02053	0.21878
5. Des.		0.01675	0.20480
Ads.	0.40032	0.13148	0.58167
1. Des.		0.08907	0.53455
2. Des.		0.06646	0.48840
3. Des.		0.05115	0.45033
4. Des.		0.04160	0.41585
5. Des.		0.03395	0.38753
Ads.	0.60048	0.21773	0.82480
1. Des.		0.14624	0.74969
2. Des.		0.10654	0.67993
3. Des.		0.08195	0.61902
4. Des.		0.06630	0.56457
5. Des.		0.05195	0.52446
Ads.	1.10088	0.44044	1.41620
1. Des.		0.29255	1.27189
2. Des.		0.21627	1.12501
3. Des.		0.16146	1.01275
4. Des.		0.12165	0.92635
5. Des.		0.09951	0.84300
Ads.	2.00160	0.86092	2.43515
1. Des.		0.56789	2.16226
2. Des.		0.41412	1.89036
3. Des.		0.30640	1.68183
4. Des.		0.22048	1.54201
5. Des.		0.17385	1.40607

Table .11: Data of Figure 2.8 (upper panel).

Soil mass (kg)	0.00810		
Water content (L)	0.00190		
Volume added(L)	0.02000		
Fraction of discarded solution	0.457		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20032	0.09431	0.23970
1. Des.		0.06247	0.20936
2. Des.		0.04273	0.18561
3. Des.		0.02884	0.17040
4. Des.		0.02078	0.15658
5. Des.		0.01598	0.14392
Ads.	0.40064	0.19891	0.45156
1. Des.		0.13060	0.39068
2. Des.		0.09138	0.33549
3. Des.		0.06313	0.29905
4. Des.		0.04579	0.26799
5. Des.		0.03193	0.24891
Ads.	0.60096	0.30466	0.66031
1. Des.		0.20317	0.55858
2. Des.		0.13768	0.48482
3. Des.		0.09572	0.42828
4. Des.		0.06911	0.38204
5. Des.		0.04766	0.35472
Ads.	1.10176	0.59985	1.09881
1. Des.		0.38607	0.93629
2. Des.		0.25955	0.80173
3. Des.		0.18026	0.69566
4. Des.		0.12842	0.61325
5. Des.		0.08910	0.56102
Ads.	2.00320	1.12476	1.90553
1. Des.		0.71654	1.62071
2. Des.		0.47379	1.39242
3. Des.		0.32539	1.20870
4. Des.		0.22130	1.08840
5. Des.		0.15827	0.98557

Table .12: Data of Figure 2.8 (lower panel).

Soil mass (kg)	0.00906		
Water content (L)	0.00094		
Volume added (L)	0.02000		
Fraction of discarded solution	0.478		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
1. Ads.	0.20032	0.06411	0.29408
2. Ads.		0.07435	0.42077
3. Ads.		0.08895	0.52608
4. Ads.		0.10272	0.61719
5. Ads.		0.11179	0.70396
6. Ads.		0.11837	0.78648
1. Ads.	0.40064	0.13138	0.58083
2. Ads.		0.16219	0.80686
3. Ads.		0.18686	1.01307
4. Ads.		0.22884	1.15201
5. Ads.		0.25139	1.28955
6. Ads.		0.26738	1.41733
1. Ads.	0.60096	0.21570	0.82818
2. Ads.		0.27056	1.12665
3. Ads.		0.31792	1.38192
4. Ads.		0.36279	1.59063
5. Ads.		0.38928	1.79232
6. Ads.		0.41300	1.97116
1. Ads.	1.10176	0.44375	1.40667
2. Ads.		0.54425	1.90073
3. Ads.		0.64657	2.27964
4. Ads.		0.71447	2.62518
5. Ads.		0.77501	2.91277
6. Ads.		0.81069	3.19100
1. Ads.	2.00320	0.85497	2.44628
2. Ads.		1.04780	3.26806
3. Ads.		1.23331	3.89391
4. Ads.		1.35634	4.45940
5. Ads.		1.47953	4.88869
6. Ads.		1.54527	5.31481

Table .13: Data of Figure 3.2 (upper panel).

Soil mass (kg)	0.00812		
Water content (L)	0.00188		
Volume added(L)	0.02000		
Fraction of discarded solution	0.457		
Adsorption time (days)	1		
Desorption time (days)	1		
	C_0 (mg L ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
1. Ads.	0.20032	0.09401	0.24008
2. Ads.		0.11475	0.31513
3. Ads.		0.12881	0.38262
4. Ads.		0.14145	0.43663
5. Ads.		0.15086	0.48378
6. Ads.		0.15763	0.52645
1. Ads.	0.40064	0.19663	0.45697
2. Ads.		0.22302	0.63711
3. Ads.		0.25392	0.77260
4. Ads.		0.27940	0.88464
5. Ads.		0.28814	1.01041
6. Ads.		0.31327	1.08125
1. Ads.	0.60096	0.30681	0.65349
2. Ads.		0.37018	0.84501
3. Ads.		0.41610	1.00550
4. Ads.		0.45194	1.13658
5. Ads.		0.47790	1.25017
6. Ads.		0.49539	1.35458
1. Ads.	1.10176	0.58698	1.13207
2. Ads.		0.70329	1.45265
3. Ads.		0.79647	1.69229
4. Ads.		0.85792	1.90271
5. Ads.		0.90674	2.07146
6. Ads.		0.92975	2.24963
1. Ads.	2.00320	1.13117	1.88601
2. Ads.		1.34317	2.38873
3. Ads.		1.49639	2.78871
4. Ads.		1.62378	3.06962
5. Ads.		1.70050	3.33016
6. Ads.		1.76230	3.53642

Table .14: Data of Figure 3.2 (lower panel).

Soil mass (kg)	0.00453				
Water content (L)	0.00047				
Volume added (L)	0.00500				
Dilution Volumes (L)	0.00500, 0.01000, 0.02000				
Adsorption time (d)	1				
Desorption time (d)	1				
	C_0 (mg L ⁻¹)	Data set 1		Data set 2	
		C (mg L ⁻¹)	S (mg kg ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20008	0.02904	0.18591	0.02777	0.18745
1. Des.		0.02071	0.17310	0.01980	0.17520
2. Des.		0.01413	0.15711	0.01459	0.15505
3. Des.		0.00987	0.13280	0.01105	0.12225
Ads.	0.40016	0.06850	0.35921	0.06806	0.35974
1. Des.		0.04883	0.32907	0.04929	0.32799
2. Des.		0.03445	0.28622	0.03522	0.28273
3. Des.		0.02292	0.23713	0.02291	0.23722
Ads.	0.60024	0.11833	0.51998	0.11306	0.52636
1. Des.		0.08024	0.47741	0.08163	0.47419
2. Des.		0.05450	0.41656	0.05518	0.41347
3. Des.		0.03521	0.34827	0.03682	0.33387
Ads.	1.10044	0.24047	0.92484	0.24109	0.92409
1. Des.		0.16827	0.82627	0.17510	0.81047
2. Des.		0.11131	0.71215	0.11403	0.69986
3. Des.		0.07259	0.56654	0.06993	0.59029
Ads.	2.00080	0.48515	1.62356	0.50279	1.60222
1. Des.		0.34783	1.40539	0.34080	1.42164
2. Des.		0.22672	1.18471	0.23037	1.16823
3. Des.		0.14200	0.94049	0.14228	0.93795

Table .15: Data of Figure 3.3 (upper panel).

Soil mass (kg)	0.00407				
Water content (L)	0.00093				
Volume added (L)	0.00500				
Dilution Volumes (L)	0.00500, 0.01000, 0.02000				
Adsorption time (d)	1				
Desorption time (d)	1				
	C_0 (mg L ⁻¹)	Data set 1		Data set 2	
		C (mg L ⁻¹)	S (mg kg ⁻¹)	C (mg L ⁻¹)	S (mg kg ⁻¹)
Ads.	0.20008	0.05564	0.16471	0.06599	0.14963
1. Des.		0.03698	0.14648	0.03859	0.14215
2. Des.		0.02367	0.12406	0.02379	0.12344
3. Des.		0.01349	0.11009	0.01432	0.10174
Ads.	0.40016	0.12573	0.30837	0.13083	0.30095
1. Des.		0.08448	0.26469	0.08625	0.25995
2. Des.		0.05377	0.21506	0.05253	0.22144
3. Des.		0.03008	0.18903	0.03008	0.18911
Ads.	0.60024	0.20067	0.44498	0.20756	0.43494
1. Des.		0.13477	0.37544	0.13387	0.37783
2. Des.		0.08390	0.30591	0.08399	0.30546
3. Des.		0.04968	0.23774	0.04734	0.26124
Ads.	1.10044	0.39168	0.78114	0.39364	0.77828
1. Des.		0.24899	0.68315	0.24592	0.69139
2. Des.		0.15991	0.52950	0.15732	0.54281
3. Des.		0.09109	0.43581	0.09086	0.43814
Ads.	2.00080	0.74687	1.36967	0.74334	1.37482
1. Des.		0.50457	1.10284	0.48237	1.16246
2. Des.		0.30118	0.90905	0.29891	0.92070
3. Des.		0.16945	0.75377	0.16603	0.78818

Table .16: Data of Figure 3.3 (lower panel).

Abstract

The primary objective of this thesis is to investigate the sorption kinetics of organic chemicals in soil. The goal is to improve the predictability of organic chemical movement to groundwater and contribute to a better understanding of sorption. Throughout this work great care is taken in the synthesis of data acquisition and mathematical modeling.

In chapter 2 hysteretic or nonsingular sorption/desorption isotherms of chlortoluron in a fresh field-moist silt loam and a fresh field-moist loamy sand containing 1.1 and 0.7 % organic C, respectively, are utilized to estimate sorption parameters of a two-stage model. These parameters are successfully used to a) predict rate studies and b) predict sorption/desorption isotherms at different solution to soil ratios in both soils. The successful prediction demonstrates that the effect of hysteresis is only apparent and simply caused by nonequilibrium sorption. In contrast the successful prediction of sorption/desorption isotherms measured with soil samples initially air-dried (a common practice in sorption studies) fails. It is shown that structural changes within the soil organic matter (the main sorbent of chlortoluron) take place during drying which are not readily reversible. Rehydration of both air-dried soils to field-moisture for 80 h (silt loam) and 500 h (loamy sand), is necessary before the sorption properties of the respective field-moist soils are reestablished. The use of air-dried soil in sorption studies with organic chemicals must therefore be questioned.

The same soils are used to investigate the suitability of different batch techniques to study kinetic sorption of chlortoluron (chapter 3). In addition to the decant-refill method (described in chapter 2) where part of the supernatant is replaced by solute-free solution two other techniques are investigated. The first technique is similar to the decant-refill method; however, part of the supernatant is replaced by solute containing solution instead. In the second technique desorption is induced by successive dilution of the supernatant with time. Nonideal sorption isotherms of chlortoluron are observed independent of the method. After fitting the two-stage model to data obtained by the decant-refill method the model is used to independently predict the two other methods with the same set of kinetic parameters. The good agreement between model and data indicates that the different nonideal isotherms observed with each technique can be explained by slow kinetics. All isotherm phenomena are explained by a single set

of sorption parameters and therefore unified by a single model. The ability of the model to describe nonideal isotherms is further tested on three data sets taken from the literature where nonideality phenomena remained unexplained or were explained by other causes than slow kinetics. Two of these three sets contain data on parathion sorption in a sandy loam while the other contains data on 2,4,5-T sorption in a silt loam. All data sets can be described by the two-stage model thereby falsifying the causes originally proposed for nonideal sorption behavior of each data set.

Chapter 4 resolves an apparent inconsistency between dimethylphthalate (DMP) batch and column experiments in two sands containing 2.25 and 0.7 % organic C. In an earlier investigation it was found that the retardation coefficients obtained by fitting a linear two-stage model to column data were about 50 % smaller than those calculated from the distribution coefficient of a 14-day isotherm. In chapter 4 the two-stage model is used to estimate kinetic sorption parameters by fitting the model simultaneously to the complete set of batch data consisting of a 3- and a 14-day isotherm as well as a rate study. With the estimated set of rate parameters, the model is able to predict column data adequately. This is in contrast to the earlier findings. It is then demonstrated that the apparent differences in the retardation coefficients reported before resulted from the experimental difficulties in detecting the tailing of the nonequilibrium breakthrough curves. As complete tail data is crucial when R is estimated by curve fitting the use of column data is limited in case of slow sorption.

Kurzfassung

In der vorliegenden Arbeit wird die Sorptionskinetik organischer Chemikalien in Böden untersucht. Ziel der Arbeit ist es, zu einem besseren Prozeßverständnis zu gelangen, um letztendlich die Verlagerung solcher Stoffe und die damit einhergehende Gefährdung z. B. des Grundwassers besser als bisher abschätzen zu können. Schwerpunkte der Arbeit sind zum einen die Anwendung verschiedener Meßverfahren zur Untersuchung der Sorptionskinetik, zum anderen die Auswertung von Meßdaten mit einem mathematischen Modell.

In Kapitel 2 wird das Sorptions/Desorptionsverhalten des Herbizids Chlortoluron in einem feldfeuchten Sand (C_{org} -Gehalt: 1.1 %) sowie einem feldfeuchten Löß (C_{org} -Gehalt: 0.7 %) untersucht. Die in den Böden gemessenen Sorptions/Desorptionsisothermen zeigen eine deutliche Sorptionshysterese. Unter der Annahme, daß die Hysterese durch kinetische Sorption bedingt ist, werden an beiden Isothermen durch Anpassung eines zweistufigen Modells Sorptionsparameter ermittelt. Die Gültigkeit dieser Annahme wird anschließend durch eine unabhängige Vorhersage von Daten getestet. Hierzu wird das Modell, unter Verwendung der ermittelten Sorptionsparameter, zur Simulation von Sorptions/Desorptionsisothermen bei geändertem Boden/Lösungsverhältnis sowie zur Simulation von Ratenstudien genutzt. Der Vergleich berechneter und gemessener Daten zeigt in allen Fällen eine gute Übereinstimmung. Im Gegensatz dazu ist die erfolgreiche Vorhersage von Sorptions/Desorptionsdaten unmöglich, wenn der Boden vor Beginn des Experiments luftgetrocknet wird. Offensichtlich führt die Lufttrocknung des Bodens zu einer Strukturveränderung der organischen Bodensubstanz (dem wichtigsten Sorbenten), die kurzfristig nicht reversibel ist. In Wiederbefeuchtungsversuchen wird gezeigt, daß es in Gegenwart von Wasser etwa 80 (Löß) bzw. 500 Stunden (Sand) dauert, bis die ursprünglichen Sorptionseigenschaften wieder hergestellt sind. Von der üblichen Praxis, den Boden vor Versuchsbeginn luftzutrocknen, ist daher abzuraten.

An den gleichen Böden wird in Kapitel 3 untersucht, inwieweit verschiedene Schüttelversuchstechniken zur Untersuchung der kinetischen Sorption von Chlortoluron geeignet sind. Neben der in Kapitel 2 beschriebenen klassischen Sorptions/Desorptionsmethode, bei welcher ein Teil der Lösung wiederholt durch herbizidfreie Lösung ersetzt wird, werden zwei weitere Techniken angewendet. Die eine ähnelt der ersten Methode – es wird lediglich herbizidhaltige Lösung als Er-

satzlösung verwendet. Bei der anderen Methode wird die Desorptionsphase des Experiments durch sukzessive Verdünnung mit herbizidfreier Lösung erreicht. Unabhängig von der gewählten Methode weicht die beobachtete Isotherme von einer Gleichgewichtsisotherme ab. Nach der Anpassung des Sorptionsmodells an die mit der klassischen Sorptions/Desorptionsmethode gemessenen Isothermen werden die ermittelten Sorptionsparameter wiederum zur unabhängigen Vorhersage der beiden anderen Verfahren benutzt. In beiden Fällen wird eine sehr gute Übereinstimmung der modellierten und gemessenen Daten erzielt. Das heißt, daß alle in den verschiedenen Verfahren beobachteten Effekte auf langsame Sorption zurückzuführen sind, weshalb methodisch bedingte Artefakte auszuschließen sind. Um zu zeigen, daß die Möglichkeiten des Modells nicht nur auf die Sorption von Chlortoluron beschränkt sind, wurden zusätzlich Literaturdaten ausgewertet. Zwei dieser Literaturdatensätze enthalten Sorptionsdaten über Parathion in einem sandigen Lehm, der dritte Sorptionsdaten über 2,4,5-T in einem schluffigen Lehm. Alle Daten zeigen einen Isothermenverlauf, der von einer Gleichgewichtsisotherme abweicht – von den jeweiligen Autoren wurde dieser entweder gar nicht oder durch experimentelle Artefakte erklärt. Der Isothermenverlauf kann in allen Fällen mit Hilfe des kinetischen Modells durch langsame Sorption erklärt werden.

In Kapitel 4 wird das kinetische Modell zur Aufklärung einer scheinbaren Inkonsistenz zwischen Dimethylphthalat Schüttel- und Säulenexperimenten in zwei Sandböden (C_{org} -Gehalt: 2.25 und 0.7 %) benutzt. Im Rahmen einer früheren Untersuchung wurde gezeigt, daß der mit einem kinetischen Modell aus Säulenversuchsdaten ermittelte Retardationskoeffizient R um etwa 50 % kleiner als der aus dem Verteilungskoeffizienten eines 14-tägigen Schüttelversuchs ermittelte R -Wert war. Im Unterschied dazu werden die kinetischen Sorptionsparameter hier durch eine Modellanpassung an alle Schüttelversuchsdaten (zwei Isothermen mit Schüttelzeiträumen von 3 und 14 Tagen, sowie eine Ratenstudie über 14 Tage) bestimmt. Mit den so bestimmten Sorptionsparametern ist es möglich, die Säulenversuchsdaten mit einem gekoppelten Transport- und Sorptionsmodell vorherzusagen. Weitere Untersuchungen zeigen, daß die vorher beschriebene Inkonsistenz beider Versuchsmethoden vermutlich auf experimentelle Schwierigkeiten bei der Identifizierung des sog. "Tailing" einer Durchbruchkurve zurückzuführen ist. Da die im Tailing enthaltene Information aber für die eindeutige

Identifizierung kinetischer Parameter durch Modellanpassung wichtig ist, müssen Säulenversuchsdaten mit Vorsicht interpretiert werden.

LEBENS LAUF

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