The modeling of reactive solute transport with sorption to mobile and immobile sorbents

1. Experimental evidence and model development

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Abstract. Modeling carrier-influenced transport needs to take into account the reactivity of the carrier itself. This paper presents a mathematical model of reactive solute transport with sorption to mobile and immobile sorbents. The mobile sorbent is also considered to be reactive. To justify the assumptions and generality of our modeling approach, experimental findings are reviewed and analyzed. A transformation of the model in terms of total concentrations of solute and mobile sorbents is presented which simplifies the mathematical formulations. Breakthrough data on dissolved organic carbon are presented to exemplify the need to take into account the reactivity of the mobile sorbent. Data on hexachlorobiphenyl and cadmium are presented to demonstrate carrier-introduced increased mobility, whereas data on anthracene and pyrene are presented to demonstrate carrier-introduced reduced mobility. The experimental conditions leading to the different findings are pointed out. The sorption processes considered in the model are both equilibrium and nonequilibrium processes, allowing for different sorption sites and nonlinear isotherms and rate functions. Effective isotherms, which describe the sorption to the immobile sorbent in the presence of a mobile sorbent and rate functions, are introduced and their properties are discussed.

Introduction

Dissolved organic carbon (DOC) in soils and aquifers is considered a sorbent and carrier for organic contaminants. The knowledge of the interaction between hydrophobic organic chemicals (HOC) and soil or aquifer materials in the presence of mobile carriers, such as DOC, plays an important role in understanding the transport behavior of the HOC. Several studies have focused on the influence of the chemical characteristics of the contaminant on solubility enhancement by DOC [e.g., Kile and Chiou, 1989]. Enhanced transport of pesticides and HOC mediated by the presence of DOC in soils and other porous media has been documented by a number of studies [e.g., McCarthy and Zachara, 1989]. In these studies it is generally assumed that DOC is nonreactive with respect to interactions with bulk soil material (BSM). However, there is evidence that the carrier DOC itself undergoes adsorption to the soil matrix [David and Vance, 1991; Jardine et al., 1990].

Simulation models considering the mobility of HOC in soils have gained increasing interest in recent years. The fate of a particular contaminant under a specific combination of environmental conditions can best be estimated by simultaneously considering all relevant processes and integrating them in a modeling approach. Therefore a three-phase system [McCarthy and Zachara, 1989] accounts for the distribution between the aqueous phase, the bulk soil, and the mobile sorbent, which can be considered a third phase or pseudophase [Edwards et al., 1991]. Nonideal transport as a consequence of nonlinearity and nonequilibrium sorption phenomena of both the carrier and the contaminant have to be taken into account also. Weber et al. [1991] emphasized the increasing experimental evidence of sorption nonlinearity in soils and sediments, while Brusseau et al. [1991] discussed a number of processes leading to rate-limited sorption of organic chemicals.

This paper is the first part of a comprehensive experimental, modeling, and simulation approach to the phenomenon of carrier-influenced transport in porous media and describes the experimental evidence for the relevant processes to be taken into account. Based on the experimental evidence, a bicomponent model is developed, which takes into account a system of equilibrium and nonequilibrium sorption processes and allows for both nonlinear isotherms and rate functions. Effective isotherms, which describe the sorption to the immobile sorbent in the presence of a mobile sorbent and rate functions, are introduced and their properties are discussed.

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for the contaminant and DOC for the carrier. Nevertheless, the model and analysis are much more general, applying to a wide range of contaminants and carriers.

Experimental Evidence

Based on the literature as well as on our own experimental results, several processes are described with respect to their relevance in carrier-influenced transport of HOC. The processes considered in detail are (1) facilitated transport of contaminants (cotransport); (2) sorption of the carrier DOC in soils, that is, the carrier itself acts as a reactive solute; and (3) transport of HOC with a reactive carrier (cosorption of HOC). For each process, an experimental example is given, which is used in part 2 for numerical simulation.

Facilitated transport of different contaminants has been described by a number of investigators. Magee et al. [1991] reported a reduction of the retardation factor of phenanthrene in a soil column filled with sand in the presence of DOC as carrier. Enfield et al. [1989] reported enhanced mobility of polycyclic aromatic hydrocarbons (PAH) and hexachlorobiphenyl (HCB) in the presence of different organic carrier mol-

cules. Kan and Tomson [1990] showed facilitated transport for naphtalene in the presence of surfactants (Triton X-100) and a protein (bovine serum albumin). Abdul et al. [1990] conducted column experiments to investigate the wash-out efficiency for a number of nonpolar organic contaminants. They found humic acid solutions more effective than water in removing nonpolar organic contaminants. Dunnivant et al. [1992a] reported facilitated transport of cadmium (Cd) and high-performance liquid chromatography (HCB) in columns packed with aquifer materials in the presence of DOC. The experimental conditions in the studies described above can be summarized as follows: sandy soil and aquifer materials have been used as a porous medium. The experiments were run with packed and homogenized small HPLC or glass columns or with larger columns [Abdul et al., 1990; Dunnivant et al., 1992a]. Pulse-type upper boundary conditions and steady state saturated flow conditions were applied. Moreover, in the experiments of Dunnivant et al. [1992a] the porous medium was saturated with DOC before starting the experiment to inhibit any retardation due to sorption of DOC to BSM. However, none of the investigations mentioned focused on the transport behavior and mobility of the DOC itself.

In all these studies, carrier DOC was assumed to be nonreactive in porous media. This assumption holds true in aquifers and riverbed systems, where DOC is mainly composed of small and hydrophilic subcomponents, which is the consequence of a sum of hydrogeochemical processes including sorption, fixation, and filtering of the larger, less mobile components of DOC. In soils, however, natural DOC is known to be retarded due to sorption to the bulk soil material, especially DOC leached out of the forest floor. Experimental data show the significant affinity of DOC to BSM [Jardine et al., 1989; David and Vance, 1991; Dunnivant et al., 1992b; Guggenberger and Zech, 1992]. Therefore experiments focusing on the influence of DOC on contaminant mobility have to take into account a potential sorption of DOC.

We show results of breakthrough experiments for HCB and Cd, representative for the studies indicating enhanced mobility, (Figure 1) presented by Dunnivant et al. [1992a]. For both HCB and Cd increased mobility was observed with increasing solute carrier DOC concentration. This observation is due to the formation of a carrier-pollutant complex composed of Cd or HCB and of the carrier DOC, leading to an increase of the apparent solubility of the pollutant. As a consequence of the experimental conditions (the column was presaturated with DOC), all sites providing sorption sites for DOC are already occupied and the carrier acts more or less as a nonreactive solute. Therefore the complex also is not reactive and is transported without retardation through the porous media. This results in increased mobility for both HCB and Cd.

The soil material used for our experiments was the Bs material of a frigid, sandy, siliceous, spodic Udipsamment with mor-type humus collected near Forchheim, Germany. Immediately after collection, the material was packed into the column without any further treatment. The porous material was not saturated with DOC prior to the experiments. The DOC used for the column experiments was prepared by leaching of forest floor material originating from the same site as the Bs material. For the leaching we used an aqueous solution with the chemical composition of the natural precipitation at the Forchheim experimental site. The columns were run under unsaturated and steady state flow conditions. The solutes and carriers were fed continuously to the porous medium. A de-
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A detailed description of the experiments can be found in work by K. U. Totsche et al. (manuscript in preparation, 1996).

The breakthrough of DOC through the Bs horizon, showing a clear deviation from the behavior of the tracer (Cl-), is given in Figure 2. The DOC concentration in the outflow remains approximately constant at 30% of the DOC inflow level. We consider two possible explanations for this observation. The first one assumes that the sorption of DOC is composed of two different types of reactions, a fast instantaneous reaction and a slow, kinetically controlled sorption reaction responsible for the extensive tailing. This type of combined sorption reaction can be described in terms of the two-site/two-region model discussed by van Genuchten and Wagener [1989]. The second explanation states that the observed breakthrough curve represents the breakthrough of only one distinct subcomponent of DOC. Several reports have described the specific sorption of the hydrophobic fraction of DOC to soil material rich in iron and aluminum oxides, such as Bs horizons [Jardine et al., 1989; Guggenberger and Zech, 1992]. The DOC used in the experiments described above was comprised of 34% hydrophilic and 66% hydrophobic components. The breakthrough curve was consistent with a selective retardation of the hydrophobic fraction in the Bs material (Totsche et al., manuscript in preparation, 1996). Therefore DOC mobility is influenced by sorption reactions to the immobile soil matrix. This may be due to combined instantaneous or kinetically controlled sorption reactions or due to the specific sorption of one or more subcomponents of the natural DOC. Consequently, it has to be expected that the pollutants complexed to the DOC or to its subcomponents are subject to similar sorption reactions as the DOC. When modeling transport of solutes in the presence of mobile carriers such as DOC one has to take into account the reactivity of the carrier itself as well as its subcomponents.

In contrast to the findings of, for example, Dunnivant et al. [1992a], we found reduced mobility for both pyrene and anthracene in soil columns containing Bs material (Figure 3). As indicated before, the experimental conditions leading to these observations were different to the experimental set up in the experiments of, for example, Dunnivant et al. [1992a]. For both anthracene and pyrene we did not observe complete breakthrough. This is due to very low water solubilities (anthracene, $3.7 \times 10^{-4}$ mol m$^{-3}$; pyrene, $7.2 \times 10^{-4}$ mol m$^{-3}$ [Karcher et al., 1988]), the high $K_{OC}$ (anthracene, $K_{OC} = 15.848$ m$^{3}$ kg$^{-1}$; pyrene, $K_{OC} = 67.608$ m$^{3}$ kg$^{-1}$ [Karcher et al., 1988]), and the unsaturated flow conditions. In the case of no DOC present, anthracene is found after approximately 50 pore volumes have been exchanged (Figure 3a). But it takes almost 140 pore volumes for the detection of anthracene in the column outflow in the presence of DOC. In the case of pyrene, the situation is even more pronounced (Figure 3b). It takes almost 160 pore volumes for pyrene to appear in the effluent in the absence of DOC. With DOC present, pyrene is detected significantly after approximately 350 pore volumes have been exchanged. The stronger retardation of pyrene compared to anthracene is not only the consequence of lower water solubility of pyrene, but is also due to its very high affinity to the hydrophobic subcomponents of DOC ($K_{DOM} = 41.687$ m$^{3}$ kg$^{-1}$). As we learned from the DOC column experiments the hydrophobic subcomponent is specifically retained by the Bs material. Consequently, this specific retardation can be observed also for the carrier-bound pyrene.

The decrease of anthracene and pyrene mobility in the presence of natural DOC may be the consequence of two different processes: In a system where HOC, DOC, and immobile BSM is present, the sorption of the DOC to the BSM leads to an

![Figure 2. Measured breakthrough of both chloride and DOC through an unsaturated column filled with the Bs material of an Udipsamment. Circles denote chloride breakthrough; diamonds, DOC at the $1.1 \times 10^{-2}$ kg m$^{-3}$ level; triangles, DOC at the $2.0 \times 10^{-2}$ kg m$^{-3}$ level; pv, pore volumes; and $C_j/C_{0j}$, reduced concentrations.](image)

Table 1. Physical and Chemical Parameters for the Column Experiments

<table>
<thead>
<tr>
<th></th>
<th>PAH</th>
<th>Dunnivant et al. [1992]</th>
</tr>
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<tr>
<td></td>
<td>DOC*</td>
<td>Anthracene*</td>
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<tr>
<td>$L$, m</td>
<td>0.072</td>
<td>0.072</td>
</tr>
<tr>
<td>$d$, m</td>
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<td>0.1</td>
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<td>$C_{DOC}$, kg m$^{-3}$</td>
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<tr>
<td></td>
<td>HCB†</td>
<td>Cd†</td>
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<tr>
<td>$C_{DOC}$, kg m$^{-3}$</td>
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<td>(0, 5.2, 20.4, 58.1)$\times 10^{-3}$</td>
</tr>
</tbody>
</table>

PAH, polycyclic aromatic hydrocarbons; DOC, dissolved organic carbon; HCB, hexachlorobiphenyl; Cd, cadmium; L, column length; d, column diameter; Q, volumetric flux; $\Gamma$, suction pressure; $\rho$, bulk density; $\theta$, volumetric water content; $C_{DOC}$, concentration of DOC in mobile phase.

*Steady state, unsaturated, continuous feed.

†Steady state, saturated, pulse type.
The experimental findings, modeling approaches not only have to take into account the increase of solubility in the presence of a mobile carrier but also must consider the reactivity of the carrier itself. Furthermore, the situation is complicated by the fact of nonequilibrium and nonlinear adsorption reaction not only for the organic chemicals, but also for the carrier and the complex. The studies of, for example, Karickhoff [1980] or Maxin and Kögel-Knabner [1995] show that the sorption of HOC to the BSM can be kinetically controlled, whereas the partition of HOC between water and DOC can be considered an equilibrium process. However, the sorption isotherm for the sorption of HOC to the BSM and to DOC can be nonlinear [Weber et al., 1991; Maxin and Kögel-Knabner, 1995]. Summarizing, the processes to be taken into account are as follows (Figure 4): sorption of HOC to BSM; sorption of DOC to BSM; formation of HOC-DOC compounds; and sorption of HOC-DOC compound to BSM.

The Model

The proposed model is developed for the understanding and numerical simulation of the reactive carrier influenced transport of reactive HOC through porous media. It considers both equilibrium and nonequilibrium sorption of the HOC to the BSM. The presence of dissolved organic carbon as a mobile sorbent leads to the formation of compounds build of DOC and HOC. The formation of the carrier-bound HOC reduces the mass concentration of free solute HOC. Thus both the sorbed and the dissolved concentration of HOC will be affected. The model considers further the sorption of the carrier-bound HOC to the BSM (Figure 4). Analogous to the sorption of free HOC, the model states two possible mechanisms for the sorption of the carrier-bound HOC: instantaneous equilibrium sorption sites and kinetically controlled nonequilibrium sorption sites. This conceptual approach results in a fractionation of the BSM into different sorption sites referring to the corresponding processes and involved chemical species (Figure 5): type $\Psi_{Hf}$, equilibrium sorption sites for free HOC; type $\Phi_{Hf}$, nonequilibrium sorption sites for free HOC; type $\Psi_{Hb}$, equilibrium sorption sites for carrier-bound HOC; and type $\Phi_{Hb}$, non-equilibrium sorption sites for carrier-bound HOC; and type $\Phi_{Hb}$, non-equilibrium sorption sites for carrier-bound HOC; and type $\Phi_{Hb}$,

Figure 3. Measured breakthrough of (a) anthracene and (b) pyrene. Triangles denote breakthrough without DOC; circles, breakthrough with $3.5 \times 10^{-2} \text{ kg m}^{-3}$ DOC present in liquid phase.

increase of potentially HOC-binding sorption sites. Solid phase organic matter content is increased by the sorption of DOC to the BSM, increasing the amount of both equilibrium and nonequilibrium sorption sites for HOC. This process of HOC retardation is independent of a potential formation of a HOC-DOC complex. Calculation of solid phase DOC in fact showed that during the experiment, soil organic matter content increased.

The second possible process is as follows: In a system where HOC, DOC, and immobile BSM is present, the presence of DOC and HOC leads to the formation of a HOC-DOC complex, increasing the apparent solubility of the HOC. As a consequence of dissolved organic material (DOM) reactivity, the complex can also be sorbed to the immobile solid phase. This may lead to a reduced mobility of the HOC in the presence of DOC, although the apparent solubility of the HOC is higher than the water solubility of the free HOC. Brusseau [1991] presented experiments that showed the increased sorption of organic chemicals in the presence of a low-polarity cosolute (cooperative adsorption).

Up to now we have failed to identify whether the first or the second process is responsible for the observations. Both processes may have to be taken into account with different influence in different porous media. However, as a consequence of

Figure 4. Schematic representation of the interactions between the carrier and the substance in the liquid phase and the bulk soil matrix for the general situation where both equilibrium and nonequilibrium reactions are allowed. $\Psi$ denotes the equilibrium reactions, $\Phi$ denotes kinetic reactions, and $K$ denotes linear isotherms. See notation list for additional information.
nonequilibrium sorption sites for carrier-bound HOC. For an explanation of the abbreviations, see notation section, below.

In the following we denote with \( p_c \) the fraction of the bulk density for the type \( \alpha \). We also take into account the equilibrium and nonequilibrium sorption of the carrier DOC (Figure 4), such that DOC appears in exactly the same forms as HOC and analogous collections of sorption sites can be attributed: type \( \Psi_{DF} \), equilibrium sorption sites for free DOC; and type \( \Psi_{DF} \), nonequilibrium sorption sites for free DOC.

Additionally, if we consider the HOC-DOC compound from the viewpoint of total DOC, types \( \Psi_{DB} \) and \( \Psi_{DB} \), which are identical with \( \Psi_{HH} \) and \( \Psi_{HH} \), also appear. Reasonable relations between the different collections of sorption sites will be discussed in the section on effective isotherms and rate functions.

From now on we use the following indices to identify the various quantities: \( \Psi \) for equilibrium sorption, and \( e \) for nonequilibrium sorption. The corresponding isotherm forms (related to the rate functions in the case of nonequilibrium sorption) are denoted as follows: \( H \) for HOC; \( D \) for DOC; \( f \) for free, that is, not carrier-bound; and \( b \) for carrier-bound. This may lead to up to three subscripts per variable, but it is nevertheless a minimal notation system for the quantities considered here.

The knowledge about the sorption process mentioned and in particular about the formation of the HOC-DOC compounds is still scarce. At present, reaction mechanisms and stoichiometry of reactions involving HOC and naturally occurring DOC are essentially unknown. Only recently have laboratory batch experiments leading to sorption isotherms and rate function description been performed.

Therefore we have to use this type of information in the formulation of the model; in particular, we have to use mass concentrations instead of molar concentrations. Often only the total DOC concentration is accessible experimentally. We use it as a reference to describe the formation of the HOC-DOC compounds in terms of an isotherm. For this process we neglect kinetic effects. This is in accordance with experimental findings [Maxin and Kögel-Knabner, 1995; McCarthy and Jimenez, 1985], but also sets the basis for a transformation of the model. This transformed model is considerably simpler than the original formulation. In this way we are able to set up a model which uses only information on a two-phase system but is capable of making quantitative statements about the overall chemistry in terms of effective isotherms and effective rate functions and also showing the interplay of chemistry and transport. This final model will be given by (13), together with (11) and (12), the definitions for the contaminant transport. Equation (19), together with (18) and (21) (scenario A), or (23a) and (25), together with (24), (26), and (27) (scenario B), will account for the carrier transport.

Mathematical Formulation

The following discussion holds true independent of the spatial dimension. For the general discussions one may think of laboratory (soil column) or field situations, with saturated or partially unsaturated, stationary or instationary flow regime. Owing to the tracer situations, the quantities related to the flow regime are assumed to be independent of the concentrations of the chemicals. We restrict our discussions to the case were only sorption acts as a sink or a source. For easier comprehension, chemical, photochemical, or biological degradation will not be considered here although these processes might be incorporated without difficulties. This assumption is valid for extremely hydrophobic organic chemicals, such as PAHs.

The volumetric mass flux is assumed to be the sum of the advective flux on the one hand and the dispersive and diffusive fluxes on the other. Combining this with the conservation of mass leads to the well-known advection-dispersion equation:

\[
L(C) = \frac{\partial (\theta C)}{\partial t} - \text{div} \left( \theta D \nabla C - q C \right) = P \tag{1}
\]

We use \( L(C) \) to abbreviate the linear part of the differential operator \( (L(C) = 0 \) describes inert transport). Here \( C \) \([ML^{-3}]\) denotes the mass concentration of the solute under consideration relative to the water-filled part of a representative elementary volume (REV); \( P \) \([ML^{-3}T^{-1}] \), the volumetric consumption/production rate; \( \theta \) [dimensionless], the volumetric water content; \( D \) \([L^2T^{-1}] \), the diffusion/dispersion coefficient, in general a matrix; \( q \) \([LT^{-1}] \), the specific discharge; \( \overline{x} \) \([L]\) and \( \overline{t} \) \([T]\), space and time variables, respectively; \( \text{div} \) and \( \nabla \), divergence and gradient in space; and \( \partial / \partial t \) or \( \partial \), the partial derivative with respect to time. The whole notation is summarized below.

We will now specify the term \( P \), which represents the sources and/or sinks. The chemical processes to be considered here are nonlinear equilibrium and nonequilibrium sorption reactions. As shown in the conceptual derivation of the model, this leads to a subdivision of the BSM in distinct fractions that perform different chemical sorption processes (Figure 5). Thus we get for the source/sink \( P(x, t) \),

\[
P(x, t) = -\rho_{eq} \partial_s \Psi(C(x, t)) - \rho_{neq} \partial_s S(x, t) \tag{2}
\]

where \( \rho_{eq} \) and \( \rho_{neq} \) are the bulk density of fractions of the BSM assigned to equilibrium or nonequilibrium sites, respectively, and \( \Psi(C(x, t)) \) \([MM^{-1}] \) and \( S(x, t) \) \([MM^{-1}] \) denote the mass concentration of the chemical sorbed to equilibrium or nonequilibrium sites, respectively.

In the following a mass concentration in solution \( C_a \) is always defined relative to the water-filled part of an REV, whereas mass concentrations \( \Psi_a \) or \( S_a \) are defined relative to the part of mass of porous skeleton attributed to sorption sites of type \( \psi_a \) or \( \varphi_a \), respectively. For the transport of HOC through a porous medium there exist two possible transport pathways: the advective-dispersive flow of the free (solute) HOC \( C_{HF} \) and the advective-dispersive transport of the carrier-bound HOC \( C_{HB} \). In combining (1) and (2) to describe the reactive transport of the HOC and identifying the adequate
fractions of the BSM, the transport of free HOC is described by

\[ \partial_t (\Theta C_{Hf}) + \rho_{Hf} \eta_i (\Theta C_{Hf}) + \rho_{Hf} \partial_S C_{Hf} - \text{div} (\Theta \partial_S C_{Hf} - q C_{Hf}) = F \]  

(3)

where \( \rho_{Hf} \) and \( \rho_{Hf} \eta_i \) denote the bulk density of the fraction of the BSM providing equilibrium sorption sites and nonequilibrium sorption sites for the free HOC, \( C_{Hf} \) is the mass concentration of free HOC in liquid phase, \( \Psi_{Hf} \) is the mass concentration of free HOC sorbed to the fraction of BSM providing equilibrium sorption sites, \( S_{Hf} \) is the mass concentration of free HOC sorbed to the fraction of BSM providing nonequilibrium sorption sites, and \( F \) is the rate of gain of free HOC due to the formation of carrier-bound HOC.

Analogous to the transport of free HOC, we find for the carrier-bound HOC the following equation:

\[ \partial_t (\Theta C_{Hb}) + \rho_{Hb} \eta_i (\Theta C_{Hb}) + \rho_{Hb} \partial_S C_{Hb} - \text{div} (\Theta \partial_S C_{Hb} - q C_{Hb}) = -F \]  

(4)

where \( \rho_{Hb} \) and \( \rho_{Hb} \eta_i \) denote the bulk density of the fraction of the BSM providing equilibrium sorption sites and nonequilibrium sorption sites for the carrier-bound HOC, \( C_{Hb} \) is the mass concentration of carrier-bound HOC in liquid phase, \( \Psi_{Hb} \) is the mass concentration of carrier-bound HOC sorbed to the fraction of BSM providing equilibrium sorption sites for carrier-bound HOC, \( S_{Hb} \) is the mass concentration of carrier-bound HOC sorbed to the fraction of BSM providing nonequilibrium sorption sites for carrier-bound HOC, and \( -F \) due to the definition of \( F \), is the rate of gain of carrier-bound HOC attributable to the formation of carrier-bound HOC.

More precisely, \( C_{Hb} \) measures the mass fraction of HOC of the HOC-DOC compound related to the water-filled part of an REV. With respect to the formation of the HOC-DOC compounds, this concept allows us to identify the loss rate in terms of the gain rate for the free HOC without knowledge on the chemical nature of the reaction.

The kinetics of the nonequilibrium adsorption will be described in a general fashion by

\[ \partial_t S_{Hf} = g_{Hf}(C_{Hf}, S_{Hf}) \]  

(5)

for the case of sorption of free HOC and

\[ \partial_t S_{Hb} = g_{Hb}(C_{Hb}, S_{Hb}) \]  

(6)

for the case of carrier-bound HOC. The properties of the rate functions \( g_{Hf} \) and \( g_{Hb} \) will be discussed in detail later. To become a complete model, a description of the rate \( F \) generally has to be added. Assuming that the formation process HOC-DOC is in equilibrium, in the next section we can transform the model, avoiding the knowledge of \( F \) at the expense of a generalized "isotherm" describing the equilibrium relation of the formation process.

Furthermore, the system (3)–(6) has to be supplemented with appropriate initial and boundary conditions. As the usual choices provide no problems in the following transformations, we will not do this explicitly.

The Transformed Model: Effective Isotherms and Rate Functions

The equations still contain the unspecified term \( F \). Our objective is to transform the model such that \( F \) does not appear explicitly anymore. We choose the total mass concentration \( C_H \),

\[ C_H = C_{Hf} + C_{Hb} \]  

(7)

as a new variable.

By adding (3) and (4), the governing transport equation for the total mass concentration of HOC in the liquid phase then becomes

\[ \partial_t (\Theta C_H) + \rho_{Hf} \eta_i (\Theta C_{Hf}) + \rho_{Hf} \partial_S C_{Hf} + \rho_{Hb} \eta_i (\Theta C_{Hb}) + \rho_{Hb} \partial_S C_{Hb} - \text{div} (\Theta \partial_S C_H - q C_H) = 0 \]  

(8)

Equation (8) in combination with (5) and (6) represents the overall transport of reactive chemicals through porous media in the presence of reactive carriers. It will further be referred to as the general statement of the transport model. Implicit in the formulation of (8) is the assumption that the dispersion/diffusion matrix \( D \) is identical for both the free and the carrier-bound part of the HOC. The aim of the following transformations is to derive a formulation for the rate of the partial mass concentrations \( C_{Hf} \) and \( C_{Hb} \) to the total mass concentration \( C_H \) of the HOC in the liquid phase.

For further discussion we assume that the formation of carrier-bound HOC is an equilibrium reaction, which means that the association of HOC and DOC is fast compared to the mean pore water velocity in the porous medium or to the sorption process of HOC to BSM. Analytical data obtained in batch kinetic experiments support the validity of this assumption [McCarthy and Jimenez, 1985; Maxim and Kögel-Knabner, 1995]. The mass concentration of carrier-bound HOC, \( C_{Hb} \), can then be expressed in terms of the mass concentration of total DOC
present in liquid phase, \( C_D \), and the “sorption isotherm” of HOC sorption to the carrier molecule DOC, \( \Pi(C_{\text{HI}}) \):

\[
C_{\text{Hi}} = C_D \Pi(C_{\text{HI}})
\]  

(9)

Here we refer to the total concentration of DOC due both to experimental restrictions and to a desired partial decoupling of the problem; obviously, the presence of DOC influences the dynamics of HOC, but we want to have the dynamics of the appearing DOC concentration to be independent of the HOC concentrations. Substituting (9) in (7) we get for the total mass concentration of HOC, \( C_H \), present in liquid phase:

\[
C_H = C_{\text{Hi}} + C_D \Pi(C_{\text{HI}})
\]  

(10)

Now we can express the mass concentration of free HOC and carrier-bound HOC in liquid phase, \( C_{\text{Hi}} \) and \( C_{\text{Hi}} \), as a function of the total mass concentration of HOC and the total mass concentration of DOC in liquid phase:

\[
C_{\text{Hi}} = G(C_D, C_H)
\]  

(11a)

\[
C_{\text{Hi}} = C_H - G(C_D, C_H) = C_D \Pi[G(C_D, C_H)]
\]  

(11b)

where \( G(C_D, C_H) \) denotes the implicit expression of the dependency of the mass concentration of free HOC on the mass concentration of DOC and the total mass concentration of HOC given by (10). This unique resolution is guaranteed under minimal assumptions on \( \Pi \); for example, monotonicity of \( \Pi \), but in general no explicit formula is available. With this, both the equilibrium sorption of free HOC and carrier-bound HOC can be expressed as a function of the total mass concentration of HOC and DOC present in liquid phase:

\[
\Psi(x, t, C_H) = \frac{\rho_{\text{H}}}{\rho_{\text{H}}} \Psi_{\text{H}}(G(C_D(x, t), C_H)) + \frac{\rho_{\text{H}}}{\rho_{\text{H}}} \Psi_{\text{H}}(C_H - G(C_D(x, t), C_H))
\]  

(12)

where \( \Psi(x, t, C_H) \) denotes the total mass concentration of HOC composed of free and carrier-bound HOC sorbed to sorption sites of the BSM providing equilibrium sorption sites, and \( \rho_{\text{H}} \) denotes the bulk density of the fraction of BSM providing equilibrium sorption sites both for the free and the carrier-bound HOC. Equation (12) represents the overall sorption of HOC attributable to the sorption of free HOC and carrier-bound HOC to equilibrium sorption sites and is called the “effective isotherm.” The properties of the effective isotherm will be discussed in a subsequent section of this paper.

With (12), the general transport model can be expressed in an equivalent form in terms of the effective isotherm:

\[
\begin{align*}
\partial_t (\theta C_H) + \rho_{\text{H}} \partial_x \Psi(x, t, C_H) + \rho_{\text{H}} \partial_x S_{\text{H}} &= 0 \\
\partial_t S_{\text{H}} &= f_{\text{H}}(x, t, C_H, S_{\text{H}})
\end{align*}
\]  

(13a)

\[
\text{where}
\]

\[
f_{\text{H}}(x, t, C, S) = g_{\text{H}}(C_D(x, t), C, S)
\]  

(13c)

for the case of sorption of free HOC, and

\[
\partial_t S_{\text{H}} = f_{\text{H}}(x, t, C_{\text{Hi}}, S_{\text{H}})
\]  

(13d)

where

\[
C_{\text{Hi}} = \alpha C_{\text{Hi}} + \alpha C_D \Pi(C_{\text{HI}})
\]  

(14a)

\[
S_{\text{H}} = \alpha S_{\text{H}}.
\]  

(14b)

where the index \( Db \) refers to the mass of DOC of the HOC-DOC colloids. Consequently, \( C_{\text{DF}} \) denotes the mass concentration of DOC particles, where none of the binding sites are occupied by an HOC particle.

An equilibrium description of the formation of carrier-bound HOC based on corresponding kinetic equations will not have the form (9) but rather

\[
C_{\text{H}} = C_{\text{DF}} \Pi(C_{\text{HI}})
\]  

(15)

Taking \( C_{\text{DF}} = \alpha C_{\text{Hi}} \) into account, this is equivalent to

\[
C_{\text{H}} = \frac{\Pi(C_{\text{HI}})}{1 + \alpha \Pi(C_{\text{HI}})} C_D
\]  

(16)

This is identical to the form (9), but with a modified isotherm, which will be nonlinear, even if \( \Pi \) from the equilibrium description (15) is linear. For small values of \( C_{\text{Hi}} \) the representation (16) can be approximated by (9), but possibly not for large values of \( C_{\text{Hi}} \) as \( \alpha \) is also expected to be very large. The quantity \( \alpha \Pi(C_{\text{HI}}) \) has to be small compared to 1 to allow for this approximation, where
Thus in general, if we determine an isotherm $\Pi$ for the description (9) by batch experiments, we actually determine the function appearing in (16) and thus have to expect its nonlinearity, being determined by the parameter $\alpha$, which is in general unknown. On the other hand, if we have reasons to believe that (15) holds true with a fixed functional relationship for $\Pi$, but with unknown parameters, for example, with a linear $\Pi$, we can use a batch experiment measurement to approximate these parameters and the unknown $\alpha$ by a fitting procedure.

One could also think of a chain of reactions, where in each reaction one available binding site captures one HOC particle. Elsewhere we will demonstrate that under reasonable assumptions this leads to the same description of the reaction as (15) does, if $C_{Db}$ denotes the mass concentration of HOC attached to DOC particles, taking all possible numbers of occupied sorption sites into account.

**Scenario A**

With respect to sorption-free HOC, the carrier-bound HOC and free DOC act as different species; in particular, the collections of sorption sites are pairwise disjoint. Then the justification of (3)–(6) is clear, but in general, the description of $C_D$ depends on $C_{Hf}$. In the following we use a notation analogous to the different fractions of HOC with $H$ in the index substituted by $D$. Following the procedure applied for HOC we arrive at the following equations. For

$$ C_D = C_{Df} + C_{Db} \quad (18) $$

we find

$$ \frac{\rho_{\psi Df}}{\rho_{\psi D}} \psi_{Df}(C_D) + \frac{\rho_{\psi Db}}{\rho_{\psi D}} \psi_{Db}(C_{Db}) + \frac{\rho_{\psi D}}{\rho_{\psi D}} \delta S_{Df} + L(C_D) = 0 \quad (19a) $$

$$ \delta S_{Df} = g_{Df}(C_{Df}, S_{Df}) \quad (19b) $$

$$ \delta S_{Db} = g_{Db}(C_{Db}, S_{Db}) \quad (19c) $$

and by (14)

$$ C_{Db} = \alpha \Pi(C_{Hf})C_D \quad (20a) $$

$$ C_{Df} = [1 - \alpha \Pi(C_{Hf})]C_D \quad (20b) $$

By neglecting $C_{Db}$ (and $S_{Db}$) we can avoid the dependence on $C_{Hf}$. Such an assumption seems to be doubtful, even if $C_{Hf}$ is several orders of magnitude smaller than $C_{Df}$, as we expect $\alpha$ to be very large.

Nevertheless, in the case of linear isotherms and rate functions, being the same for free and carrier-bound HOC, (19a)–(19c) reduce to a linear problem for $C_D$ and $S_{Df}$, independent of $C_{Hf}$. Let

$$ \frac{\rho_{\psi Df}}{\rho_{\psi D}} g_{Df}(C, S) = k_C - k_d \frac{\rho_{\psi Db}}{\rho_{\psi D}} S \quad (21c) $$

$K$, $k_C$, $k_d > 0$ are constants; $\rho_{\psi Df}$, $\rho_{\psi Db}$ are, for example, the fractions of bulk density related to equilibrium and nonequilibrium sorption sites for DOC. Then

$$ \frac{\rho_{\psi Df}}{\rho_{\psi D}} \psi_{Df}(C_D) + \frac{\rho_{\psi Db}}{\rho_{\psi D}} \delta S_{Df} + L(C_D) = 0 \quad (22a) $$

$$ \delta S_D = k_C S_D - k_d S_D \quad (22b) $$

where $S_D$ is defined by

$$ S_D = \frac{\rho_{\psi Df}}{\rho_{\psi D}} S_{Df} + \frac{\rho_{\psi Db}}{\rho_{\psi D}} S_{Db} \quad (22c) $$

**Scenario B**

With respect to sorption, free DOC and the carrier-bound HOC compounds are indistinguishable, but they act as different species compared to HOC; in particular, the first collections of sorption sites are the same and disjoint from the last one. Then it is clear that for the total concentration of DOC equations of the following type hold true:

$$ \frac{\rho_{\psi Df}}{\rho_{\psi D}} \psi_{Df}(C_D) + \frac{\rho_{\psi D}}{\rho_{\psi D}} \delta S_{Df} + L(C_D) = 0 \quad (23a) $$

$$ \delta S_D = g_D(C_D, S_D) \quad (23b) $$

The problem lies here in the justification of $\psi_{Df}$ and $g_{Df}$: Because of (14a) and (14b), the fraction of the total DOC in solution in form of carrier-bound HOC is $\alpha \Pi(C_{Hf})$, and thus is also in the sorbed phase related to equilibrium sorption sites, that is, with reference to the collections of equilibrium sorption sites of DOC the sorbed mass concentration is $\alpha \Pi(C_{Hf})\psi_{Df}(C_{Df})$. By (14a) and (14b) this means that for HOC in the form of carrier-bound HOC,

$$ \frac{\rho_{\psi Df}}{\rho_{\psi D}} \psi_{Df} + \frac{\rho_{\psi Db}}{\rho_{\psi D}} \psi_{Db}(C_D) = \frac{\rho_{\psi Db}}{\rho_{\psi D}} \psi_{Db}(C_{Db}) \quad (24) $$

where $\psi_{Db}$ denotes the sorbed mass concentration of carrier-bound HOC related to the mass fraction containing the equilibrium sorption sites. Thus (24) defines a generalized isotherm analogous to (12), as $\psi_{Hf} = \psi_{Df}(x, t, CHf)$ is linear in $C_{Hf}$, but $x$, $t$ is dependent by means of its $C_D$ dependence. For the nonequilibrium sorption reaction we cannot argue in the same way, as due to the time dependence of $C_{Hf}$ we cannot expect the fraction of the total DOC in form of carrier-bound HOC to be $\alpha \Pi(C_{Hf})S_D$.

For the special case of a linear rate function, that is,

$$ \delta S_D = k_C S_D - k_d S_D \quad (25) $$

for constants $k_C$, $k_d$, by means of (14a) and (14b) $C_D$ can be split in $C_{Df}$ and $C_{Db}$ and thus also $S_D$ such that

$$ S_D = \frac{\rho_{\psi Df}}{\rho_{\psi D}} S_{Df} + \frac{\rho_{\psi Db}}{\rho_{\psi D}} S_{Db} \quad (26) $$

The only requirement is that the initial condition for $S_D$ is such that a splitting like (26) exists, which is evident. Then $S_{Df}$ and $S_{Db}$ can be defined by means of the rate functions given in (21c) and (21d), respectively. According to (14a) and (14b), $S_{Hf}$ then also fulfills the rate function

$$ \delta S_{Hf} = \frac{\rho_{\psi Db}}{\rho_{\psi D}} k_C S_{Hf} - k_d S_{Hf} \quad (27) $$
Special Cases

In this section we will discuss how to apply the model to special cases, for example, to batch sorption experiments or linear sorption reactions, which will relate our work to the modeling approaches.

Linear Sorption of HOC to Carrier DOC

Assume that the partition of HOC between carrier DOC and liquid phase is a linear function of the total mass concentration of HOC in the liquid phase, that is,

$$
\Pi(C_{\text{H}}) = K_{\text{HD}} C_{\text{H}}
$$

(28)

where $K_{\text{HD}}$ denotes the partition coefficient of HOC between carrier DOC and liquid phase. This assumption seems to be valid for the case when the concentration of HOC is very small compared to the concentration of carrier DOC. This situation is usually met in surface and subsurface horizons of soils. Then $C_{\text{HB}}$, the concentration of carrier-bound HOC, can be written as

$$
C_{\text{HB}} = C_{\text{D}} K_{\text{HD}} C_{\text{H}}
$$

(29)

With that, $G(C_{\text{D}}, C_{\text{H}})$ is explicitly given by

$$
G(C_{\text{D}}, C_{\text{H}}) = \frac{1}{1 + C_{\text{D}} K_{\text{HD}}} C_{\text{H}}
$$

(30)

and we get for the effective isotherm $\Psi(x, t, C_{\text{H}})$

$$
\Psi(x, t, C_{\text{H}}) = \frac{\rho_{\text{HB}}}{\rho_{\text{H}}} \left( \frac{1}{1 + C_{\text{D}} K_{\text{HD}}} C_{\text{H}} \right)
$$

(31)

If we further assume that $\Psi_{\text{HF}}$ and $\Psi_{\text{HB}}$ are also linear sorption isotherms then

$$
\Psi_{\text{HF}}(C_{\text{H}}) = K_{\text{HF}} C_{\text{H}}
$$

(32a)

$$
\Psi_{\text{HB}}(C_{\text{H}}) = K_{\text{HB}} C_{\text{H}}
$$

(32b)

where $K_{\text{HF}}$ and $K_{\text{HB}}$ denote the partition coefficient for the free and the carrier-bound HOC, respectively, and the effective isotherm is explicitly given by

$$
\Psi(x, t, C_{\text{H}}) = \frac{\rho_{\text{HF}}}{\rho_{\text{H}}} \left( \frac{1}{1 + C_{\text{D}} K_{\text{HD}}} C_{\text{H}} \right) K_{\text{HF}} C_{\text{H}}
$$

(33)

Under the restriction of no sorption of carrier-bound HOC to the bulk soil material, that means $K_{\text{HB}} = 0$, and the effective isotherm reduces to

$$
\Psi(x, t, C_{\text{H}}) = \frac{\rho_{\text{HF}}}{\rho_{\text{H}}} \left( \frac{1}{1 + C_{\text{D}} K_{\text{HD}}} K_{\text{HF}} C_{\text{H}} \right)
$$

(34)

This is the form of the effective isotherm used by Kan and Tomson [1990], Dunningall et al. [1992a] and Magee et al. [1991]. The application of the model with such restrictions is limited to the case of nonreactive carrier-influenced transport of reactive solutes. As has been discussed in the section on experimental evidence, in the case of DOC as carrier molecule the assumption of DOC being a nonreactive carrier is no longer valid for the case of transport through natural soils, and the sorption and desorption of DOC has to be taken into account.

Lafrence et al. [1989] suggested a three-site transport model for reactive chemicals in porous media, which can also be considered as a special case of the general model if the following assumptions made by the authors are introduced. These assumptions are two types of sorption sites, one instantaneous, which should be describable by nonlinear Freundlich-type sorption isotherms and nonequilibrium sorption sites, accessible to the free dissolved chemical. A third nonequilibrium site should be accessible to the carrier-bound substance.

They restrict their discussions to the case where only monovalent complexation reactions are involved in the formation of carrier-bound chemicals. This corresponds to a description like (9) with linear II. Little is known regarding the chemical and structural properties of DOC as a carrier molecule in soils. Consequently, we consider the restriction to only monovalent complexation reactions as unjustified. If we think of the DOC as spherical, huge macromolecules, one can imagine that the generally much smaller HOC can be incorporated in the interior of the DOC macromolecule. Another possible pathway could be the formation of micelle-like structures as described by Wershaw [1986].

This means that the assumption of DOC being a nonreactive chemical is no longer valid. Consequently, the assumption that the sorption of carrier-bound HOC is much greater compared to the sorption of carrier DOC alone does not seem to meet with the natural situation. This assumption holds for the case in which the sorption of the carrier-bound molecule is due to a specific sorption mechanism, which depends on a functional group of the reactive chemical. In general, we cannot exclude nonspecific sorption mechanisms, and therefore a model for carrier facilitated transport should take into account the sorption of the carrier molecules itself. Enfield et al. [1989] developed a different approach to simulate the influence of macromolecules on reactive chemical transport. Their fundamental assumption is that the solute carrier macromolecule does not undergo sorption reactions itself. They divided the total flow domain into two subdomains governed by two distinct "mobile" phases: a mobile aqueous phase and a mobile organic phase. Each phase was assigned its own flow regime which is characterized by different dispersion coefficients and mean pore water velocities. For each domain they applied an advective-dispersion equation to describe the transport in two mobile phases. The transfer between the mobile phases is described by rate functions acting as sinks for one phase and as source for the other phase. The interaction between mobile phases and immobile solid phases is described by rate functions, too. All rate functions are assumed to be of the first-order, that is, linear, type.

The conceptual division of the flow domain into a mobile organic and a mobile aqueous phase seems to be appropriate to simulate carrier-facilitated transport. But one has to note that there actually is no organic liquid phase with intrinsic mobility present. The mobility of the organic macromolecules depends on their dissolution in the aqueous phase. So the proposed division of the flow domain is a pragmatic way of describing the transport phenomena observed in porous media.

In contrast, a mechanistic approach to describe the fact that a part of the porous medium is not accessible to the mobile phase would be to consider the exclusion of smaller pores for the dissolved macromolecules. We will discuss the conse-
The fundamental property of batch experiments is their homogeneity in space. So \( C_H^b, S_H^b, S_{Hb}^b \) are independent of space and \( \text{div} \left( \theta \frac{\partial C_H}{\partial t} \frac{\nabla C_H}{\Delta x} - q_{C_H^b} \right) = 0 \). With that, (13a) reduces to

\[
\theta \frac{\partial C_H}{\partial t} + \rho_{PHb} \nabla \left[ G \left( C_H^0(x, t), C_H^b \right) \right] = 0
\]

or \( \theta C_H + \rho_{PHb} \Psi(t, C_H^0) + \rho_{PHb} S_H^b + \rho_{PHb} S_{Hb}^b = 0 \) constant. The rate functions for the sorption at nonequilibrium sites will be

\[
\frac{\partial S_H^b}{\partial t} = f_{Hb}(t, C_H^b, S_H^b)
\]

The equations for \( C_{Hb} \), for example, (23), simplify analogously.

Batch experiments are an appropriate method to determine capacity and kinetics of the sorption of HOC to BSM in the absence and presence of carrier DOC. These experiments can be used to determine the adequate sorption isotherm or the rate functions \( g \).

Equations (37a)-(37c) are the statement of the general model in the batch experiment case. The problem is to solve the ordinary differential equations (37a)-(37c) for known initial values at the initial time, say, \( t = 0 \).

\[
C_{Hb}(0) = C_{Hb}^0, S_H^b(0) = S_{Hb}^0, S_{Hb}(0) = S_{Hb}^0
\]

**Kinetic Rate Functions**

If we are interested in the kinetics of the sorption process, we have to integrate (37a) for distinct times \( t > 0 \) over the interval \([0, t]\). The conservation of mass then leads for every distinct time \( t \) to the problem

\[
\Theta C_H + \rho_{PHb} \Psi(t, C_H^0) + \rho_{PHb} S_H^b + \rho_{PHb} S_{Hb}^b
\]

\[
= \Theta C_{Hb} + \rho_{PHb} \Psi(0, C_H^0) + \rho_{PHb} S_{Hb}^b + \rho_{PHb} S_{Hb}^b
\]

\[
\frac{\partial S_H^b}{\partial t} = f_{Hb}(t, C_H^b, S_H^b)
\]

\[
\frac{\partial S_{Hb}^b}{\partial t} = f_{Hb}(t, C_H^b, S_{Hb}^b)
\]

**Equilibrium Sorption Isotherms**

If we are interested in the equilibrium sorption isotherms, we have to solve (38a)-(38c) for the time \( t \rightarrow \infty \). We expect the stabilization

\[
C_{Hb}(t) \rightarrow C_{Hb}^b
\]

\[
S_H^b(t, C_H^b) \rightarrow S_{Hb}^b
\]

\[
S_{Hb}(t, C_H^b) \rightarrow S_{Hb}^b
\]

\[
C_{D}(t) \rightarrow C_{D}^b
\]

The rate functions for the sorption of the free HOC and the carrier-bound HOC to the nonequilibrium sites are zero. Usually, the sorbed concentrations are only functions of the dissolved total concentration of HOC (compare (3a) and (3b) in part 2):

\[
f_{Hb}(\infty, C_H^b, S_H^b) = 0 \Rightarrow S_H^b = S_{Hb}^b(C_H^b)
\]

\[
f_{Hb}(\infty, C_H^b, S_{Hb}^b) = 0 \Rightarrow S_{Hb}^b = S_{Hb}^b(C_{Hb})
\]

Here \( f_{Hb}(\infty, C, S) \) is given by (13b), and \( C_D = C_D^b \) and \( f_{Hb}(\infty, C, S) \) are given in an analogous way by (13c). Equation (38a) implies

\[
\Theta C_{Hb}^0 + \rho_{PHb} \Psi(C_{Hb}^0) + \rho_{PHb} S_{Hb}^0 + \rho_{PHb} S_{Hb}^0 = \Theta C_{Hb}^0
\]

\[
+ \rho_{PHb} \Psi(C_{Hb}) + \rho_{PHb} S_{Hb}^0 + \rho_{PHb} S_{Hb}^0 = \Theta C_{Hb}^0
\]
where \( \theta C_{H0} \) is the total mass concentration of HOC added to the system at time \( t = 0 \). The superscript "eq" denotes equilibrium. For given \( C_{H0} \), (41) is a nonlinear equation for \( C_{H} \), or if (40a) and (40b) cannot be resolved explicitly, (40a), (40b), and (41) are (nonlinear) equations for \( C_{H}^{eq}, S_{eq}^{H}, \) and \( S_{neq}^{H} \). They can be resolved numerically.

**Conclusions**

Using experimental evidence, we have shown the need for a mathematical model which not only takes into account the processes leading to carrier-facilitated transport but also the carrier introduced reduced mobility of solutes in porous media. We have presented a model to describe the transport of a solute in porous medium, which undergoes equilibrium and nonequilibrium adsorption to an immobile sorbent (the soil matrix), but also equilibrium adsorption to a mobile sorbent, for example, DOC. The carrier itself, the free HOC and the complex bound fraction of the HOC is allowed to undergo equilibrium and nonequilibrium adsorption to the soil matrix. We thus have the interplay of the transport with various competing processes: the reduction in mobility due to the adsorption to the soil matrix, a diminishing of this adsorbed fraction, for example, DOC. The carrier, itself, the free HOC and the complex bound fraction of the HOC is allowed to undergo equilibrium and nonequilibrium adsorption to the soil matrix. We have set up a model to incorporate all these processes. By transforming the model in terms of total concentrations of HOC and DOC we simplify the model and have a direct expression for the overall effect of the processes mentioned by means of effective isotherms and rate functions. In this way we are able to identify quantitatively whether we end up with an increase or decrease of mobility. This will be worked out in part 2 of this paper.

**Notation**

- \( H \): hydrophobic organic chemical (HOC) pollutant.
- \( D \): dissolved organic compound (DOC), carrier molecule.
- \( f \): free.
- \( b \): bound to mobile sorbent.
- \( eq, neq \): equilibrium and nonequilibrium, respectively.
- \( \alpha \): ratio of mass of HOC-DOC particle to HOC particle.
- \( \partial/\partial t, \partial_1 \): differentiation with respect to time.
- \( \text{div} (\_\_) \): divergence and gradient in space.
- \( \theta \): volumetric water content with respect to unit volume of porous medium \([L^3L^{-3}]\).
- \( \Pi \): mass of HOC bound to carrier DOC relative to the total mass of dissolved carrier (not in (15)–(17)) \([MM^{-1}]\).
- \( \rho \): density of bulk soil material (BSM) related to unit volume of porous medium \([ML^{-3}]\).
- \( \rho_{eq}, \rho_{neq} \): bulk density of fractions of the BSM assigned to equilibrium and nonequilibrium sites, respectively \([ML^{-2}]\).
- \( \rho_{Hb} \): bulk density of the BSM providing equilibrium sorption sites for carrier-bound DOC \([ML^{-3}]\).
- \( \rho_{Hf} \): bulk density of the fraction of the BSM providing equilibrium sorption sites for carrier-bound HOC \([ML^{-3}]\).
- \( \rho_{Hf} \): bulk density of the fraction of the BSM providing equilibrium sorption sites for free HOC \([ML^{-3}]\).
- \( \rho_{Hf} \): bulk density of the fraction of the BSM providing nonequilibrium sorption sites for carrier-bound DOC \([ML^{-3}]\).
- \( \rho_{Hf} \): bulk density of the fraction of the BSM providing nonequilibrium sorption sites for free DOC \([ML^{-3}]\).
- \( \rho_{Hb} \): bulk density of the fraction of the BSM providing nonequilibrium sorption sites for carrier-bound HOC \([ML^{-3}]\).
- \( \rho_{Hf} \): bulk density of the fraction of the BSM providing nonequilibrium sorption sites for free HOC \([ML^{-3}]\).
- \( \Psi \): mass concentration related to fraction of mass of BSM sorbed to equilibrium sites; also total mass concentration of HOC composed of free and carrier-bound HOC sorbed to equilibrium sorption sites; effective isotherm \([MM^{-1}]\).
- \( \psi_{Hb} \): mass of carrier-bound HOC sorbed at equilibrium to the fraction of BSM providing equilibrium sorption sites \([MM^{-1}]\).
- \( \psi_{Hf} \): mass concentration of free HOC sorbed at equilibrium to the fraction of the BSM providing equilibrium sorption sites \([MM^{-1}]\).
- \( C \): mass concentration of solute related to the water-filled pore volume \([ML^{-3}]\).
- \( C_D \): total mass concentration of DOC dissolved in liquid phase \([ML^{-3}]\).
- \( C_{Db} \): mass concentration of carrier-bound DOC dissolved in liquid phase \([ML^{-3}]\).
- \( C_{Df} \): mass concentration of free DOC dissolved in liquid phase \([ML^{-3}]\).
- \( C_H \): total mass concentration of HOC \([ML^{-3}]\).
- \( C_{Hb} \): mass concentration of carrier-bound HOC dissolved in liquid phase \([ML^{-3}]\).
- \( C_{Hf} \): mass concentration of free HOC dissolved in liquid phase \([ML^{-3}]\).
- \( D \): matrix of sum of molecular diffusion and mechanical dispersion \([L^2T^{-1}]\).
- \( F \): rate of gain of mass of free HOC due to the formation of carrier-bound HOC \([ML^{-3}T^{-1}]\).
- \( g_{Db} \): reaction rate of the nonequilibrium sorption of carrier-bound DOC \([MM^{-1}T^{-1}]\).
- \( G_{Df} \): reaction rate of the nonequilibrium sorption of free DOC \([MM^{-1}T^{-1}]\).
- \( g_{Hf} \): reaction rate of the nonequilibrium sorption of free HOC \([MM^{-1}T^{-1}]\).
- \( g_{Hb} \): reaction rate of the nonequilibrium sorption of carrier-bound HOC \([MM^{-1}T^{-1}]\).
- \( G \): mass concentration of free HOC in liquid phase in the presence of carrier DOC \([ML^{-3}]\).
- \( J \): volumetric flux \([ML^{-2}T^{-1}]\).
- \( f_{Hf} \): effective rate function for free HOC sorption to nonequilibrium sites \([MM^{-1}T^{-1}]\).
References


