

Mobile Organic Sorbent Affected Contaminant Transport in Soil: Numerical Case Studies for Enhanced and Reduced Mobility

Kai Uwe Totsche* and Ingrid Kögel-Knabner

ABSTRACT

Mobile organic sorbents (MOS) such as dissolved and colloidal phase organic matter control flow of water and transport of solutes in soils. We studied the effect of MOS on contaminant fate by systematic numerical case studies. The scenarios considered were (i) enhanced mobility, (ii) reduced mobility due to cosorption, and (iii) reduced mobility due to cumulative sorption. The enhanced mobility and cosorption scenario require contaminant sorption to the MOS. The cosorption and cumulative sorption scenario require sorption of MOS to the immobile sorbent. Simulations were run for physicochemically different fractions of dissolved organic matter and two model contaminants. Mobile organic sorbents mobility is characterized by a wide range of retardation parameters. Continued import of MOS to subsoil material high in MOS-specific sorption sites will increase the solid phase organic matter content. Enhanced mobility was observed for soils without MOS-specific sorption sites or for situations where MOS are in sorptive equilibrium with the immobile sorbent. Cosorption resulted in reduced contaminant mobility. The extent to which reduced mobility was observed depended on the ratio of the affinities of the free contaminant and the MOS-bound contaminant. As the sorption of the MOS-bound contaminants is controlled by the properties of the MOS, the characterization of these properties is a crucial step for the estimation of the effect of MOS on contaminant mobility. Cumulative sorption resulted in reduced contaminant mobility as well. However, this result is the consequence of the increase of the sorption capacity due to the sorption of MOS, a long-term process that may last for years to decades.

MOBILE ORGANIC SORBENTS such as dissolved and colloidal phase organic matter affect flow of water and transport of solutes in soils (McCarthy and Zachara, 1989; Murphy and Zachara, 1995; Kögel-Knabner and Totsche, 1998; Totsche, 2001). Major processes between the solution and the solid phase, such as sorption, partitioning, speciation, and ion exchange, are influenced by the interactions with MOS. Their presence affects the solute solubility due to complexation, solubilization, carrier association, and the solvophobic effect. In recent years, research has focused on processes leading to mobility enhancement of organic and inorganic pollutants (Magee et al., 1991; Kan and Tomson, 1990; Grolimund et al., 1996; Elimelech and Ryan, 2002; Kretzschmar et al., 1999; Baumann et al., 2002; Saiers, 2002). The issue was to understand to what extent colloids may facilitate contaminant transport in porous media with respect to risk assessment, soil and groundwater reclamation, and

cleanup. Major compounds that have been shown to increase the solubility and thus the mobility of nutrients and contaminants are surfactants (Edwards et al., 1991; Haulbrook et al., 1993; Rahman et al., 1994; Liu and Chang, 1997), cosolvents (Nkedi-Kizza et al., 1985, 1987; Brusseau et al., 1991), (hydr)oxides, clay and other minerals (Saiers and Hornberger, 1996; Karathanasis, 1999; Degueldre et al., 2001), humic substances (Kan and Tomson, 1990; Ding and Wu 1997; McCarthy and Zachara, 1989; Dunnivant et al., 1992; Totsche et al., 1997; McCarthy, 1998; Kinniburgh et al., 1999) and humin-coated inorganic colloids (Amirbahman and Olson, 1993; Kretzschmar and Sticher, 1997). In contrast to aquatic environments (Buffle et al., 1998; Wilkinson et al., 1999; Degueldre et al., 2000; Jin and Flury, 2002), the majority of dissolved and colloidal-size solution phase constituents in soils is either biotic or organic in nature, or composed of inorganic matter with organic coatings.

Due to their chemical properties (i.e., chemical diversity and high concentration of functional groups), these substances interact both with components of the immobile solid phase and with other dissolved and colloidal phase components of the liquid phase. Contaminant facilitated transport in the presence of MOS applies to such environmental conditions where MOS have to be considered a nonreactive mobile-phase constituent; that is, neither filtration nor sorption or partitioning of MOS to the immobile solid phase occurs. This is the case for porous media that is either in sorptive equilibrium with MOS or has unfavorable conditions for MOS sorption or attachment. In soils, however, MOS have to be considered reactive and are subject to immobilization due to sorptive interactions with the immobile soil (Murphy and Zachara, 1995; Kaiser et al., 1997; Weigand and Totsche, 1998). Common MOS sorbents are iron-, manganese-, and aluminum-(hydr)oxides; clay minerals; and organic matter (Kaiser et al., 1996; Jardine et al., 1989; McCarthy et al., 1993; Weigand and Totsche, 1998; Kaiser and Zech, 1998). In such environments, MOS may cause reduced overall contaminant mobility due to immobilization of MOS and thus immobilization of the MOS-associated contaminants (Lee et al., 1989; Totsche et al., 1997). The underlying process has been described as cosorption. Also, mobile organic sorbents sorption can lead to an increase of the organic C content of the bulk soil, thus increasing potential contaminant binding sites, a process referred to as cumulative sorption (Totsche et al., 1997).

In this paper, we analyze the effect of MOS on the mobility of contaminants in different environmental set-

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Abbreviations: BTC, breakthrough curve; HM, heavy metals; HOC, hydrophobic organic compounds; MOS, mobile organic sorbents; PAH, polycyclic aromatic hydrocarbons.

tings by means of numerical case studies. The objective is to find qualitative and quantitative criteria to distinguish between the effects on contaminant mobility that derive from processes which lead to MOS-mediated enhanced or reduced contaminant mobility. This knowledge is of prime importance for a reliable assessment of contaminant fate and for the interpretation of laboratory and field-scale contaminant breakthrough data. In particular, we will introduce and discuss three different scenarios of MOS-affected transport in porous media: cotransport, cosorption, and cumulative sorption. Within the cotransport scenario, the carrier MOS are considered nonreactive with respect to the immobile solid phase but are allowed to interact with the contaminants. This scenario will help to understand the phenomena of MOS-facilitated transport. In the cosorption and cumulative sorption scenarios, the MOS are allowed to interact with the immobile solid phase. These scenarios will help to understand reduced solubility and thus reduced mobility of solutes in the presence of MOS. All scenarios are based on either field data or experimental data.

MODELING

Mobile Organic Sorbent-Affected Solute Transport in Soils

Mobile organic sorbents are characterized by a great chemical, structural, and shape diversity and a wide size range (Fig. 1).

The thorough modeling of the motion of MOS would require information on the position, orientation, size, shape, and velocity of each individual particle within the solution phase. Unfortunately, this information is

not currently available. A simpler approach could be based on the calculation of the orientation and position distributions of the MOS particles. The distributions are governed by the advection–diffusion/dispersion equation. The application of this approach, however, assumes size and shape symmetry to allow neglecting any possible coupling between rotary and translational motion (Brenner, 1974), an assumption in general not justified for natural colloidal material. A widely used approach for modeling colloid deposition and transport is based on filtration theory, that is, physical and chemical deposition and straining (Ibaraki and Sudicky, 1995; Kretzschmar et al., 1997; Wan and Tokunaga, 1997; Huber et al., 2000). Release, redistribution, transport, and retardation of mobile organic sorbents within the vadose zone are controlled by a complex interplay of biological and physicochemical interactions and processes (Chu et al., 2001; Bunn et al., 2002; Münch et al., 2002). To cover the processes of biogenic and pedogenic MOS formation in surface soil horizons, which can result in high initial concentration during MOS release (First Flush; Kaiser and Zech, 1998; Weigand and Totsche, 1998; Münch et al., 2002), MOS aggregation, and MOS aging, a more complex conceptual framework is required.

In the following, we introduce a model that considers the transport of nutrients and contaminants in the presence of mobile and immobile sorbents. The model represents an extension of previous work (Totsche, 1995; Knabner et al., 1996; Totsche et al., 1996; Prechtel et al., 2002). The extensions comprise the consideration of multiple nonlinear sorbents for the MOS and the solutes, different additional formulations of sorption isotherms, and additional rate laws to account for kinetic interactions. Unsaturated, steady-state transport is con-

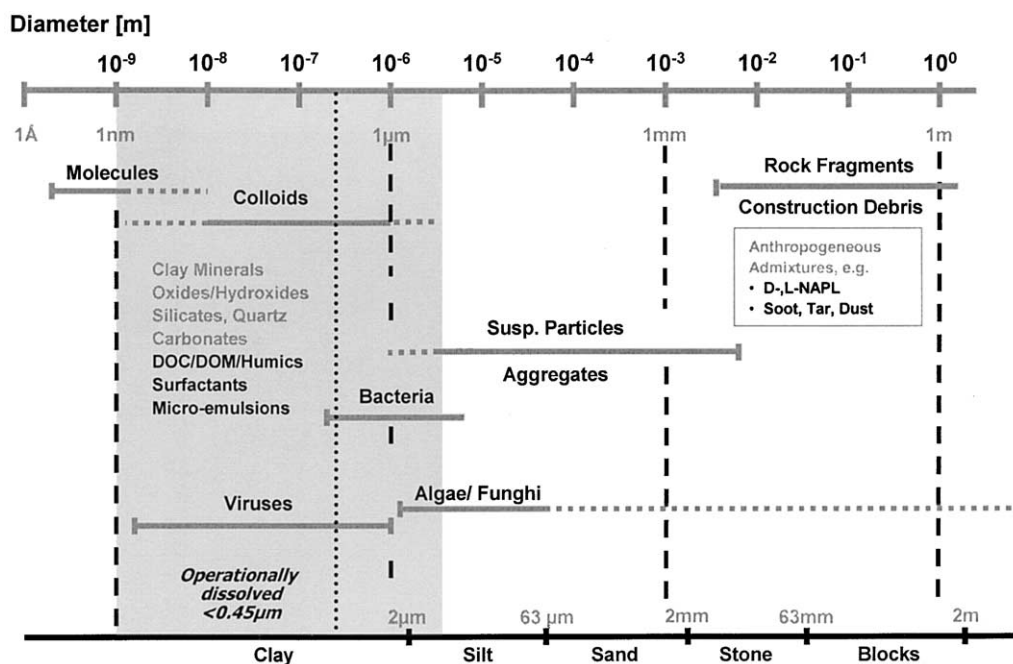


Fig. 1. Size class spectra of particles and aggregates of different origin in the soil environment. The shaded area represents the region of mobile materials. The dotted line designates the upper size limit of the operationally defined dissolved fraction. Note the small and medium-sized colloidal particles are part of this fraction, too.

sidered by allowing the water content to be defined as a function of depth and soil materials. At present, accumulation of colloidal material at the water–air interface is not taken into account. The mobile sorbents are considered reactive; that is, they are allowed to interact with the immobile solid phase and with each other (Fig. 2). Thus, MOS aggregation reactions can be modeled.

Advective, diffusive, and dispersive transport and equilibrium and nonequilibrium sorption of both solutes and MOS to multiple immobile phase sorbents are considered, to account for patchy or layered chemical heterogeneity (Sun et al., 2001; Luthi et al., 1998).

Transport of reactive solutes in the presence of a mobile sorbent is conceptualized by assuming at least two interacting constituents, the mobile organic sorbent and the freely dissolved solute, such as a contaminant. These constituents undergo association reactions resulting in three aqueous phase components: the free solute C_H ($M L^{-3}$), the free MOS C_D ($M L^{-3}$), and the MOS-associated solute C_{Hb} ($M L^{-3}$). Solubility enhancement, or the increase of the apparent solubility of the contaminant, results from solute–MOS association in the aqueous phase. In the presence of MOS, total aqueous concentration of the solute C_H ($M L^{-3}$) is given by the sum of free and MOS-associated solute

$$C_H = C_{Hf} + C_{Hb} \quad [1]$$

One may note that C_H , the total aqueous concentration of the solute is much higher than predicted by the

K_D (K_{OC}) or its aqueous solubility. If MOS and thus also the associate have to be considered as nonreactive with respect to the immobile solid phase, overall interactions of the solute with the immobile solid phase are reduced. Compared with the reference state (i.e., no MOS present), enhanced mobility due to cotransport is observed. In contrast, if MOS and the associate are subject to interactions with the immobile solid phase, total aqueous concentration of the solute will be smaller than predicted by the pure solid- and aqueous-phase equilibrium distribution K_D (K_{OC}) coefficient. We then observe reduced mobility.

Transport of both the solute and the MOS are modeled with the advection–dispersion equation:

$$\partial_t(\theta C) - \nabla(\theta D \nabla C - qC) = P \quad [2]$$

Here, ∂ denotes the differential operator, θ denotes the volumetric water content ($L L^{-3}$), C ($M L^{-3}$) is the mass concentration of the solute with respect to the water filled part of the pore volume, D ($L^2 T^{-1}$) is the coefficient of longitudinal dispersion, q ($L T^{-1}$) is the volumetric flux density, and P ($M L^{-3} T^{-1}$) is a volumetric source–sink term. In the general situation, P is the sum of both biological processes and physicochemical interactions. At present only sorptive interactions are considered within the model.

Sorptive Interactions

Sorption can be spontaneous, kinetically controlled, linear, or nonlinear. As the sorption sites are not the

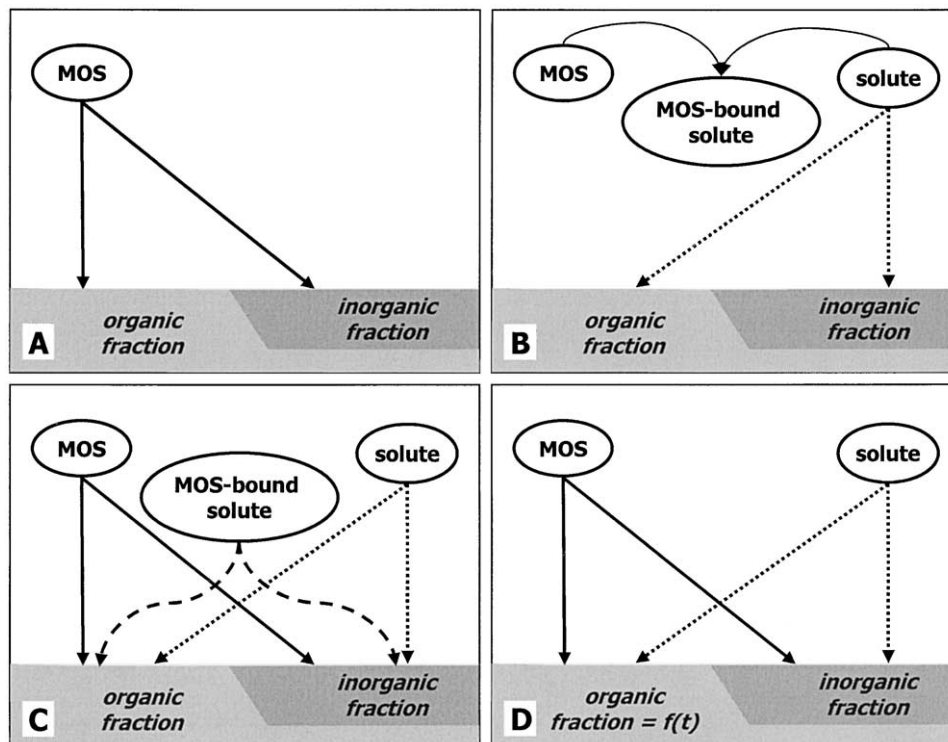


Fig. 2. Interaction pathways considered by the numerical case studies. The interactions can be of linear or nonlinear type, spontaneous or kinetically controlled. (A) Conceptual model for the transport of mobile organic sorbents (MOS) through soil. (B) Conceptual model for MOS enhanced contaminant mobility (Scenario A). (C) Conceptual model for reduced mobility due to cosorption (Scenario C). (D) Conceptual model for reduced mobility due to cumulative MOS-sorption (Scenario D). Note that for Scenario C the organic fraction of the bulk solid phase is a function of time. The solid phase is composed of different organic and inorganic sorbents. Effects of the mobile sorbents on solution phase properties like surface tension can be considered as well.

same for the solute, the MOS, and the associate, the bulk soil is considered to be composed of different disjoint fractions, each providing sorption sites for individual sorption reactions. Therefore, P can be written as

$$P(x,t) = -\rho_{\text{eq}}\partial_t\Psi[C(x,t)] - \rho_{\text{neq}}\partial_t S(x,t) \quad [3]$$

ρ_{eq} and ρ_{neq} (M L^{-3}) are the fractions of bulk density providing sorption sites for equilibrium and nonequilibrium sorption, and $\Psi[C(x,t)]$, $S(x,t)$ (M M^{-1}) are the amounts of mass sorbed to equilibrium and nonequilibrium sorption sites. Transport of total solute will take place in both the free and in the MOS-associated form. The corresponding equations are

$$\partial_t(\theta C_{\text{Hf}}) + \rho_{\Psi\text{Hf}}\partial_t\Psi_{\text{Hf}}(C_{\text{Hf}}) + \rho_{\phi\text{Hf}}\partial_t S_{\text{Hf}} - \nabla(\theta D\nabla C_{\text{Hf}} - q C_{\text{Hf}}) = F \quad [4]$$

for the free solute and

$$\partial_t(\theta C_{\text{Hb}}) + \rho_{\Psi\text{Hb}}\partial_t\Psi_{\text{Hb}}(C_{\text{Hb}}) + \rho_{\phi\text{Hb}}\partial_t S_{\text{Hb}} - \nabla(\theta D\nabla C_{\text{Hb}} - q C_{\text{Hb}}) = -F \quad [5]$$

for the MOS associated solute. F ($\text{M L}^{-3} \text{T}^{-1}$) denotes the consumption rate of free solute due to the formation of MOS-associated solute, and $-F$ [$\text{M L}^{-3} \text{T}^{-1}$] is the production rate. Provided the production rate of MOS-bound solute equals the consumption rate of free solute, the addition of Eq. [5] and [6] will give the overall transport equation for total mass of solute:

$$\partial_t(\theta C_{\text{H}}) + \rho_{\Psi\text{Hf}}\partial_t\Psi_{\text{Hf}}(C_{\text{Hf}}) + \rho_{\phi\text{Hf}}\partial_t S_{\text{Hf}} - \rho_{\Psi\text{Hb}}\partial_t\Psi_{\text{Hb}}(C_{\text{Hb}}) + \rho_{\phi\text{Hb}}\partial_t S_{\text{Hb}} - \nabla(\theta D\nabla C_{\text{H}} - q C_{\text{H}}) = 0 \quad [6]$$

For simplicity we will continue for the special case of linear contaminant–MOS association and Freundlich-type sorption reactions for both the equilibrium and the nonequilibrium interactions of the free and the MOS-bound solute. The interactions considered are partitioning or sorption following a Freundlich- or Langmuir-type Isotherm. Furthermore, a dual-mode sorption mechanism is available, which superimposes a linear sorption process with a nonlinear interaction following Polanyi-potential theory to cover sorption to microporous solids, as well. A number of lab and field studies have shown that soils provide different sorbents for MOS. Among others, the pedogenic iron oxides and the soil organic matter are important sorbents (Kaiser et al., 1996; Jardine et al., 1989; McCarthy et al., 1993; Weigand and Totsche, 1998; Kaiser and Zech, 1998). Thus, we have to consider individual soil constituents, given as mass fractions of the bulk soil mass. Sorption to an individual fraction of the bulk soil is then given by

$$\begin{aligned} \Psi_{\text{Hf}}(C_{\text{Hf}}) &= K_{\text{Hf}} C_{\text{Hf}}^p \\ \Psi_{\text{Hb}}(C_{\text{Hb}}) &= K_{\text{Hb}} C_{\text{Hb}}^q \end{aligned} \quad [7]$$

where p and q are the respective Freundlich exponents for the different fractions. It is also well established that sorption and release of MOS are highly rate limited (Kaiser et al., 1996; Weigand and Totsche, 1998; Münch et al., 2002). Rate-limited sorption can be calculated by

$$\begin{aligned} \partial_t S_{\text{Hf}} &= k_{\text{Hf}}[\varphi_{\text{Hf}}(C_{\text{Hf}}) - S_{\text{Hf}}] \\ \partial_t S_{\text{Hb}} &= k_{\text{Hb}}[\varphi_{\text{Hb}}(C_{\text{Hb}}) - S_{\text{Hb}}] \end{aligned} \quad [8]$$

Within the code, other rate laws (e.g., diffusion-limited sorption) are available as well. For the simulation scenarios presented here, we use a constant rate independent on the concentrations.

The Effective Isotherm

With the association reaction expressed in terms of an instantaneous linear equilibrium interaction, that is

$$C_{\text{Hb}} = C_{\text{D}} K_{\text{DOM}} C_{\text{Hf}} \quad [9]$$

we are able to identify the partial mass concentrations of free and MOS-bound solute in terms of total mass concentration of solute and MOS:

$$\begin{aligned} C_{\text{Hf}} &= \frac{1}{1 + K_{\text{DOM}} C_{\text{D}}} C_{\text{H}} \\ C_{\text{Hb}} &= \frac{K_{\text{DOM}} C_{\text{D}}}{1 + K_{\text{DOM}} C_{\text{D}}} C_{\text{H}} \end{aligned} \quad [10]$$

Here, C_{D} (M L^{-3}) denotes the total solute mass concentration of the MOS, and K_{MOS} ($\text{L}^3 \text{M}^{-1}$) is the partitioning coefficient or the solute between the aqueous phase and the MOS. Using Eq. [7] in combination with Eq. [10], equilibrium sorption of free and MOS-bound solute can be reformulated in terms of total mass concentration of solute C_{H} and MOS C_{D} :

$$\begin{aligned} \Psi(x,t,C_{\text{H}}) &= \rho_{\Psi\text{Hf}}/\rho_{\Psi\text{H}}\Psi_{\text{Hf}}(C_{\text{Hf}}) + \rho_{\Psi\text{Hb}}/\rho_{\Psi\text{H}}\Psi_{\text{Hb}}(C_{\text{Hb}}) \\ &= \rho_{\Psi\text{Hf}}/\rho_{\Psi\text{H}} K_{\text{Hf}} \left(\frac{1}{1 + K_{\text{DOM}} C_{\text{D}}} C_{\text{H}} \right)^p + \\ &\quad \rho_{\Psi\text{Hb}}/\rho_{\Psi\text{H}} K_{\text{Hb}} \left(\frac{K_{\text{DOM}} C_{\text{D}}}{1 + K_{\text{DOM}} C_{\text{D}}} C_{\text{H}} \right)^q \end{aligned} \quad [11]$$

Equation [11], the effective isotherm, computes the overall equilibrium sorption of total solute due to the partial sorption of free and MOS-bound solute to the corresponding fractions of sorption sites. With Eq. [11], overall transport of total solute (Eq. [6]) can be expressed in terms of the effective isotherm:

$$\partial_t(\theta C_{\text{H}}) + \rho_{\Psi\text{H}}\partial_t\Psi(x,t,C_{\text{H}}) + \rho_{\phi\text{Hf}}\partial_t S_{\text{Hf}} + \rho_{\phi\text{Hb}}\partial_t S_{\text{Hb}} - \nabla(\theta D\nabla C_{\text{H}} - q C_{\text{H}}) = 0 \quad [12]$$

The transport equation for the mobile organic sorbents is given by an individual advection-dispersion equation, also. Linear steady-state movement of the MOS is then represented by

$$\partial_t(\theta C_{\text{D}}) + \rho_{\Psi\text{D}}\partial_t\Psi_{\text{D}}(C_{\text{D}}) + \rho_{\phi\text{D}}\partial_t S_{\text{D}} - \nabla(\theta D\nabla C_{\text{D}} - q C_{\text{D}}) = 0 \quad [13]$$

Equation [12]—in combination with Eq. [13] for MOS transport and with Eq. [5] and [6], which also have to be expressed in terms of total concentrations—represents the overall transport model for reactive solutes in the presence of mobile reactive MOS. Within this paper, flow of the mobile phase is assumed to be at steady state. By doing so, we are able to analyze the effect of

the physicochemical interactions on the breakthrough behavior of the solutes. We are well aware of the fact that this assumption holds only for column experiments. The effect of transient and nonhomogenous flow on MOS-affected solute transport is highly relevant for the evaluation of field transport of contaminants. Unfortunately, data on such transport conditions are currently not available, so our analysis is restricted to steady-state flow conditions.

A Priori Estimator for MOS-Affected Contaminant Transport

In the special situation of equilibrium interactions, we can estimate the effect of MOS on the transport of solutes by calculation of the ratio of the weighted isotherms of the free solute and the carrier-bound solute for the maximum observed concentration of the solute and the maximum expected concentration of the carrier:

$$\beta = \frac{\rho_{\Psi_{\text{Hb}}} \Psi_{\text{Hb}}(C_{\text{Hb max}})}{\rho_{\Psi_{\text{Hf}}} \Psi_{\text{Hf}}(C_{\text{Hf max}})} \quad [14]$$

for the general case and

$$\beta = \frac{\rho_{\Psi_{\text{Hb}}} K_{\text{Hb}}}{\rho_{\Psi_{\text{Hf}}} K_{\text{Hf}}} \quad [15]$$

for the equilibrium partitioning case (Totsche, 1995; Totsche et al., 1996). If β is smaller than unity, enhanced mobility is observed. For the equilibrium case, the breakthrough time t_{BTC} and the dimensionless breakthrough time pV_{BTC} of a solute in the presence of MOS can be estimated a priori using the effective isotherm.

$$t_{\text{BTC}} = \frac{L}{q} \left\{ \theta + \left[(\rho_{\Psi_{\text{Hf}}} + \rho_{\Psi_{\text{Hb}}}) \left(\frac{\rho_{\Psi_{\text{Hf}}} K_{\Psi_{\text{Hf}}} C_{\text{Hf}}^{\rho_{\Psi_{\text{Hf}}}} + \frac{\rho_{\Psi_{\text{Hb}}} K_{\Psi_{\text{Hb}}} C_{\text{Hb}}^{\rho_{\Psi_{\text{Hb}}}}}{\rho_{\Psi_{\text{Hf}}} + \rho_{\Psi_{\text{Hb}}} C_{\text{Hf}} + C_{\text{Hb}}} \right) \right] \right\}$$

and

$$pV_{\text{BTC}} = \frac{q t_{\text{BTC}}}{\theta L} \quad [16]$$

NUMERICAL CASE STUDIES

All numerical case studies presented here are based on experimental and field data given in the literature.

Table 1. Parameters used for all simulation scenarios.

Parameter	Symbol (unit)	Value
Water content	θ (L)	0.35
Specific discharge	q (m s ⁻¹)	1.667×10^{-5}
Dispersivity	λ (m)	0.001
Bulk density	d_b (kg m ⁻³)	1500
Length	L (m)	0.05
Inflow concentration HOC [†]	C_{HOC} (kg m ⁻³)	5×10^{-5}
Inflow concentration heavy metal	C_{HM} (kg m ⁻³)	5×10^{-3}
Inflow concentration MOS [‡]	C_{MOS} (kg m ⁻³)	$(0, 1, 5, 10, 50, 100) \times 10^{-3}$
Peclet number	Pe (L)	50

[†] Hydrophobic organic compounds.

[‡] Mobile organic sorbents.

\parallel $Pe = L/\lambda$.

Details on experimental conditions, MOS sorption parameters, and contaminant–MOS interaction parameters can be found elsewhere (Dunnivant et al., 1992; Münch et al., 2002; Totsche et al., 1997; Kögel-Knabner and Totsche, 1998; Kögel-Knabner et al., 2000; Weigand and Totsche, 1998; Kaiser et al., 1997; Kaiser and Zech, 1997, 1998). All simulations were run with the same model domain and flow regime; the respective parameters are summarized in Table 1. The numerical code used is written in C and C++ programming language and can be run on both workstations (e.g., GNU C++ compiler) and PCs.

We assume a soil horizon of 0.05-m length, advection-dominated steady-state flow regime (Peclet number, $Pe = 50$) homogeneously composed of sorbents for both the MOS and the solute and unsaturated flow conditions ($\theta < \theta_{\text{sat}}$). A continuous feed upper boundary condition is used for both the solutes and the MOS. All aqueous phase components are subject to the same dispersion. This assumption is based on the fact that only few data on the dispersivity of MOS are available which result from column experiments. The calculated dispersivities of the MOS did not significantly differ from the dispersivities of the conservative tracer. This assumption, however, should be checked experimentally in more detail. No sinks other than sorption-like interactions with the immobile solid phase are allowed; in particular, no chemical or biological degradation is acting on the substances. Sorption of the free solute, the MOS, and the MOS-associated solute are described by linear or nonlinear Freundlich-type interactions. The association reaction between contaminant and MOS is assumed to be fast compared with the flow velocity and with the interactions with the solid phase. Thus, an equilibrium sorption is used for the interactions between the contaminants and the MOS. Table 2 summarizes the parameter sets used for the individual scenarios.

The scenarios cover typical contaminant transport situations in soils and aquifers. We consider two contaminant types: heavy metal (HM) and hydrophobic organic contaminant (HOC). The sorption of the HM to the bulk soil is characterized by a lower partition coefficient ($K_{\Psi_{\text{Hf}}} = 0.5 \text{ m}^3 \text{ kg}^{-1}$) and sorption to hydrophilic MOS, while the sorption of the hydrophobic contaminants is characterized by a higher partition coefficient ($K_{\Psi_{\text{Hf}}} = 50 \text{ m}^3 \text{ kg}^{-1}$) to the bulk soil and sorption to the hydrophobic MOS.

Table 2. Specific parameter sets for the individual scenarios.†

Parameter	Scenarios																			
	MOS		A HOC		A HM		B HOC		B HM		B Special case HOC		B Special case HM		B Special case nonlinear		C Low affinity linear		C High affinity nonlinear	
	Fig. 3	Fig. 4c,d	Fig. 4a,b	Fig. 5c,d	Fig. 5a,b	Fig. 6c,d	Fig. 6a,b	Fig. 8	Fig. 10a	Fig. 10b										
ρ_{HOC} [10^3 kg m^{-3}], %	0.0	0.03 (2)	0.03 (2)	0.03 (2)	0.03 (2)	0.0015 (0.1)	0.0015 (0.1)	0.0015 (0.1)	0.03 (2)	0.03 (2)	0.03 (2)	0.0015 (0.1)	0.0015 (0.1)	0.0015 (0.1)	0.03 (2)	0.03 (2)	0.03 (2)	0.03 (2)	0.03 (2)	0.03 (2)
ρ_{HM} [10^3 kg m^{-3}], %	0.0	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)
ρ_{VD} [10^3 kg m^{-3}], %	1.47	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	1.47 (98)	0.12 (8)	0.12 (8)	0.12 (8)	0.12 (8)	0.12 (8)	0.12 (8)
K_{HOC} [$\text{m}^3 \text{ kg}^{-1}$]	0.0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
K_{HM} [$\text{m}^3 \text{ kg}^{-1}$]	0.0	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
ρ_{HOC} [$\text{m}^3 \text{ kg}^{-1}$]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ρ_{HM} [$\text{m}^3 \text{ kg}^{-1}$]	0.015, 0.187, 0.935, 1.870, 5.610	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
ρ_{VD} [$\text{m}^3 \text{ kg}^{-1}$]	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
K_{HOC} [$\text{m}^3 \text{ kg}^{-1}$]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\rho_{\text{HOC}} = \rho_{\text{VD}}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

† A: Scenario A, cotransport; B: Scenario B, cosorption; Scenario C, cumulative sorption; HM: heavy metal; HOC: hydrophobic organic contaminant; MOS: mobile organic sorbent.

RESULTS AND DISCUSSION

Transport of Mobile Organic Sorbents

Figure 3 gives the breakthrough of MOS of varying affinity to soil normalized to the inflow concentration C_{0D} .

The most important feature is the wide range of mobilities as indicated by the breakthrough curves (BTC). The mobility of MOS or fractions of MOS can be as high as the mobility of conservative tracers or as low as hydrophobic contaminants (Table 3).

This broad range of mobilities reflects the diverse physicochemical nature of MOS as reported in the literature (e.g., Kaiser et al., 1996; Kaiser and Zech, 1998; Münch et al., 2002). The affinity is calculated as the product of the fraction of the bulk density, which provides MOS-specific sorption sites (ρ_{VD}), and the respective sorption model (Ψ_{VD}). This product determines the retardation of MOS, as the sorption of MOS depends on both the amount of specific sorption sites and on the individual MOS sorption isotherm. The parameter values used for the simulation scenario were taken from batch and column experiments with different porous media, different MOS types, and typical MOS concentrations in soils (Kaiser et al., 1996; Weigand and Totsche, 1998; Jardine et al., 1989; McCarthy, 1998). The MOS types considered are the hydrophilic fraction, the hydrophobic fraction, and an intermediate fraction of the dissolved organic matter. The three fractions are different with respect to sorption to the components of the immobile solid phase and with respect to the association with other solution phase components. While the hydrophilic MOS fraction is more mobile and seems to relate to the transport of HM (Guggenberger et al., 1994), the hydrophobic fraction is more strongly retarded and interacts with more hydrophobic pollut-

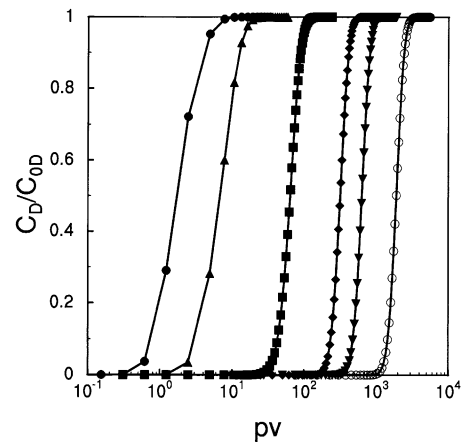


Fig. 3. Breakthrough of mobile organic sorbents (MOS) with different affinity to soil. The interaction parameters are chosen such that the corresponding breakthrough curves represent different MOS or MOS fractions. filled circles, $\rho_{\text{VD}}K_{\text{VD}} = 0.18$, MOS hydrophilic, low content of sorbing minerals; triangles, $\rho_{\text{VD}}K_{\text{VD}} = 1.8$, MOS hydrophilic, higher content of sorbing minerals; squares, $\rho_{\text{VD}}K_{\text{VD}} = 22.4$, MOS intermediate, low content of sorbing minerals; diamonds, $\rho_{\text{VD}}K_{\text{VD}} = 112$, MOS intermediate, higher content of sorbing minerals; inverted triangles, $\rho_{\text{VD}}K_{\text{VD}} = 224$, MOS hydrophobic, low content of sorbing minerals; circles, $\rho_{\text{VD}}K_{\text{VD}} = 673$, MOS hydrophobic, high content of sorbing minerals.

Table 3. Affinities and respective breakthrough times calculated for the different mobile organic sorbent (MOS) fractions.

MOS type†	MOS			
	$\rho_{\Psi D}K_{\Psi D}$	$\rho_{\Psi BTC}$	$\rho_{\Psi D}$	$K_{\Psi D}$
Hydrophilic, l.a.	0.45	2.3	0.03	15
Hydrophilic, h.a.	1.8	6.1	0.12	15
Intermediate, l.a.	28	81	0.03	935
Intermediate, h.a.	112	321	0.12	935
Hydrophobic, l.a.	168	481	0.03	5610
Hydrophobic, h.a.	673	1924	0.12	5610

† l.a., low amount of specific sorption sites; h.a., high amount of specific sorption sites.

ants like PAH (Kukkonen et al., 1990). When these different fractions travel through soil, selective sorption results in a relative decrease of the larger and more reactive MOS fractions in favor of the smaller, less reactive and thus more mobile MOS fractions. Additionally, competitive sorption reactions are known for mobile organic sorbents (Kaiser and Zech, 1997). Thus, the passage of MOS from the source horizons down to deeper soil and groundwater results in a chromatographic separation of MOS. Weigand and Totsche (1998) showed that overall transport of MOS originating from organic C-rich soil horizons like the forest floor can be understood and modeled by superimposing the breakthrough of two fractions, which are characterized by markedly different interaction parameters, just like the hydrophilic MOS differ from the hydrophobic MOS. While one fraction, comprising approximately 30% of overall MOS, was characterized by a spontaneous and low-affinity interaction with the immobile bulk solid phase, the remaining 70% were characterized by high-affinity, nonlinear and nonequilibrium interactions with the immobile solid phase. With that approach, the authors were able to predict the breakthrough of mobile organic sorbents through goethite-coated quartz sand at different flow velocities. With this in mind, the first two BTCs (solid circles, solid rectangles) given in Fig. 3 represent hydrophilic and thus mobile fractions of MOS through soils low in MOS-specific sorbents, while the last two BTCs (open circles, inverse solid triangles) represent the hydrophobic and thus less mobile fractions of MOS in soils with a high amount of MOS-specific sorption sites. The other BTCs (solid squares, solid diamonds) represent situations of intermediate MOS in soils with either high or low content of MOS-specific sorption sites.

Effect of Mobile Organic Sorbents on the Transport of Solutes in Soils

In the following, the effect of MOS on the transport of solutes will be discussed based on the results of numerical case studies of three different scenarios. Scenario A combines typical conditions for MOS-facilitated transport, while Scenarios B and C have the conditions for reduced mobility of contaminants in the presence of MOS.

Scenario A: Enhanced Mobility

The assumptions for Scenario A are as follows (conditions for the respective model parameters for this and all other scenarios are given in brackets):

- The solute sorbs to the mobile organic sorbents ($K_{MOS} > 0$).
- The solute sorbs to the immobile sorbents ($K_{\Psi HF} > 0$).
- The MOS do not sorb to the immobile bulk solid phase ($K_{\Psi D} = 0$).
- The properties of the MOS-bound contaminant are governed by those of the MOS; that is, no sorption of the associate occurs ($K_{\Psi D} = K_{\Psi HB} = 0$).

This set of assumptions applies for soil horizons that are either equilibrated and saturated with MOS or low in MOS sorbents, such as pedogenic oxides or clay minerals (e.g., eluvial [E] horizons). Soil horizons that are potentially sorbing MOS but partially saturated with MOS were found to be the A horizons, and Bh horizons of spodosols (Kaiser et al., 1996). Similar conditions may also be found in aquifers (McCarthy, 1998) and sediments with high input of MOS. Such conditions also prevail in those sediments and aquifer environments where MOS is mainly composed of low molecular weight, hydrophilic and therefore more mobile constituents. This nonreactive property of MOS is the result of a combination of several processes—filtering, sorption, ion exchange, flocculation, microbial transformation, and mineralization—acting on MOS during its passage from forest floor and organic-rich surface horizons to aquifers (Jardine et al., 1990; McCarthy et al., 1993; Weigand and Totsche, 1998). Although even low-molecular weight MOS undergoes association with HOC, the sorptive capacity of this type of MOS for HOC is considerably lower (Raber and Kögel-Knabner, 1997).

In Fig. 4 the BTCs obtained for this scenario with both contaminant types, the heavy metal (a,b) and the dummy HOC (c,d) are given. For the contaminant, the total (C_H ; a,c) and the free concentration (C_{HF} ; b,d) are shown. All concentrations are normalized to the inflow concentration C_0 of the respective solute.

The presence of MOS results in a progressively earlier breakthrough of the two different contaminants. First arrival and complete breakthrough is affected by the MOS in solution. With increasing MOS concentration C_D , from 0 to 0.100 kg MOS m^{-3} , breakthrough of the total solute is shifted to smaller porevolumes (Fig. 4a and 4c). The breakthrough of the free solute C_{HF} is also faster at higher MOS concentrations. The effluent concentration of the free solute (Fig. 4b and 4d) reduces from $C_{HF} = 0.9C_H$ for $C_D = 5$ to $C_{HF} = 0.5C_H$ for $C_D = 100.0$. The reduced effluent concentration of the free solute is due to the higher proportion of MOS-associated contaminant at higher MOS concentration (Eq. [11]). The increasing amount of MOS-associated solute leads also to increased mobility of the total solute, as the overall interactions of the total solute are more and more dominated by the interactions with the (nonreactive) MOS. Such situations have been observed in column experiments for HM and hydrophobic organic pollutants (Dunnivant et al., 1992; Kan and Tomson, 1990) where the solid phase materials were preequilibrated with MOS. Thus MOS-facilitated transport of the contaminants was to be observed. The relative effect of MOS on contaminant mobility is similar for both types

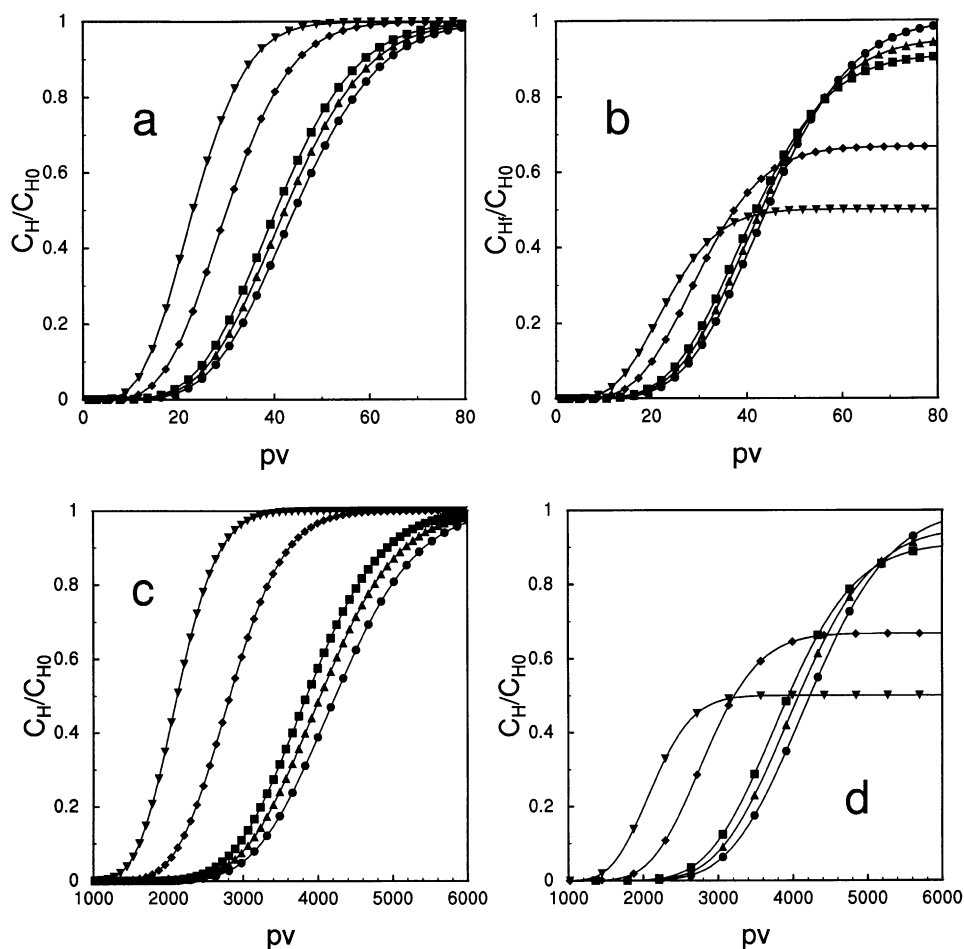


Fig. 4. Breakthrough of (a,b) a dummy heavy metal and (c,d) a dummy hydrophobic contaminant in the presence of increasing concentrations of mobile organic sorbents (MOS) for Scenario A, enhanced mobility. Given are the breakthrough curves for the free C_{Hf} and the MOS-bound solute C_{Hb} . For this scenario, no sorption of the MOS to the immobile solid phase is allowed ($\rho_{\psi D}K_{\psi D} = 0$). The symbols represent the following MOS concentrations (kg m^{-3}): circles, 0; triangles, 0.005; squares, 0.01; diamonds, 0.05; inverted triangles, 0.1.

of contaminants. Because of the difference in the affinity to the bulk solid phase of HM and HOC, the breakthrough times for HM are generally much shorter than for HOC (Tables 4 and 5).

It is important to note from Fig. 4b and 4d that the

breakthrough of the free solute is not only reduced with increasing MOS concentration, but also shifted to smaller pore volumes. With progressing propagation of the contaminant front in the soil, the interaction equilibrium between the three phases is continuously reestab-

Table 4. Expected breakthrough times for the respective solutes according to the specific scenarios: linear solute interactions, linear and nonlinear mobile organic sorbents (MOS).

C_{MOS}	$p v_{BTC}^{\dagger}$											
	A		B		B High affinity‡, linear solute§, linear MOS¶		B Low affinity#, linear solute, linear MOS		B High affinity, linear solute, nonlinear MOS††		B Low affinity, linear solute, nonlinear MOS	
	HOC	HM	HOC	HM	HOC	HM	HOC	HM	HOC	HM	HOC	HM
0	4286	44	4286	44	215	3.1	215	3.1	215.2	3.1	215.3	3.1
1	4244	43	4244	44	219	9.4	213	3.2	213.4	3.6	213.2	3.1
5	4082	42	4085	45	235	33.5	205	3.3	206.6	6.1	205.1	3.06
10	3897	40	3903	46	254	61.2	196	3.4	199	9.5	195.8	3.0
50	2858	30	2879	51	357	216.1	145	4.1	158.4	31.5	143.9	2.7
100	2143	22	2175	54	428	322.6	110	4.6	131.4	48.4	108.3	2.4
β	0	0	0.0147	1.47	2.99	299	0.024	2.4	2.992	299	0.024	2.4

† Number of exchanged porevolumes needed for the effluent concentration to reach 50% of the inflow concentration level.

‡ High affinity of the MOS to the immobile solid phase.

§ Linear sorption of solute to the solid phase.

¶ Nonlinear sorption of MOS to solid phase.

Low affinity of MOS to the immobile solid phase.

†† Nonlinear sorption of MOS to the solid phase.

Table 5. Expected breakthrough times for the respective solutes according to the specific scenarios. Nonlinear solute interaction, linear and nonlinear MOS.

C_{MOS}	B Low affinity, nonlinear solute, Linear MOS				B High affinity, nonlinear solute lin- ear MOS				B Low affinity, nonlinear solute, nonlinear MOS				B High affinity, nonlinear solute nonlinear MOS			
	HOC		HM		HOC		HM		HOC		HM		HOC		HM	
	pV_{BTC}	β	pV_{BTC}	β	pV_{BTC}	β	pV_{BTC}	β	pV_{BTC}	β	pV_{BTC}	β	pV_{BTC}	β	pV_{BTC}	β
0	18.2	0.0	1.3	0.0	18.2	0.0	1.3	0.0	18.2	0.0	1.3	0.0	18.2	0.0	1.3	0.0
1	18.1	0.29	1.4	15.0	24.4	37.3	8	1896	18.0	0.01	1.3	1.2	18.2	1.5	1.8	150.0
5	17.5	0.30	1.6	15.1	47.8	37.5	31	1880	17.3	0.02	1.4	1.5	18.8	1.9	4.4	190.9
10	16.9	0.30	1.8	15.2	74.7	37.7	59	1893	16.5	0.02	1.4	1.7	19.7	2.11	7.8	211.8
50	13.5	0.31	2.9	15.9	225.5	39.6	214	1983	11.9	0.02	1.5	2.2	26.4	2.69	30.3	269.7
100	11.3	0.33	3.7	16.6	329.3	41.3	321	2071	8.9	0.024	1.5	2.4	32.0	2.99	47.5	299.2
β_{in}	0.024		2.4		2.9		299		0.024		2.4		2.99		299	

lished, as the bulk phase consumes contaminant from the aqueous phase. Consequently, the free solute concentration is supplied continuously with contaminant from the MOS-associated fraction.

Scenario B: Reduced Mobility due to Cosorption

The assumptions for Scenario B are:

- The solute sorbs to the mobile organic sorbents ($K_{MOS} > 0$).
- The solute sorbs to the immobile sorbents ($K_{\Psi_{HF}} > 0$).
- The MOS are considered reactive and sorb to the immobile solid phase ($K_{\Psi_{D}} > 0$).
- The physicochemical properties of the MOS-bound solutes are dominated by those of the MOS; that is, the MOS-bound solutes sorb to the immobile solid phase in the same way as the MOS ($K_{\Psi_{Hb}} = K_{\Psi_{Hb}} > 0$).

These assumptions hold for soil horizons with an excess sorption capacity for MOS. Such situations are found in B horizons of Inceptisols, Alfisols, and illuvial B horizons of Spodosols, rich in MOS-sorbing minerals and low in organic C (Kaiser et al., 1996; Weigand and Totsche, 1998).

Figure 5 shows the MOS-mediated breakthrough of the two different dummy solutes at increasing MOS concentrations. The respective transport scenario for the MOS breakthrough is indicated by the dashed line within Fig. 5a and 5b (Fig. 3, solid rectangles). With progressing time, the amount of MOS sorbed to the immobile solid phase increases until the MOS-specific sorption sites are completely occupied by the MOS molecules. From then on, the amount of MOS entering the soil equals the amount of MOS leaving the soil. For HOC and HM we observe the expected reduction of the free concentration C_{HF} as the consequence of the association with the MOS. In the case of the dummy HM, the BTCs for the different MOS concentrations are congruent in the beginning of the breakthrough and start to diverge markedly after the effluent concentration level of the contaminant exceeds $C/C_0 = 0.2$. This breakthrough behavior is seen for the free C_{HF} (Fig. 5a) and the total concentration C_H (Fig. 5b). With progressing time, the divergence grows because the amount of MOS in the mobile phase increases. With that, the amount of MOS providing sorption sites for the HM in

the mobile phase also increases. While in the beginning of the breakthrough almost all MOS are consumed by the solid phase, the progressing saturation of the solid phase with the MOS results in an increase of the liquid-phase MOS concentration. With that, the extent of the association reaction grows until the equilibrium is established.

According to the difference in affinity to the immobile solid phase between the two contaminants (HM and HOC), and especially because of the difference in the affinity contrast to the MOS, the effects on the contaminant breakthrough are different. While we observe reduced mobility for the heavy metal, the mobility of the HOC is still increased. In case of the HM, the breakthrough time increases from $pV_{BTC} = 44$ for the reference situation with no MOS present to $pV_{BTC} = 54$ for 0.100 kg MOS m^{-3} (Tables 4 and 5). With the MOS present in the mobile phase, the breakthrough of the heavy metal is delayed. The presence of MOS results in reduced mobility.

Reduced mobility, however, is not observed for the hydrophobic contaminant. The breakthrough time decreases from $pV_{BTC} = 4286$ for the reference situation with no MOS present to $pV_{BTC} = 2175$ for 0.1 kg MOS m^{-3} present in the mobile phase (Table 3). The difference compared with the heavy metal solute is due to the fact that the equilibration of the immobile solid phase with the inflowing MOS is accomplished much faster than the equilibration with the HOC. This results in a quasi-nonsorbing situation for the MOS and thus for the MOS-bound contaminant at the onset of the contaminant breakthrough. The solid phase is no longer an effective sorbent for the MOS. The cosorption conditions prevail only at the beginning of the breakthrough. The soil column is completely saturated with MOS after about 120 pore volumes (see also Fig. 3, solid rectangles). Because of the high affinity of HOC to the organic matter of the bulk phase, first breakthrough of HOC compounds occurs after about 1000 pore volumes have been exchanged. Thus, the conditions of cotransport dominate this scenario for most of the duration of the breakthrough.

This is also reflected in β (Eq. [14] and [15]), which is a measure to estimate the effect of MOS on the mobility of a solute. If $\beta < 1$, the mobility is enhanced compared with the reference situation without MOS. If $\beta > 1$,

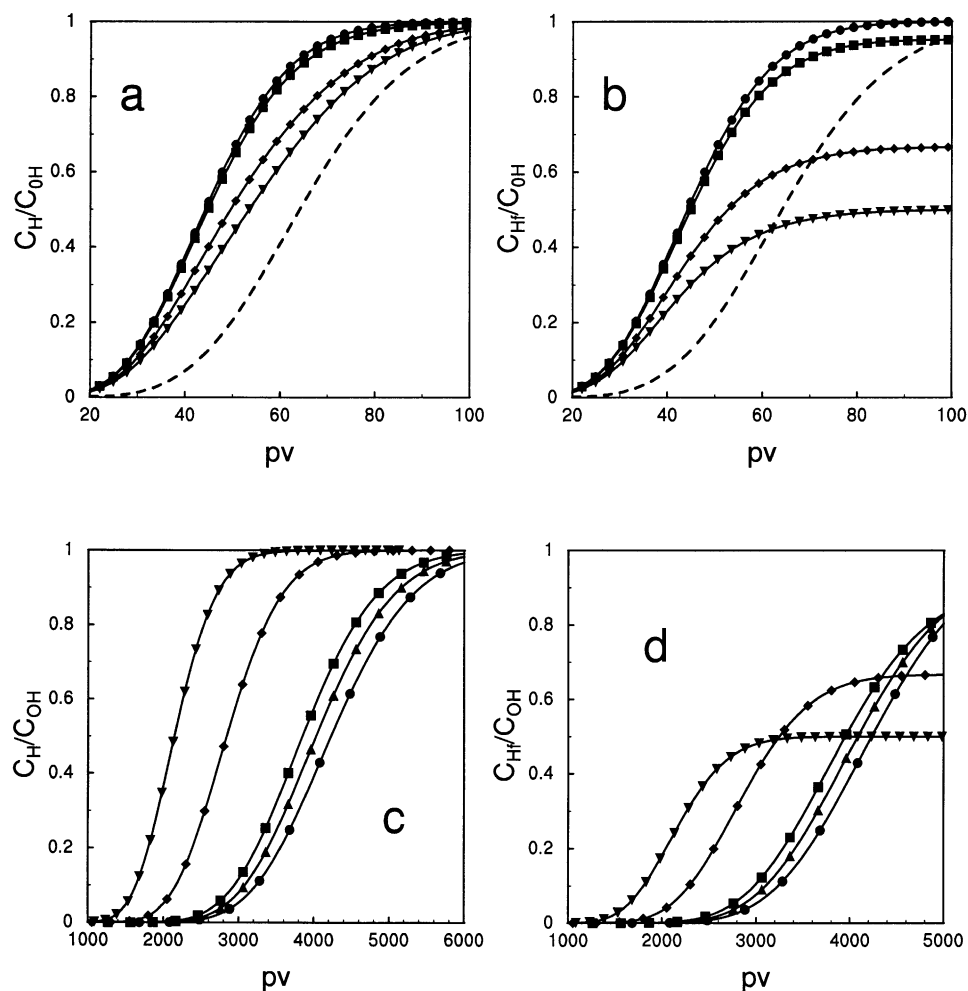


Fig. 5. Breakthrough of (a,b) a heavy metal and (c,d) a hydrophobic contaminant in the presence of increasing concentrations of mobile organic sorbents (MOS) for Scenario B, reduced mobility due to cosorption. Given are the breakthrough curves for the free C_{Hf} and the MOS-bound solute C_{Hb} . For this scenario, sorption of the MOS to the immobile solid phase is allowed ($\rho_{\Psi D}K_{\Psi D} = 22$). As MOS model substance, the hydrophilic MOS fraction ($K_{\Psi D} = 0.015 \text{ m}^3 \text{ kg}^{-1}$) was chosen which sorbs nonspecifically to the bulk solid phase ($\rho_{\Psi D} = 1470 \text{ kg m}^{-3}$). The dashed line (a,b) gives the breakthrough of this MOS fraction for both solutes. The symbols represent the following MOS concentrations (kg m^{-3}): circles, 0; triangles, 0.005; squares, 0.01; diamonds, 0.05; inverted triangles, 0.1.

the mobility is reduced compared with the reference situation. In the HOC transport scenario $\beta = 0.0147$, which is an indication of mobility enhancement. Compared with Scenario A, the enhanced mobility scenario, where no sorption of the MOS and the MOS-bound HOC occurs, the breakthrough is delayed. The difference in the breakthrough times for the two scenarios increases with the MOS concentration, starting from virtually no difference at low concentrations ($\Delta p_{v_{BTC}} = 0$ at $0.001 \text{ kg MOS m}^{-3}$) to approximately 30 pv at $0.100 \text{ kg MOS m}^{-3}$ (Tables 4 and 5). It is therefore important to note that the presence of reactive MOS does not result in all cases in reduced mobility. Whether or not increased or reduced mobility is observed depends at first on the extent of the ratio between the affinity of the free contaminant ($\rho_{\Psi Hf}K_{\Psi Hf}$) to that of the MOS-bound contaminant ($\rho_{\Psi Hb}K_{\Psi Hb}$), that is, the β value. As the sorption, and therefore retardation, of the MOS-bound contaminants is predominantly controlled by the type and moieties of the MOS itself, the characterization of the MOS properties and moieties is a crucial step for

the estimation of the effect of MOS on the mobility of contaminants.

Special Case. A special scenario was simulated for the transport of contaminants in porous media low in sorbed MOS and low in specific immobile sorbents for the contaminants. Under such conditions the sorption of the MOS to the immobile bulk soil is even higher than the sorption of the contaminants.

Figures 6a and 6b show the breakthrough of HM in the presence of intermediate MOS with high amount of specific sorption sites for this type of MOS while Fig. 6c and 6d show the breakthrough of HOC in the presence of hydrophobic MOS with a high amount of MOS-specific sorption sites.

For both cases, the effect of the reduced amount of specific contaminant sorption sites is dramatic. For the reference situation (i.e., no MOS present in the liquid phase) the breakthrough time drops from $p_v = 44$ to $p_v = 3.1$ for the heavy metal and from $p_v = 4286$ to $p_v = 215$ for the HOC (Table 3). This reflects the well known but often neglected fact that the retardation is

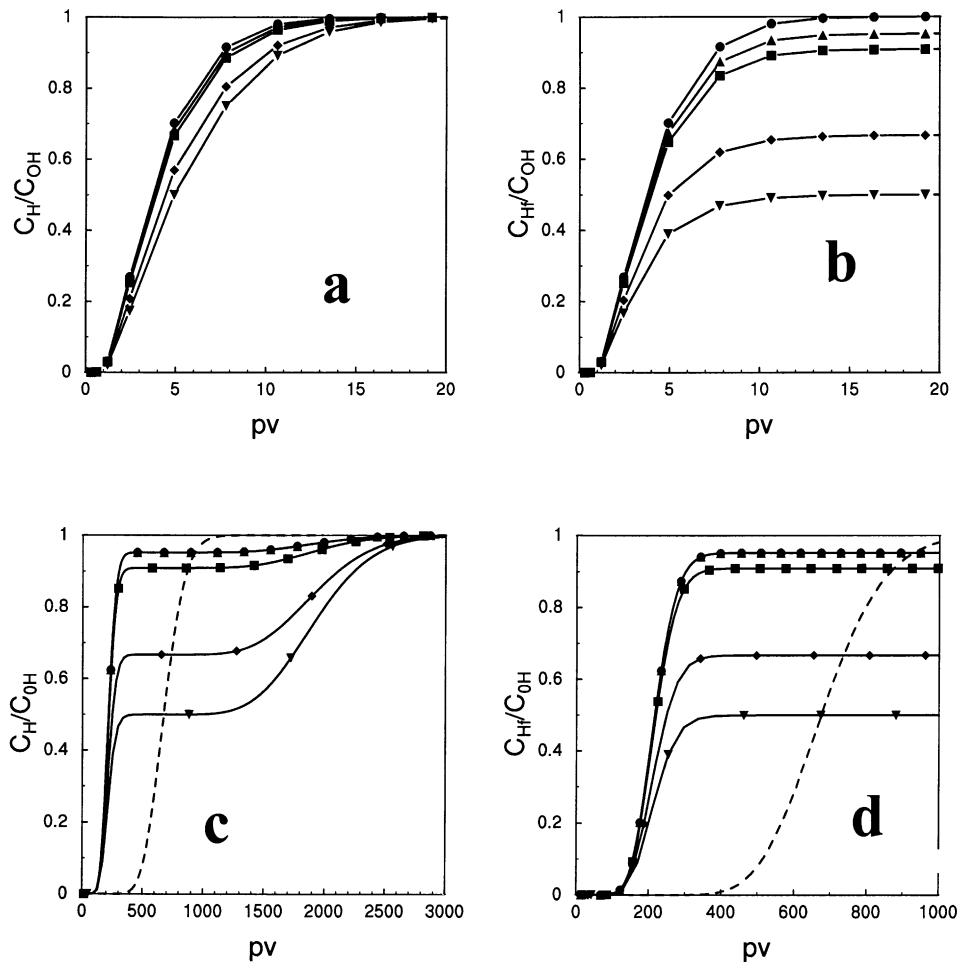


Fig. 6. Breakthrough of (a,b) a heavy metal and (c,d) a hydrophobic contaminant in the presence of increasing concentrations of mobile organic sorbents MOS) for Scenario B. Given are the breakthrough curves for the free C_{Hf} and the MOS-bound solute C_{Hb} . As MOS model substance, the hydrophobic MOS fraction ($K_{\Psi D} = 1.870 \text{ m}^3 \text{ kg}^{-1}$) was chosen which sorbs specifically to the bulk solid phase ($\rho_{\Psi D} = 120 \text{ kg m}^{-3}$). The dashed line (a,b) gives the breakthrough of this MOS fraction for both solutes. The symbols represent the following MOS concentrations (kg m^{-3}): circles, 0; triangles, 0.005; squares, 0.01; diamonds, 0.05; inverted triangles, 0.1.

both the result of the sorption isotherm and of the amount of accessible sorption sites. The observed breakthrough time and as such the retardation are affected if one or the other is varied.

The effect of the special case scenario on the breakthrough of the solutes is minor as long as β is close to 1. Figure 6a and 6b show this situation exemplarily for the breakthrough of the heavy metal. The sigmoidal shape of the BTCs is conserved and the heavy metal mobility is still reduced with $\beta = 2.4$ ($\beta = 1.47$, high amount of specific heavy metal-sorption or HOC-sorption sites), while the HOC mobility is still enhanced with $\beta = 0.024$ ($\beta = 0.0147$, Tables 4 and 5).

However, the effect on the breakthrough markedly changes for the HOC (Fig. 6c, 6d). The most prominent feature of the total HOC breakthrough behavior is the change of the graph from sigmoidal shape (Fig. 5c, $K_{\Psi D} = K_{\Psi Hb} = 15$) to the shoulder shape (two changes in curvature from convex to concave back to convex and finally to concave) for the high affinity case (Fig. 6c, $K_{\Psi D} = K_{\Psi Hb} = 1870$). The shoulder is observed exclusively for the breakthrough of total solute. The free solute and the MOS still exhibit a sigmoidal BTC.

Because the breakthrough of the total solute is the consequence of the superposition of the BTC of the free solute and the MOS-associated solute, the initial breakthrough observed for the total solute is essentially the breakthrough of the free solute in the high affinity MOS-sorption case. This is revealed by the congruence of the BTC for the free and the total solute for about 1000 exchanged pore volumes. Then the BTC for the free and the total solute deviate because the breakthrough of the free solute is completed. The BTC for total solute asymptotically approaches the BTC of the MOS, which also represents the breakthrough of the MOS-associated solute. The delay in the breakthrough of the MOS and thus the MOS-associated HOC is determined by (i) the affinity of the solute to the MOS, (ii) the total concentration of the MOS, and (iii) the affinity of the MOS to the immobile solid phase. The limiting situations of the formation of a shoulder as a consequence of the increase of the concentration are depicted in Fig. 7.

While for the low MOS concentration both the free and the MOS-bound fraction of the solute are of sigmoidal shape, the high MOS-concentration results in the evolution of the shoulder. For both situations, we as-

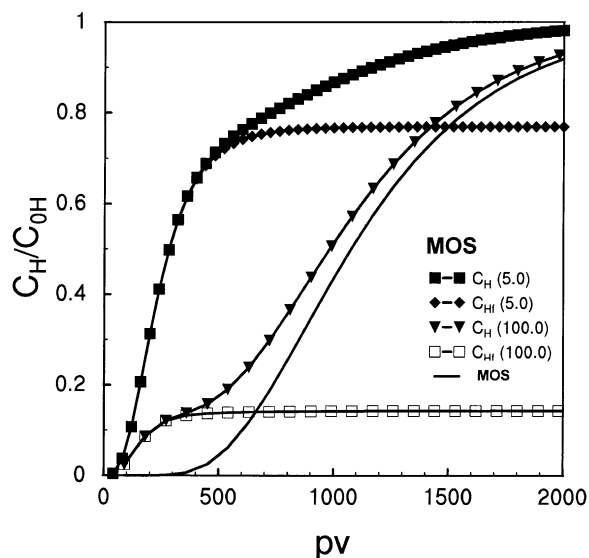


Fig. 7. Breakthrough of HOC in the presence of mobile organic sorbents (MOS) according to Scenario B, cosorption. Given is the limit situation for the evolution of a shoulder in the breakthrough curve.

sume the presence of hydrophobic MOS and a low amount of MOS-specific sorption sites.

The evolution of a shoulder or even a plateau will be more pronounced the stronger the differences are between the affinity of the MOS-bound solute and the free solute with respect to sorption to the immobile phase. Therefore the formation of the shoulder for the total solute is a strong indication for reduced mobility and for the fact that the MOS affect the sorption of the solute to the immobile phase. In soil horizons high in specific sorption site for MOS, such as the iron- and manganese oxide-rich subsoil horizons of spodosols or the sesquioxide enriched horizons of gleysols, such a transport scenario will result in an enrichment of contaminants only in the MOS-sorption layers. This scenario might help us understand the depth profiles found at rural and forested sites, which are affected solely by atmospheric imissions of hydrophobic organic contami-

nants like polycyclic aromatic hydrocarbons (PAH). Hartmann (1995) and Pichler (1995) found enriched PAH concentrations in subsoil horizons high in organic matter content. Large amounts of PAH were found particularly in soil horizons rich in iron or manganese oxides. These soil minerals are known to be specific sorbents for the MOS and thus for the MOS-bound PAHs. The process of cosorption is thus an effective process for the reduction of contaminant concentration in the seepage water and as such adds to the filter function of soils.

The specific situation of a low amount of specific sorption sites for the solute was further modified by assuming a nonlinear, convex shaped Freundlich-sorption isotherm ($p > 1$) of the solutes to the immobile solid phase. Without any MOS present, such an isotherm results in increased tailing as small concentrations travel much faster than high concentrations (Fig. 8a, 8b).

This is still the case for the onset of the breakthrough of the solute in the presence of MOS, as long as the liquid concentration of MOS is small due to MOS sorption to the immobile solid phase. As soon as the sorption sites for MOS are equilibrated with MOS and the liquid phase MOS concentration starts to increase, the formation of the MOS-bound contaminant fraction dominates the overall breakthrough of the contaminant. This results in an abrupt change of the increase of the effluent concentration of the total solute (Fig. 8a). The slope of the BTC diminishes, and the breakthrough is delayed to high pore volumes. Thus, the sorption of the MOS-bound solute enforces the effect of the nonlinear convex sorption characteristic. For the breakthrough of the free solute, the development of a maximal export concentration is observed. The maximum peaks just in front of the onset of the breakthrough of the MOS. This maximum is the consequence of the fact that the sorption sites for the free solute are already at equilibrium, resulting in maximal free solute concentration, while the formation of the MOS-bound fraction has not started so far. A peak effluent concentration is the marked consequence

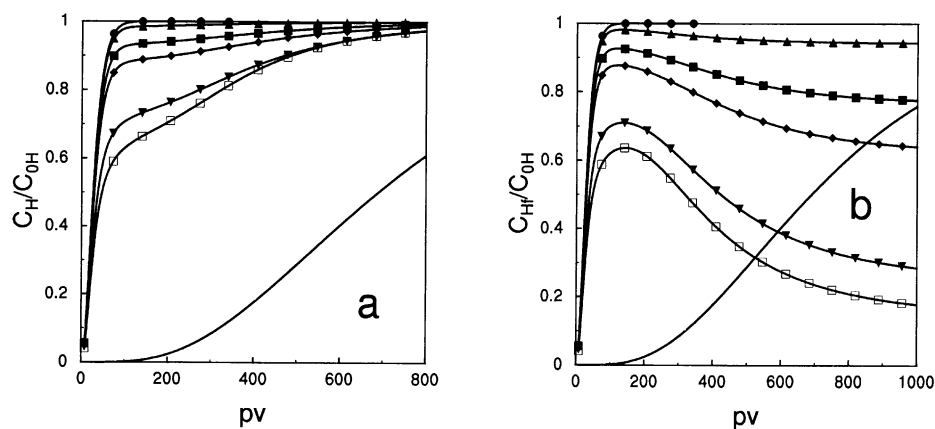


Fig. 8. Breakthrough of a hydrophobic contaminant in the presence of increasing concentrations of mobile organic sorbents (MOS) for Scenario B. The sorption of the solute was assumed nonlinear following a Freundlich-type sorption isotherm with $p = 1.15$. Given are the breakthrough curves for the free C_H and the MOS-bound solute C_{HB} . As MOS model substance, the hydrophobic MOS fraction ($K_{\psi D} = 1.870 \text{ m}^3 \text{ kg}^{-1}$) was chosen which sorbs specifically to the bulk solid phase ($\rho_{\psi D} = 120 \text{ kg m}^{-3}$). The solid line indicates the breakthrough of this MOS fraction. The symbols represent the following MOS concentrations (kg m^{-3}): circles, 0; triangles, 0.001; filled squares, 0.005; diamonds, 0.01; diamonds, 0.05; open squares, 0.1.

of the cosorption scenario under nonlinear sorption conditions. The necessary requirement for the formation of the shoulder or a plateau is a much higher affinity of the MOS, and thus of the MOS-bound solute, compared with the affinity of the free solute.

In a qualitative manner, the same holds for concave-shaped Freundlich-type with $p < 1.0$ or Langmuir- or saturation-type sorption isotherms. In fact, the effect of MOS and the formation of a shoulder or a peak effluent concentration are even more pronounced. Concave-shaped sorption isotherms result in a self-sharpening concentration front, as the low concentrations travel slower than the high concentrations. This results in a steeper and narrower peak than the convex-shaped sorption isotherms (data not shown).

Based on the experimental finding and on the field evidence, reduced contaminant concentrations due to the dynamics of MOS might also be observed without the requirement of the formation of a MOS-bound fraction of the contaminant. One may assume that first MOS are sorbed to specific sorption sites. The sorbed MOS then adds to the soil organic matter and thus to the sorption sites for the free contaminants. This scenario is studied next.

Scenario C: Reduced Mobility due to Cumulative Sorption

The assumptions for Scenario C are:

- No formation of the MOS-bound solute is required (i.e., $K_{MOS} = 0.0$).
- The solute sorbs to specific sorption sites of the immobile phase ($\rho_{\Psi_{HF}} > 0$; $K_{\Psi_{HF}} > 0$).
- The MOS are considered reactive and sorb to MOS-specific sorption sites of the bulk solid phase ($\rho_{\Psi_D} > 0$; $K_{\Psi_D} > 0$).

For the following discussion, we will focus on the consequences of the sorption of MOS for the solid phase organic matter and for the sorption of subsequent solutes.

In Fig. 9, the depth profiles of the bulk density $\rho_{\Psi_{HF}}$

of the organic matter fraction is plotted for a sequence of MOS concentrations (0, 5, 10, 50, and 100 g MOS m^{-3} , Fig. 9a) and for a sequence of exchanged pore volumes (10, 100, 200, 280, 400, and 700). These profiles were obtained by assuming that the sorption of MOS leads to an increase of the soil organic matter content. This assumption may apply to illuvial horizons of spodosols, where the continuous sorption of humic substances to iron, aluminum and manganese (hydr)oxides leads to the formation of C-rich spodic horizons. More general, the release of MOS from organic materials, the transport from organic C-rich surface soil horizons to deeper soil horizons and the subsequent sorption, precipitation or flocculation within the subsurface is one of the major soil forming processes. Besides the direct input of organic materials by flora and fauna, transport from organic C-rich horizons is the dominant process which results in enrichment of organic matter in the subsurface. Given a fixed amount of MOS-specific sorption sites, the successive import of MOS results in the progressive saturation of these sites and such in an increase of the overall amount of organic matter in the subsurface. The organic matter content is controlled by the total concentration level and the type and properties of the MOS. Figure 9a shows the course of the depth profiles for different mean MOS concentrations calculated for the fixed time of 280 exchanged pore volumes. With respect to the sorbed MOS concentration, the system is still not completely equilibrated. Figure 9b shows the course of the depth profiles for a fixed concentration of 50 g MOS m^{-3} and different snapshots in time. The sorption of MOS results in the propagation of the solid phase organic matter front. The specific bulk density of organic matter increases from $\rho_{\Psi_{HF}} = 0.0300$, which resembles the initial condition, to $\rho_{\Psi_{HF}} = 0.0254$, the final condition after 1000 pore volumes have been exchanged.

Unfortunately, the sorbed MOS cannot be distinguished analytically from initially present soil organic matter. Soil organic matter, in particular, is the dominant sorbent for hydrophobic organic contaminants like

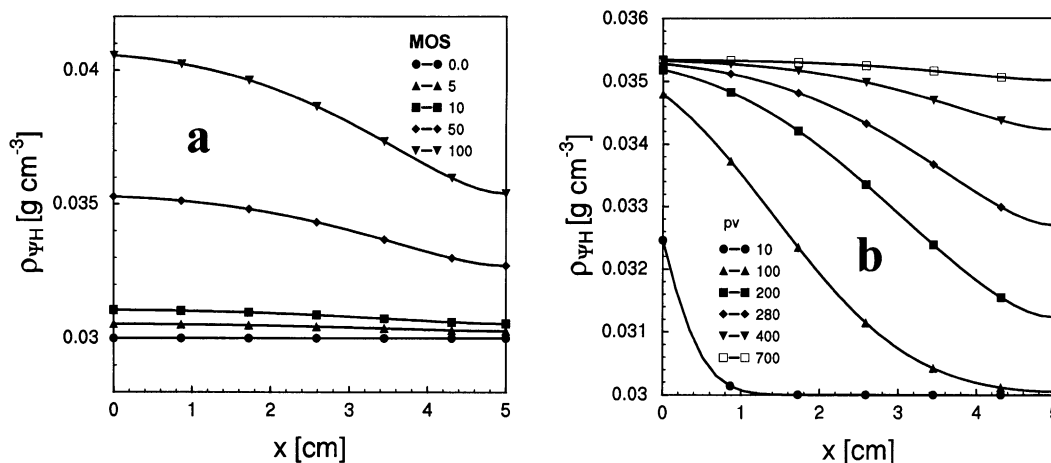


Fig. 9. Depths profiles of the fraction of the bulk solid phase which provides sorption sites for the hydrophobic organic contaminants. (a) Depth profiles for increasing mobile organic sorbents (MOS) concentrations as calculated after 280 pore volumes have been exchanged. (b) Depth profiles for 0.050 kg MOS m^{-3} for different moments. Initially, the amount of organic matter was set to 0.03 10^{-3} kg m^{-3} .

PAH. Thus, the sorption of MOS not only results in an increased mass fraction of the bulk soil organic matter (indicated by the bulk density fraction $\rho_{\psi H}$), but also in an increase of the sorption sites for hydrophobic organic contaminants. Thus, Fig. 9a and 9b can be interpreted in terms of an increase of specific HOC sorption sites in time. This increase should affect the transport of solutes with particular affinity to soil organic matter. This effect is shown in Fig. 10.

We study two different scenarios with respect to the properties of the MOS and the soil. Figure 10a shows the effect on solute breakthrough for intermediate MOS in a soil with a high amount of MOS-specific sorption sites while Fig. 10b shows the effect on solute breakthrough for hydrophobic MOS in a soil with a high amount of MOS-specific sorption sites. For both cases the breakthrough is delayed. This is the consequence of the increase of the organic matter due to the sorption of MOS. In general, the onset of the breakthrough is neither affected by the intermediate nor by the hydrophobic MOS. This reflects the important fact that the cumulative-sorption scenario does not require a formation of MOS-bound solute. As the sorption of MOS has to persist for a very long time to result in an increase of the solid phase organic matter, the initial breakthrough of the solute remains unchanged compared with the reference situation.

With progressing time the individual BTCs for the different MOS concentrations deviate from the reference state (without any MOS present). For both cases, the effect on the breakthrough of the solute is marked. But only the hydrophobic MOS result in an effect on the shape and curvature of the solute BTC. The long-lasting increase of the specific bulk density (i.e., the organic matter content) as a result of the sorption of MOS results in a dramatically prolonged breakthrough behavior of the solute. The BTCs exhibit a plateau much smaller than the respective equilibrium contaminant-effluent concentration. During the ongoing MOS sorp-

tion process, the contaminant sorption has to be considered a transient process. Under natural MOS release and transport conditions this reduced contaminant concentration may last for very long times (years to decades). Once the MOS-sorption sites are equilibrated, the effluent concentration of the contaminants will dramatically increase as soon as the contaminant sorption sites are saturated. This can be seen in Fig. 10b after approximately 1600 pore volumes have been exchanged.

The cumulative-MOS sorption scenario has important consequences for contaminant fate in porous media. First of all, this scenario causes transient sorbent properties (i.e., a time-dependent solid phase composition). Contaminant sorption parameters obtained for such situations may hold just for the moment. The sorption isotherm will prove time dependent as long as the MOS sorption equilibrium is not established. Soil materials with a high content of MOS-specific sorption sites should therefore be tested for prevailing conditions favorable for cumulative sorption. The estimation of the contaminant sorption parameters can then be constrained by the sorption behavior of the MOS.

The increase of the soil organic matter content due to cumulative MOS sorption can reduce the porosity and as such the permeability of the porous media (e.g., Abadzic and Ryan, 2001). Thus, cumulative sorption will also affect the flow of water and other liquid and gaseous phases through soils high in MOS-specific sorbents.

The concentration of the contaminants in the seepage water of soils subject to cumulative MOS sorption is reduced as long as the cumulative MOS sorption persists. Once completed, the contaminant concentration will increase markedly. With that, soil and groundwater protective values may be violated. Risk assessment studies aimed at groundwater protection have to consider such transient MOS sorption conditions when estimating the long-term contaminant concentration within the liquid phase.

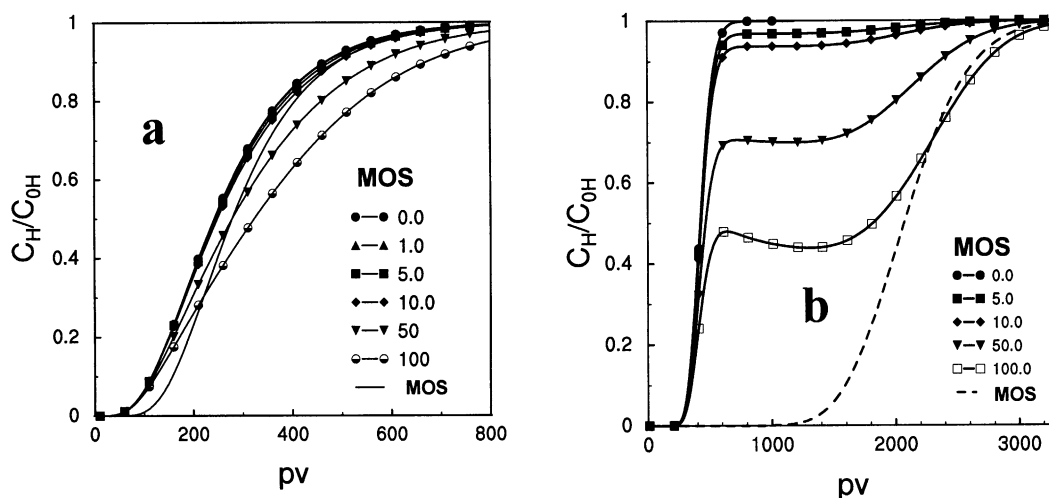


Fig. 10. Breakthrough of a hydrophobic organic contaminant in the presence of increasing concentrations of mobile organic sorbents (MOS) for Scenario C, the cumulative sorption scenario. Given are two situations. (a) Linear hydrophobic organic compounds interaction of the hydrophobic organic compounds with the solid phase organic matter and intermediate MOS ($K_{\psi D} = 1.870 \text{ m}^3 \text{ kg}^{-1}$) with a high amount of MOS-specific sorption sites.

Up to now, we studied the effect of increased contaminant specific sorption sites by considering the effect of cumulative MOS sorption. In principle, the same holds for the opposite case, that is, a time-dependent decrease of organic matter and consequent loss in contaminant-specific sorption sites. Such a decrease could be the result of microbial degradation of organic matter due to changed environmental and climatic conditions. This would result in increased release of MOS and contaminants as well. Such conditions have to be addressed in future work on the fate of contaminants affected by mobile organic sorbents.

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