Transport of heavy metals in saturated columns – Experiments and modelling

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ABSTRACT: The transport of heavy metals in groundwater is influenced by chemical and physico-chemical processes. Actually, the model CoTAM presented in this paper enables to simulate advection and dispersion for a one-dimensional case and considers rate dependent processes of sorption and desorption. The main algorithm works with the method of finite differences to solve the partial differential equations using a Crank-Nicholson scheme and the Newton-Raphson method to solve nonlinear equation systems. Sorption and desorption processes are included in this algorithm as the Henry, Freundlich, and two-site Langmuir isotherms. The isotherm parameters were obtained separately from column and batch experiments. Comparing measured breakthrough curves of cadmium and copper with the modelled curves, it was obvious that rates of slow sorption processes received from batch experiments cannot be used to simulate sorption in a system with flowing groundwater, sufficiently. Fitting those parameters was necessary to get a good coincidence of measured and simulated breakthrough curves.

1 INTRODUCTION

The infiltration of waste water compounds afflicts the quality of groundwater in a serious way. To estimate possible dangers gaining from that input and to take effective precautions, the processes affecting the transport of solute compounds in groundwater have to be understood. Besides the hydraulic situation in any aquifer many authors (e.g.: Stumm et al. 1976; Calmano 1989) consider sorption as one of the most important processes controlling the transport of any solute compound. Sorption of solute heavy metals on solid surfaces in the aquifer is the reason for lower concentrations of those metals than had to be expected according to thermodynamical calculations.

Expressions describing the partitioning of adsorbate between dissolved and adsorbed phases at constant temperature are known as adsorption isotherms. The isotherms most commonly used to describe adsorption at the solid solution interface are the Henry, Freundlich, and the Langmuir isotherms with

$$C_s = K_d \cdot C_l \quad [\text{mol/g}] \tag{1}$$

$$C_s = k \cdot C_l^{1/n} \quad [\text{mol/g}] \tag{2}$$

$$C_s = \frac{p \cdot K \cdot C_l}{1 + k \cdot C_l} \quad [\text{mol/g}] \tag{3}$$

with
$\quad C_s \quad$ sorbed concentration [mol/g]
$\quad C_l \quad$ concentration of solute [mol/cm^3]
$\quad K_d, k, n, p, K \quad$ parameters of isotherms

Leckie et al. (1980) conducted batch experiments with heavy metals and metalloids and found it impossible to describe the observed processes with Freundlich or Langmuir isotherms. They expected the surfaces to have different kinds of sorbing sites. A multi-site model was developed in which they implied a combination of Langmuir isotherms. Pierce & Moore (1981) simulated the sorption of arsenate and arsenite with a combination of Langmuir and Freundlich isotherms, while Flühler & Jury (1983) and Selim et al. (1988) used a two-site Langmuir model.

Generally, the kinetic of those processes consists of two phases. Leckie et al. (1980), Nyffeler et al. (1984) and Hayes & Leckie (1986) observed a nearly complete sorption of heavy metals within

minutes followed by a second period of sorption. In that period equilibrium is reached within days or even months. So, additionally to isotherms for the state of equilibrium (eq. 1 - 3; 4),

$$C_s = F(C_l) = \sum_{k=1}^{k_{max}} f_k(C_l) \quad [\text{mol/g}] \qquad (4)$$

partial differential equations are needed to describe temporal changes of the adsorbed concentration. Using a two-site isotherm ($k_{max} = 2$) the following equation is needed

$$\frac{\partial C_s}{\partial t} = \sum_{k=1}^{2} r_k \cdot (f_k(C_l(t)) - C_{s,k}(t)) \quad \left[\frac{\frac{\text{mol}}{\text{g}}}{\text{s}}\right] (5)$$

with

r rate constant of sorption [1/s]
t time [s]

The two-site model describes the processes of sorption sufficiently well, however, a good fit is not a proof for that theory (Sposito 1982; Selim et al. 1988).

Parallel to the two-site model the surface-complexation model was developed (Stumm 1976). According to that model hydroxyl groups of an amphoteric character are the reactive parts of a surface. These hydroxyl groups are able to form complexes with kations in the surrounding solute. Forming these surface complexes is thought to be the reason for sorption.

The sorption process affects the movement of solutes in groundwater. The combination of hydrodynamic processes like advection, dispersion, and sorption can be described with the following partial differential equation

$$\frac{\partial S}{\partial t} + \frac{\partial C_l}{\partial t} = D_l \cdot \frac{\partial^2 C_l}{\partial x^2} - v_a \cdot \frac{\partial C_l}{\partial x} \quad \left[\frac{\frac{\text{mol}}{\text{cm}^3}}{\text{s}}\right] (6)$$

with

$S = \varrho/n_e \cdot C_s$ [mol/cm^3]
C_l concentration of solute [mol/cm^3]
n_e effective porosity [cm^3/cm^3]
ϱ_b bulk density [g/cm^3]
D_l dispersion coefficient [cm^2/s]
v_a transport velocity [cm/s]

The sorbed concentration C_s can be compared directly with the concentration C_l by multipling C_s with the factor ϱ_b/n_e.

The equation (6) can also be written as

$$R \cdot \frac{\partial C_l}{\partial t} = D_l \cdot \frac{\partial^2 C_l}{\partial x^2} - v_a \cdot \frac{\partial C_l}{\partial x} \quad \left[\frac{\frac{\text{mol}}{\text{cm}^3}}{\text{s}}\right] (7)$$

with $R = 1 + \dfrac{\varrho_b}{n_e} \cdot \dfrac{\partial F(C_l)}{\partial C_l}$

Any isotherm can be used for the function $F(C_l)$. A simple model combining sorption and transport is the linear equilibrium model which is a common method for approximating solute retardation by sorption in groundwater systems (Faust & Mercer 1980; Pinder 1984).

In this case the partial differential equation (7) can be solved analytically. This solution can be used for a first estimate of the breakthrough at location X. The distribution of concentration in an endless and homogeneous column under constant flow conditions can be calculated by (Kinzelbach 1987)

$$C_l(x,t) = \frac{C_0}{2} \left[\text{erfc} \left(\frac{x - \dfrac{v_a \cdot t}{R}}{2\sqrt{\dfrac{D_l \cdot t}{R}}} \right) \right.$$
$$\left. + \exp \left(\frac{x \cdot v_a}{D_l} \right) \cdot \text{erfc} \left(\frac{x + \dfrac{v_a \cdot t}{R}}{2\sqrt{\dfrac{D_l \cdot t}{R}}} \right) \right] (8)$$

with

C_l concentration of solute [mol/cm^3]
C_0 input concentration [mol/cm^3]

and

$$\text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\xi^2)\, d\xi$$

Recent research (van Genuchten & Wierenga 1977; Isenbeck et al. 1985; Goltz & Roberts 1986) demonstrated that the linear equilibrium model does not always describe the transport of solutes adequately.

For inhomogeneous situations or nonlinear isotherms like Freundlich or Langmuir the partial differential equation (6) can only be solved with numerical methods.

In systems of one-dimension (columns) the

method of finite differences (Flühler & Jury 1983; Kinzelbach 1987) is often used.

Another possibility to solve the hydrodynamic transport equation is the method of finite elements (van Genuchten 1982; Kinzelbach 1987).

In systems of two- or three-dimensions the method of characteristics (Konikow & Bredehoeft 1978) is often used. A further way for solving multidimensional systems is the Random-Walk algorithm (Kinzelbach 1987).

The first-order reversible kinetic model (Lapidus & Amundson 1952) and the two-site model (van Genuchten & Wierenga 1977) have been used successfully to describe the transport of a number of solutes which interact with porous media in column experiments (Hoffman & Robston 1980; Selim 1988). Mansell et al. (1985) were also successful in modelling the transport of phosphate through columns with a two-site model. However, the rates of the sorption reaction gained from static batch experiments could not be used to model the movement in soils. Instead, the rate constants of sorption had to be fitted to get a good coincidence between measured and modelled data.

2 MODEL

The model used for evaluating the column experiments is based on the program DISPER presented by Flühler & Jury (1983). The algorithm of the program solves the partial differential equation (6) by a finite difference method. This numerical method requires a discretisation in time and space. The column is divided into cells of (constant) length Δx_i. Time is discretisated into time intervals Δt.

All terms of the differential equation were approximated by terms of Taylor-series. The differential equation (5) can be described by linearisation of a two-site isotherm (Flühler & Jury 1983)

$$\frac{\Delta S}{\Delta t} = \sum_{k=1}^{2} r_k \cdot \left[\frac{1}{2} \cdot \left(f_{i,k}^{j} - S_{i,k}^{j} \right) \right. \tag{9}$$
$$\left. + \frac{1}{2} \cdot \left(f_{i,k}^{j+1} - S_{i,k}^{j+1} \right) \right]$$

with $f_{i,k}^{j} := \frac{\varrho_b}{n_e} \cdot f_k(C(x_i, t_j))$

The variable $S_{i,k}^{j+1}$ was eliminated by transforming the equation (9)

$$\frac{\Delta S}{\Delta t} = \frac{\sum_{k=1}^{2} \alpha_k \cdot \left[f_{i,k}^{j+1} + \left(f_{i,k}^{j} - 2S_{i,k}^{j} \right) \right]}{\Delta t} \tag{10}$$

with $\alpha_k = \frac{r_k \cdot \Delta t}{2 + r_k \cdot \Delta t}$

The algorithm is a combination of the terms approximated by Taylor-series and the equation (10). Using cells of constant length it follows

$$\frac{C_i^{j+1} - C_i^{j}}{\Delta t} + \frac{\sum_{k=1}^{2} \alpha_k \cdot \left[f_{i,k}^{j+1} \left(f_{i,k}^{j} - 2S_{i,k}^{j} \right) \right]}{\Delta t} \tag{11}$$
$$= \frac{1}{2} D_l \frac{C_{i-1}^{j} - 2C_i^{j} + C_{i+1}^{j}}{(\Delta x)^2}$$
$$+ \frac{1}{2} D_l \frac{C_{i-1}^{j+1} - 2C_i^{j+1} + C_{i+1}^{j+1}}{(\Delta x)^2}$$
$$- \frac{1}{2} v_a \frac{C_{i+1}^{j} - C_{i-1}^{j}}{2 \cdot 2\Delta x} - \frac{1}{2} v_a \frac{C_{i+1}^{j+1} - C_{i-1}^{j+1}}{2 \cdot 2\Delta x}$$

for $i = 2, \ldots, n - 1$

The terms $f_{i,k}^{j+1}$ are dependent on the unknown concentration C_i^{j+1} so that the generated equation system cannot be solved directly. For solving this system the program DISPER uses the Newton-Raphson algorithm.

The original algorithm (Flühler & Jury 1983) is programmed by using two-site Langmuir isotherms only. The algorithm presented in this paper was expanded by Henry and Freundlich isotherms and adapted to the special situation of column experiments.

To simulate the transport of heavy metals in column experiments the number of cells must be raised from 20 to 1000 cells. The system matrix was stored according to a concept presented by Kinzelbach (1987). This concept reduced the number of matrix elements from n^2 to $3 \cdot n$.

The numerical boundary conditions were changed as follows: the mass balance of the first cell of the modelled column requires that inputs and outputs add up to zero due to advection, dispersion, and diffusion during a time interval Δt.

$$0 = A \cdot n_e \cdot \Delta t \cdot \left(v_a \cdot C_0 - v_a \cdot C_1 \right. \tag{12}$$
$$- D_l \frac{C_1 - C_2}{\Delta x_1}$$

$$+ \ D_{Diff}\frac{C_0 - C_1}{\Delta x_0} - D_{Diff}\frac{C_1 - C_2}{\Delta x_1}\Bigg) \quad [mol]$$

The terms of diffusion can be neglected in column experiments, if the transport velocity is higher than 0.1 m/d (Kinzelbach 1987).

Flühler & Jury (1983) modelled the outflow of contaminated liquid using an impervious boundary concept. This concept sets the concentration gradient at the boundary to zero.

Calculating the breakthrough curve of an ideal tracer with this concept of boundary conditions leads to a different curve from the one evaluated by the analytical solution (8).

Another possibility is given by the transmission boundary concept (Kinzelbach 1987). It approximates the concentration gradient across the boundary by using the concentration gradient between two cells before.

In simulations it was observed that the Peclet criteria ($|v_a \cdot \Delta x/ \ D_l| < 2$) could be neglected if the tracer was adsorbed. Numerical oscillation took only place if the condition

$$\left| \frac{v_{med} \cdot \Delta x}{D_l} \right| < 2 \qquad (13)$$

with $\quad v_{med}\quad$ apparent velocity of the retarded tracer.

was infrindged.

3 ANALYTICS, MATERIAL AND METHODS

All liquid samples were filtered through a 0.2 μm nylon filter. Heavy metals were measured with an Atomic Absorption Spectrometer AAS 1100 or a Atomic Emission Spectrometer with Inductive Coupled Plasma ICP/6500, Perkin Elmer.
Sorption of the tracers on the materials used in the experiments was tested and excluded. The used water (Tab. 1) was prepared artificially according to a typical groundwater type (Taylor 1989) that can be found in upper sandy aquifers, which are extended over the region with glacial deposits in North-West-Germany.

Like the water the adsorbate was artificial. The most simple system was pure quartz sand. All other systems consisted of quartz sand and an additional compound. The portions of these compounds referred to those in natural aquifers (Tab. 2).

Table 1.: Water used in the experiments			
ion	concentration [mg/l]	ion	concentration [mg/l]
Na	14.8	Cl	22.4
K	1.99	NO_3	12.8
Ca	10.7	SO_4	54.4
Mg	3.70		
Mn	0.16	pH-value	4.65
Al	3.89	Eh-value	270 mV

Table 2.: Data and compounds of the columns					
No.	Compounds added to quartz sand	portion [%-weight]	pv* [%]	α_l* [mm]	v_a* [m/d]
1	quartz sand (pure)	100	31	1	0.525
2	+ albite	10	30	1	0.528
3	+ goethite	0.5	29	2.5	0.531
4	+ montmorillonite	1	29	35	0.557
5	+ mangandioxide	0.04	30	0.5	0.537
6	+ peat	0.1	31	1	0.536
* pv :pore volume; α_l: dispersivity; v_a: velocity					

All batch experiments were conducted in PE tubes. They were filled with 200 g of solid and 250 ml of water spiked with tracers. The tubes were shaken for one minute each hour and were sampled continuously between 0.5 and 140 hours. The experiments were effected with concentrations of the tracers in a range between 50 μg/l and 100 mg/l. According to thermodynamical calculations with the program PHREEQE (Parkhurst et al., 1980) the concentrations of the tracers were in a range in which precipitation could not be expected. This was confirmed by experiments with tubes containing water spiked with tracers but without any aquifer material.
Column experiments were conducted in plexiglass pipes with a length of 1 m and an inner diametre of 4.65 cm. Set in operation, the prepared columns were streamed through with water from the bottom to the top. The stream was held constant with a peristalic pump. After conditioning the columns with water the hydraulic parameters (Tab. 2) were gained by tracer experiments with LiBr. These preparing phases were followed by the tracer experiments conducted with water spiked with 0.02 mmol/l of cadmium and copper. After 60 days the columns were streamed through by unspiked
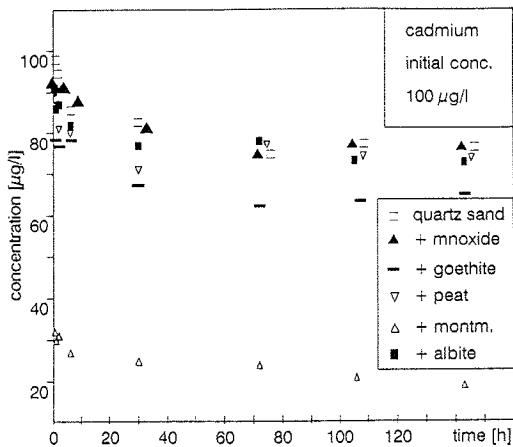
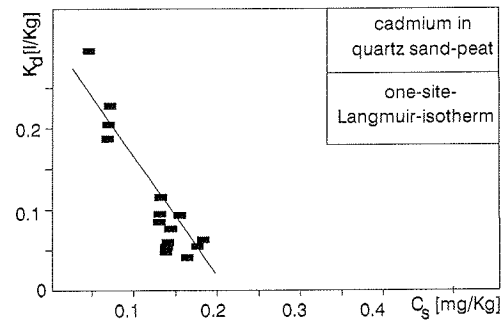Fig. 1: Temporal changes of the cadmium concentration in the solute during batch experiments

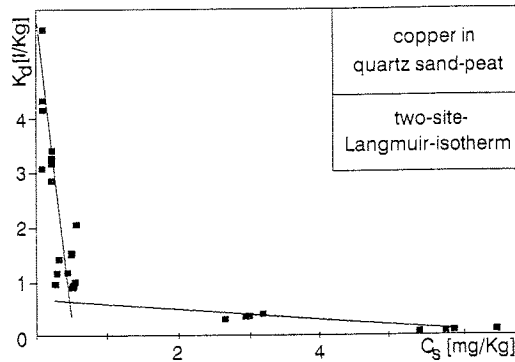Fig. 2: Distribution coefficient versus the amount of cadmium sorbed by quartz sand and peat.

Fig. 3: Distribution coefficient versus the amount of copper sorbed by quartz sand and peat
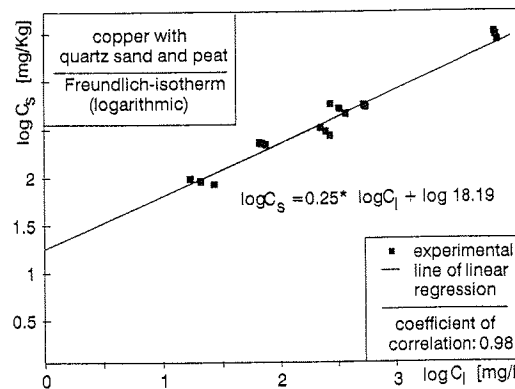
Fig. 4: Freundlich isotherm for the system of copper sorbed by quartz sand and peat.

water to get a breakthrough curve for the desorptional case.

To receive a set of data for the isothermal sorption of a heavy metal to a surface Sposito (1982) suggested a graph of distribution coefficient versus amount of sorbed metal. According to that method the parameters of a Langmuir or multisite Langmuir isotherm can be received by linear regression (Fig. 3).

The rate constants of sorption were determined by optimising the values for the kinetic parameters with the method of nonlinear regression following the criterium of the sum of least square roots (Fig. 5).

This set of data for the sorption isotherm and the kinetic rates combined with the hydraulic data of the column experiment is the basis for simulating such cases with the program CoTAM.

4 RESULTS AND DISCUSSION

4.1 Behaviour of cadmium and copper in batch experiments

Generally, sorption phenomena can be devided into two periods. At the beginning of any sorption a rapid decrease of concentration of heavy metals in the solute phase can be observed within hours. In the case of cadmium the whole reaction was finished after this rapid decrease except of the experiment with montmorillonite as an additional compound to quartz sand (Fig. 1).

In all experiments with copper the rapid decrease is followed by a slower decrease reaching equilibrium as well.

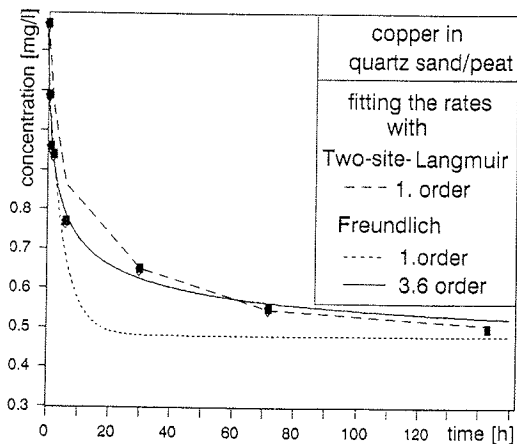As follows graphs of the states of equilibrium

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Fig. 5: Temperal changes of copper concentration during a batch experiment. Rate constants of sorption were fitted by using Langmuir and Freundlich isotherms with different orders of reaction
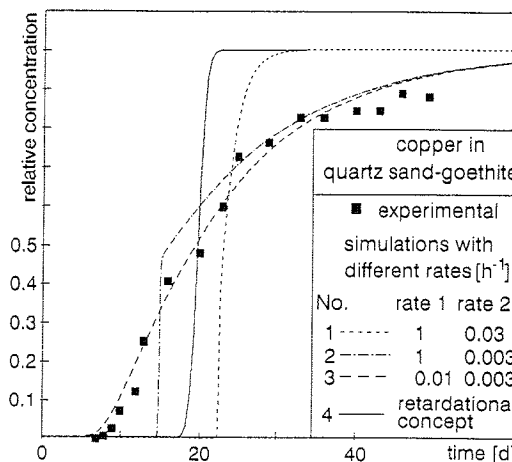

Fig. 6: Breakthrough curves of copper through the quartz sand- goethite column and four simulations. Simulation no.1: rates gained from batch experiments; no.2: the slow rate was fitted; no.3: both rates were fitted; no.4: the modelled breakthrough curve according to an analytical model with retardation (eq. 8)

are presented with the destribution coefficient K_d versus the amount of sorbed metals (Sposito 1982). Every linear part of the graph represents a single isotherm so that it is easy to distinguish between single-Langmuir and two-site Langmuir cases. The sorption of cadmium can be described with a single Langmuir isotherm (Fig. 2).

To describe the sorption of copper sufficiently two-site Langmuir isotherms were neccessary (Fig. 3).

It was also possible to calculate Freundlich isotherms which represent the sorption (Fig. 4). But trying to determine the rate constants to describe the kinetics of the reaction it was impossible to use a first order kinetic.

In the example presented in figure 5 the assumption of 3.6th. order was necessary to reach a sufficient fit. In contrast to that using Langmuir or two-site Langmuir isotherms first order kinetics were observed (Fig. 5). Generally, a kinetic of a broken order can describe a reaction, but different mechanisms of the reaction are not fully understood and just comprehended in the size of the broken order. To consider this fact only simple or two-site Langmuir isotherms were used in the presented paper.

In spite of success of surface-comlexation models as tools for understanding the basic interactions that take place at sorbing surfaces we decided to work with a multi-site isotherm model. Coatings, size of reactive surfaces, and particle size will differ

from aquifer to aquifer so that all data have to be evaluated new for every case; referring to that fact there is no practicle advantage to use the surface complexation model instead of an isotherm model.

4.2 Simulated and measured breakthrough curves

The simulation of breakthrough curves is based on the data gained from the batch experiments. First model calculations with these data showed simulated curves that were too steep and too late (Fig. 6). Better fits were received after lowering the slower rate of sorption (Fig. 6). But in the case of copper in the quartz sand-goethite column a sharp bend was observed in the breakthrough curve; additionally the simulated curves started steeper than the measured values. After lowering both rate constants – the first quicker one as well – a good fit was reached (Fig. 6).

In all batch experiments the rates for the slower second part of sorption were overestimated (Tab. 3). We expect rates gained from static batch experiments to be systematically too high to be used for modelling column experiments. The reason might be that the delivery of metal ions is dependent on the Darcy velocity. At low velocities the mass transfer in columns can be so slow that the
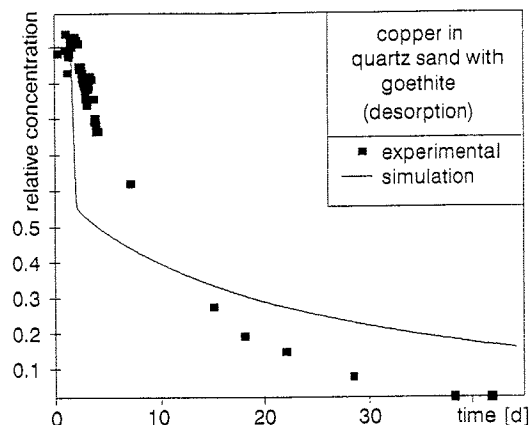
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Fig. 8: Breakthrough curves of the desorption of copper in quartz sand through the quartz sand-goethite column. The simulation presented here is based on the same isotherm and rates as for the sorption reaction (compare Fig. 6)
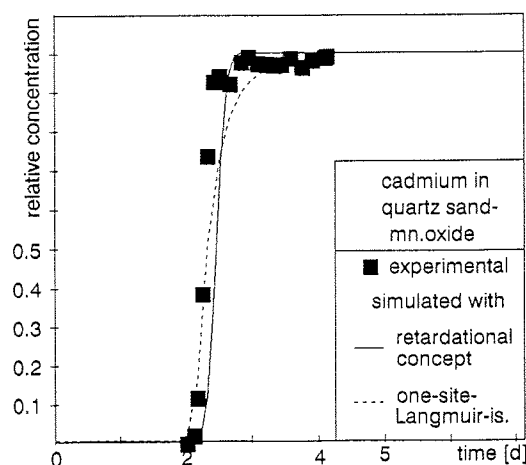

Fig. 7: Breakthrough curves of cadmium through a column filled with quartz sand and mangnese-oxide. Additionally with simulations based on the retardational concept and a one-site Langmuir isotherm (eq. 8).

kinetic of sorbing metals allows the solid to sorb more than the delivery of ions through the column offers. In contrast to that the problem of delivery and the dependence on a hydraulic situation never exists in a batch experiment because solute and solid are homogenized during periodical shaking. If the delivery of metal ions is a controlling process on sorption phenomena it is obvious that

rates gained from batch experiments, where this phenomenon is neglected are too high to be used for simulating column experiments. Batch experiments give a hint on the range of rates, but to get more exact ones they have to be determined in separate column experiments.

Using cadmium as a tracer steep breakthrough curves were observed in both cases, sorption and desorption. It was possible to simulate these data using a one-site Langmuir isotherm or the linear-equilibrium model (Fig. 7).
This model – also known as retardational concept – can only be used for types of reactions which are fully reversible and do not consist of a sum of reactions but only of one primary reaction. The fit for the cadmium breakthrough curve using this concept indicates that the sorption of cadmium is a fully reversible and a primary reaction.
The breakthrough curves of copper could be modelled with a two-site Langmuir isotherm, but not with the retardational concept (Fig. 6).

Sorptions of copper were not fully reversible as calculations of input and output of the columns showed. Using the two-site Langmuir model to get sufficient fits indicates, that the sorption of copper consists of more than one primary reaction.

Comparing the breakthrough curves of sorption (Fig. 6) and desorption (Fig. 8), it can be seen that they are of a different character. A reason for that fact is that the reactions are not fully reversible. In our example just 74 % of copper left the

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column filled with quartz sand and goethite. So, using the same isotherms with the same rates to simulate the case of desorption instead of sorption the extent of desorption would be overestimated (Fig. 8).
Until now no data are available for a separate desorption isotherm; however, the model presented is able to work with different isotherms for sorption and desorption.

5 CONCLUSION

The model CoTAM presented here is based on an algorithm of Flühler & Jury (1983) and was optimised in a way that connecting a thermodynamic model like PHREEQE (Parkhurst et al. 1980) is possibel so that types of chemical reactions different from sorption/desorption can be considered during any simulation. Using this model combined with isotherm parameters received from batch experiments it was possible to simulate the transport of cadmium and copper in saturated columns. However, the rate constants of sorption for slow reactions gained from batch experiments had to be fitted. Simulation of desorption needs isotherms and rate constants different from sorption. These data have to be determined in separate experiments.

Until now the model in connection with experiments can be used to simulate transport of heavy metals in a metre scale but not for cases of regional extent.

However, we hope the model CoTAM can help reaching better understanding of processes affecting transport of heavy metals in groundwater.

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