Short communication

Theoretical analysis of kinetic effects on the quantitative comparison of $K_d$ values and contaminant retardation factors

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1. Introduction

Experimentally-determined distribution coefficients ($K_d$ values) are commonly used to describe contaminant partitioning between liquids and solids for reversible, linear contaminant sorption behavior. $K_d$ values represent the primary parameters for the calculation of retardation factors ($R_f$) in contaminant transport models, and are hence an important utility in the evaluation of contaminant mobility in saturated porous media. With the incorporation of distribution coefficients in transport models two assumptions are inherently made: (1) local equilibrium conditions with respect to contaminant surface reactions have been validated mathematically within the characteristic time/length of the transport model (Jennings, 1987; Jennings and Kirkner, 1984; Lasaga, 1998); and (2) incorporated $K_d$ values represent equilibrium conditions for contaminant sorption reactions (United States Environmental Protection Agency, 1999). If equilibrium has been reached experimentally and in the model frame-work, then errors associated with kinetic limitations for contaminant sorption reactions to minerals will be minimized. Otherwise, kinetic errors will be introduced as it is unlikely that the individual equilibration time selected for the experimental determination of $K_d$ values will correspond to the specific sorption time-frame in the model. Furthermore, due to natural pore size heterogeneity, changes in redox chemistry and microbiological activity, local contact times between pore water solutions and mineral surfaces may vary over time and space. Hence, the best approach to minimize errors associated with kinetic limitations of contaminant sorption reactions is to use equilibrium $K_d$ values and to select characteristic times/lengths in the transport model that justify a local equilibrium assumption.
Therefore, there is a need to characterize potential kinetic effects on the experimental determination of $K_d$ values.

Contaminant transport models can be used to characterize and compare contaminant mobility at a variety of chemical solution conditions, such as pH, ionic strength or dissolved organic ligand concentrations. This is relevant if transport behavior is evaluated for systems of potentially changing chemical solution conditions, e.g., over extended time or length scales. For example, corrosion of metal waste containers may require the simulation of contaminant mobility under various pH conditions. Biodegradation of organic wastes may lead to high dissolved organic matter concentrations near the source term, but lower levels along the transport pathway entailing transport calculations at varying organic ligand concentrations. In these cases, a relative comparison of contaminant velocities at various chemical solution conditions is mathematically linked to relative differences in contaminant retardation factors and distribution coefficients. Hence, errors associated with these parameters, e.g., due to kinetic limitations, may be further propagated in their relative comparison. In the following discussion, we will focus on metal contaminants as sorbates of interest; however, similar considerations may also be applicable to other types of compounds.

Distribution coefficients are commonly computed based on the results of batch sorption studies, which allow for a time-efficient investigation of contaminant sorption behavior under a variety of chemical solution conditions. For metal contaminants, sorption data have been reported for a wide range of sorption equilibria times from minutes to weeks, even for the same metal-solid system (Dzombak and Morel, 1990). This variety in equilibration times is clearly a concern, especially since the appropriateness of equilibration times is often based on 'preliminary' experimental data, which are not reported in detail (Dzombak and Morel, 1990). The selection of appropriate equilibration times is complicated by the n-step character of metal sorption kinetics at constant pH. Kinetics are characterized by an initial fast metal uptake followed by one or more slower step(s) in which the equilibrium sorption density is approached asymptotically (Dzombak and Morel, 1990). Often it is assumed that the contribution of the slow sorption step is small and that short equilibration times are sufficient. However, the relevance of slow sorption rates may not necessarily become apparent during short-term kinetic experiments leading to a possible misinterpretation of equilibrium or steady-state conditions. Furthermore, it has been demonstrated that under certain conditions the slow sorption step can represent a significant portion of total sorption (Dzombak and Morel, 1986; Jannasch et al., 1988; Li et al., 1984; McKenzie, 1970; Vanriemsdijk and Lyklema, 1980).

In addition, variations in chemical solution conditions may affect the relative contributions of fast and slow sorption steps and the net apparent rates of contaminant sorption reactions. As chemical reactions are widely known to be governed by the elementary reactions that constitute the reaction mechanism (Stone and Morgan, 1990), this dependence on chemical solution conditions may be due to differences in the underlying mechanisms of sorption reactions and reaction pathways. For example, pH may influence the apparent metal sorption behavior due to variations in metal solution speciation and inorganic ligand complexation (Bachmef et al., 2008; Nedobukh et al., 1987), to changes in mineral surface charge, and the pH-dependence of metal (surface) precipitation reactions (Rouff et al., 2005). The presence of organic ligands may slow down metal sorption due to lower sorption rates of metal-ligand complexes (Pitois et al., 2008), the rate-limited dissociation of metal-ligand solution complexes prior to the sorption of ‘free’ metals (Bryan et al., 2007; Schmitt et al., 2003), and the formation of organic surface films causing a change in surface charge characteristics (Neiho and Loeb, 1974). For instance, changes in metal sorption kinetics in the presence of natural organic ligands have been observed for Al, Fe, Zn and Pb (Schmitt et al., 2003), americium(III) (Arringer et al., 1998), and europium(III) (Pitois et al., 2008). Effects of solution pH on metal-surface reactions have been reported for Pb(II) (Fischer et al., 2007; Rouff et al., 2005), and a variety of other metals including Mn, Cd, Ni, Zn, Cu, Al, Cr, and Hg (Fischer et al., 2007).

It becomes clear that without a critical evaluation of kinetic effects, it is unknown to what extent observed differences in $K_d$ values are due to effects of chemical solution conditions, to changes in kinetic sorption behavior, or a combination of the two. Depending on the specific kinetic characteristics of the evaluated systems, the neglect of kinetic limitations could lead to either an over- or underestimation of the effects of chemical solution conditions on contaminant sorption behavior in comparison to equilibrium conditions. Hence, $K_d$ values determined for various solution conditions at short equilibration times may be very limited in their capability to accurately quantify relative differences in contaminant sorption behavior at long-term or equilibrium conditions.

Despite the potential relevance of chemical effects on sorption kinetics, it may not be practical to perform batch kinetic experiments for all chemical solution conditions of interest in order to avoid errors associated with kinetic limitations. However, it is clearly a concern that potential errors could be propagated in cases of relative comparisons of sorption and transport parameters. Therefore, the goal of this paper is to elucidate the influence of sorption kinetics on the relative comparison of $K_d$ values and retardation factors. This comparison will refer to two systems that describe sorption of a selected contaminant onto one specific solid phase but under different chemical solution conditions. Specifically, we will provide the following:

1. A derivation of mathematical equations describing the relationships between pseudo-first order sorption kinetics and the ratios of $K_d$ values and retardation factors;
2. A series of hypothetical examples demonstrating the effects of non-equilibrium sorption conditions on the relative comparison of sorption and transport parameters in systems with various sorption characteristics;
3. A comparison of these hypothetical examples with experimental kinetic data from the literature;
4. Recommendations for the selection of appropriate experimental sorption equilibration times for systems with various sorption kinetics and affinities. These will allow researchers to minimize potential errors in the
comparison of sorption and transport parameters due to kinetic limitations while decreasing the number of kinetic experiments required.

Throughout this analysis, we assume that contaminant sorption behavior in two systems with different chemical solution conditions can be described by linear sorption isotherms. Hence, $K_d$ values represent the constant slopes of linear sorption isotherms and are independent of solute concentrations. As a consequence, retardation factors do not depend on concentration fields, as is the case for non-linear sorption isotherms (Attinger et al., 2003). While the assumption of linear sorption behavior may not always be applicable to field-related problems, it is necessary for the simplification of the mathematical analysis in this study.

In addition, our conclusions are based on the assumption of fully-reversible pseudo-first order kinetics for contaminant sorption reactions onto mineral surfaces. While first order models have been widely used to describe reactions at the mineral/water interface (Sparks, 2000), their validity is limited by the assumption of an ‘unlimited’ amount of reactive surface sites and fully-reversible surface reactions, i.e., the lack of sorption hysteresis. We primarily selected a pseudo-first order rate law for this analysis because it allows for a simple mathematical approach to determine if two systems show the same or different sorption kinetics (see 2.1 Definitions and assumptions). Nevertheless, future research is needed to characterize kinetic limitations for the comparison of retardation factors for non-linear, concentration-dependent sorption behavior and surface site limitations, ‘biphasic’ sorption/desorption reactions, and changes in desorption behavior over time.

In summary, in this study we characterize the errors that are potentially introduced in the comparison of contaminant sorption and transport behavior under various chemical solution conditions if kinetic limitations for contaminant sorption reactions are ignored. It is not our goal to provide any recommendations for the incorporation of time-dependent distribution coefficients in contaminant transport models.

2. Theoretical analysis

2.1. Definitions and assumptions

Soil minerals are known to provide specific surface sites for sorption reactions of metals and other contaminants (Stumm, 1992). For reasons of simplification, we assume that all physical and chemical processes contributing to a net overall metal sorption reaction (mass transfer, diffusion, surface complexation reactions, etc.) can be summarized by the following reversible surface reaction

$$\equiv S + M \leftrightarrow \equiv S - M \quad (1)$$

where $M$ is the metal contaminant, $\equiv S$ the reactive surface site and $\equiv S - M$ the resulting surface complex. Hence, in this study sorption kinetics represent net apparent sorption rates without considering specific solution or surface species and reaction pathways.

Further, assuming that all systems under investigation provide a large excess of reactive surface sites, metal sorption kinetics can be described by the decrease in metal solution concentration $[M]$ (mol $\text{l}^{-1}$) over time $t$ (days) based on a pseudo-first order rate law

$$\frac{d[M]}{dt} = -k_f[M] + k_r\left(\frac{\rho}{\theta}\right)[\equiv S - M] \quad (2)$$

where $\rho$ represents bulk density (kg $\text{l}^{-1}$) and $\theta$ porosity (dimensionless). In Eq. (2), the pseudo-first order forward rate constant (day$^{-1}$) is equal to $k_f = k_f[S]$; $k_r$ (kg (mol days)$^{-1}$) and $k_r$ (days$^{-1}$) represent forward and reverse rate constants for the surface reaction in Eq. (1). The concentrations of free and occupied surface sites, $[\equiv S]$ and $[\equiv S - M]$, have units of mol kg$^{-1}$.

At equilibrium, $d[M]/dt = 0$ and the dimensionless equilibrium constant for the pseudo-first order sorption reaction is equal to (Stone and Morgan, 1990)

$$K = \frac{k_f}{k_r} = \left(\frac{\rho}{\theta}\right)\frac{[\equiv S - M]_e}{[M]_e} \quad (3)$$

with metal surface and solution concentrations representing equilibrium values.

A pseudo-first order rate law was selected as it allows for a simple approach to determine if two systems show the same or different sorption kinetics. With the same sorption kinetics, both systems will reach their individual equilibrium surface concentrations at the same ‘natural’ rate, which is the sum of the individual rate constants ($k_f + k_r$) (Espenson, 1995). In this case, both systems need the same characteristic time $\tau$ (days) to reach 63.2% of their respective equilibrium surface concentrations (Stone and Morgan, 1990).

$$\tau = \frac{1}{k_f + k_r} \quad (4)$$

In fact, systems with the same pseudo-first order sorption kinetics show the same fraction of the equilibrium surface concentration ($f(t)$) sorbed at any given point in time independent of the individual equilibrium $K_d$ values approached.

Assuming linear contaminant sorption behavior, we can define the apparent distribution coefficient $K_d(t)$ (1 kg$^{-1}$) at any given time as

$$K_d(t) = \frac{[\equiv S - M]_t}{[M]_t} \quad (5)$$

and at full equilibrium conditions as

$$K_d = \frac{[\equiv S - M]_e}{[M]_e} = \left(\frac{\rho}{\theta}\right)K = \left(\frac{\rho}{\theta}\right)\frac{k_f}{k_r} \quad (6)$$

$K_d$ values are related to (dimensionless) contaminant retardation factors ($R$) based on the following expression (Stumm, 1992)

$$R = 1 + \frac{\rho}{\theta}K_d \quad (7)$$

where again $\rho$ represents bulk density in kg $\text{l}^{-1}$ and $\theta$ porosity (dimensionless). Including the time-dependence of $K_d$ values, as well as common ranges for the values of $\rho$ (1.6–2.1 kg $\text{l}^{-1}$)
and θ (0.2–0.4) (Stumm, 1992), retardation factors can typically be expected within a range from \( R_f(t) = 1 + 4K_d(t) \) to \( R_f(t) = 1 + 10K_d(t) \). For all conversions between \( K_d(t) \) and \( R_f(t) \) in this paper, we will assume intermediate values of aquifer characteristics resulting in \( R_f(t) = 1 + 7K_d(t) \). We will discuss the influence of this assumption on the presented results in the Results and discussion section.

Furthermore, retardation factors also describe the ratio between the average linear velocities (cm s\(^{-1}\)) of the groundwater solution (\( u \)) and the contaminant (\( u_i \)) measured at the point where the concentration of the solute front is one-half of the original contaminant concentration (Stumm, 1992).

\[
R_f = \frac{u}{u_i} \tag{8}
\]

Last, whenever we state the term ‘relative comparison of \( K_d \) values’ (or retardation factors) in the following, we refer to the comparison of these parameters after they have been determined experimentally for two different chemical systems A and B. It is assumed that these systems have been used to characterize the sorption of one specific contaminant to the same solid phase but under different chemical solution conditions.

2.2. General analysis

When contaminant sorption behavior is evaluated in two systems A and B based on a relative comparison of \( K_d \) values, we effectively look at the dimensionless ratio (\( r_\infty \)) of distribution coefficients at chemical equilibrium conditions (\( t \to \infty \)).

\[
r_\infty = \frac{K_{d,A}}{K_{d,B}} \tag{9}
\]

If equilibrium has not been reached, then the calculated, apparent \( K_d \) values only represent fractions (\( X, \) dimensionless) of the equilibrium distribution coefficients.

\[
K_d(t) = X(t)K_{d,\infty} \tag{10}
\]

Therefore, the ratio of \( K_d \) values under non-equilibrium conditions (\( r(t) \)) can only be equal to its ratio at equilibrium, if identical fractions (\( X_A = X_B \)) of the equilibrium values have been reached in both systems.

\[
r(t) = \frac{K_{d,A}(t)}{K_{d,B}(t)} = \frac{X_A(t)K_{d,A,\infty}}{X_B(t)K_{d,B,\infty}} = \frac{K_{d,A,\infty}}{K_{d,B,\infty}} = r_\infty (\text{only if } X_A = X_B) \tag{11}
\]

If this condition is not fulfilled, then errors are introduced in the relative comparison of \( K_d \) values, contaminant retardation factors and average linear contaminant velocities. Relative differences in \( K_d \) values are now the result of two factors: (1) the mechanistic effects of chemical solution conditions on contaminant sorption behavior; and (2) the errors introduced due to neglecting kinetic limitations. The potential relevance of kinetic effects is dependent on the resulting differences in the values of \( X_A \) and \( X_B \), as well as on the magnitudes of the compared equilibrium \( K_d \) values. Ultimately, errors associated with kinetic limitations will have to be compared to experimental errors that are introduced by performing long-term batch sorption experiments with the goal to reach sorption equilibria. For example, systems characterized by high contaminant sorption affinities, and consequently large \( K_d \) values, may require measurements of low solute concentrations possibly resulting in large analytical errors. Furthermore, the continuous shaking of batch sorption systems over extended time-frames may lead to side reactions (Sposito, 1984), such as the physical degradation of mineral particles. Nevertheless, it should still be useful to improve the understanding of the mathematical relationships between \( K_d \) values and contaminant sorption kinetics.

The total metal concentration in the system (\( |M|_{Tot} \)) is equal to the metal solution concentration at time equal zero (\( |M|_0 \)), prior to any sorption reactions to the mineral phase. Hence, the metal mass balance for any given point in time can be written as

\[
|M|_{Tot} = |M|_0 + \int_0^t \left[ |S| - |M|_t \right] dt \tag{12}
\]

Therefore, for the most general case,

\[
K_d(t) = \frac{\left[ |S| - |M|_t \right]}{|M|_t} = f(t)\frac{\left[ |S| - |M|_\infty \right]}{|M|_0 - f(t)\left[ |M|_0 \right]} \tag{13}
\]

whereas \( f(t) \) represents the (dimensionless) fraction of the equilibrium surface concentration sorbed over time, and \( |M|_0 \) (\( \text{mol L}^{-1} \)) the contaminant solution concentration at time equals zero. The mathematical function of \( f(t) \) is characterized by the sorption kinetics in a given system, whereas systems with the same pseudo-first order kinetics will have identical functions of \( f(t) \). Nevertheless, based on Eq. (13), systems with the same sorption kinetics will still show different functions of \( K_d(t) \) over time as long as different sorption equilibria are approached. Furthermore, in cases with different sorption kinetics in systems A and B (\( \tau_A \neq \tau_B \)), the individual functions of \( f(t) \) will differ as well, leading to a more complex relationship. In either case, the relative comparison of sorption distribution coefficients is affected by the selected sorption equilibration time as long as sorption equilibria have not been reached. Errors introduced by kinetic limitations will be more pronounced in systems with high contaminant surface concentrations at equilibrium (large equilibrium \( K_d \) values). We conclude that the relative comparison of \( K_d \) values is inherently sensitive to kinetic effects. This is not only the case for systems with different sorption kinetics, but also for systems with the same kinetic sorption behavior.

2.3. Derivation: \( K_d \) values and retardation factors as a function of kinetic rate constants

In the following, we will derive mathematical expressions in order to describe \( K_d \) values and retardation factors as functions of kinetic rate constants and time. Later, the derived expressions will be used in hypothetical examples, which characterize the time-dependence of these parameters for
different types of kinetic sorption behavior. For this derivation, contaminant surface reactions are based on Eq. (1); sorption kinetics follow pseudo-first order rate laws as described in Eq. (2).

First, Eq. (2) is integrated and normalized based on [M]i0, which gives the normalized metal solution concentration ([M]i) as a function of time (days):

$$\frac{[M]_i}{[M]_{i0}} = \exp\left(-\left(k_f + k_r\right)t\right) + \frac{k_r}{k_f + k_r} \left\{1 - \exp\left(-\left(k_f + k_r\right)t\right)\right\}$$

(14)

Based on the definition of characteristic time $\tau$ (Eq. (4)), this equation can be simplified to

$$\frac{[M]_i}{[M]_{i0}} = \exp\left(-\frac{t}{\tau}\right) + k_r\tau\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}$$

(15)

Considering again the metal mass balance equation (Eq. (12)), we can express the apparent $K_d$ value (Eq. (13)) at any given time in the experiment as

$$K_d(t) = \left(\frac{\theta}{\rho}\right)\left(\frac{[M]_{i0} - [M]_i}{[M]_{i0}}\right) = \left(\frac{\theta}{\rho}\right)\left(1 - \frac{[M]_i}{[M]_{i0}}\right)$$

(16)

Substitution of Eq. (15) into Eq. (16) and rearrangement gives

$$K_d(t) = \left(\frac{\theta}{\rho}\right)\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\} \times (1 - k_r\tau) \times \left(1 - \frac{t}{\tau}\right) + k_r\tau$$

(17)

With $(1 - k_r\tau) = k_f/(k_f + k_r)$ and $k_r\tau = k_i/(k_f + k_i)$ it follows that

$$K_d(t) = \left(\frac{\theta}{\rho}\right)\frac{k_f}{k_f + k_i}\left(1 - \exp\left(-\frac{t}{\tau}\right)\right) + k_i$$

(18)

This expression (Eq. (18)) can now be used to calculate apparent $K_d$ values as a function of time for a variety of pseudo-first order sorption kinetics using various values of $k_f$ and $k_r$, the ‘natural’ rate constant ($k_f + k_r$) and $\tau$. Furthermore, we can re-write Eq. (18) in the following form after dividing all terms by $k_r$ and taking into account that $K_{d,∞} = (\theta/\rho)k_f/k_i$ (Eq. (6)).

$$K_d(t) = \frac{k_f}{k_i}\frac{1 - \exp\left(-\frac{t}{\tau}\right)}{K_{d,∞}\exp\left(-\frac{t}{\tau}\right) + 1}$$

(19)

Hence, the fraction of the equilibrium $K_d$ value reached over time ($X(t)$) can be expressed as

$$X(t) = \frac{K_d(t)}{K_{d,∞}} = \frac{\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}}{\left(\frac{\theta}{\rho}\right)K_{d,∞}\exp\left(-\frac{t}{\tau}\right) + 1}$$

(20)

It follows that $X(t)$ is a function of sorption kinetics ($\tau$) as well as of the equilibrium $K_d$ value for a particular system. Therefore, the time-frame that is needed to reach a constant distribution coefficient is mathematically linked to the magnitude of its value.

For the following discussion and later calculations, we assume that typical aquifer characteristics lead to $(\rho/\theta) = 7$ (see above). Expanding this analysis to retardation factors, a relative change in retardation factors over time can be defined based on Eq. (7).

$$\frac{R_{f,A}(t)}{R_{f,B}(t)} = \frac{1 + 7K_{d,A}(t)}{1 + 7K_{d,B}(t)}$$

(21)

This time-dependent ratio can be calculated for a variety of kinetic system characteristics by substituting individual expressions of $K_d(t)$ (Eq. (18)) for systems A and B into Eq. (21). Last, this expression can also be used to characterize kinetic effects on relative differences between average linear contaminant velocities for two chemical systems A and B using Eq. (8).

$$\frac{R_{f,A}(t)}{R_{f,B}(t)} = \frac{ui_{i,A}(t)}{ui_{i,B}(t)}$$

(22)

Based on the results of this derivation (Eqs. (18), (19) and (21)), we conclude that the ratio of retardation factors for two chemical systems, A and B, will always change as a function of sorption equilibrium time as long as: (1) chemical sorption equilibria have not been reached in all systems within the experimental time-frame ($t → ∞$); and (2) equilibrium $K_d$ values are different for the two systems under investigation ($k_{f,A} ≠ k_{f,B}$ and/or $k_{r,A} ≠ k_{r,B}$). This is valid even when both systems show the same pseudo-first order sorption kinetics (same $τ$). In order for this ratio to be independent of time in non-equilibrium systems, both sets of forward and reverse rate constants would have to be identical. Therefore, both equilibrium $K_d$ values would have to be the same.

2.4. Hypothetical examples of kinetic effects on $K_d$ values and retardation factors

In the following, we will illustrate the influence of kinetic parameters on the ratios of apparent $K_d$ values and retardation factors over time in a series of hypothetical examples covering a variety of kinetic conditions. First, the ratios of $K_d$ values ($X(t) = K_d(t)/K_{d,∞}$; Eq. (20)) will be computed for a variety of sorption rates and equilibrium distribution coefficients. For illustration purposes, we will compare the time-dependent behavior of $X(t)$ with functions of $f(t)$, the fraction of the equilibrium surface concentration sorbed over time. For this purpose, the time-dependent contaminant surface concentration is calculated based on the following expression (Stone and Morgan, 1990) arbitrarily assuming an initial contaminant solution concentration of 4 mM.

$$\left[\equiv S - M_i\right] = \left(\frac{\theta}{\rho}\right)\frac{k_i}{k_f + k_i}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}$$

(23)

This equation is the result of the integration of the pseudo-first order rate law written in terms of metal-surface concentrations. Values of $f(t)$ are then computed by dividing Eq. (23) by the individual equilibrium surface concentrations.
Secondly, we will illustrate the influence of kinetic parameters on the ratio of retardation factors over time (Eqs. (21) and (22)) in four sets of examples, which focus on two systems, A and B, with different chemical solution conditions. This characterization is particularly useful as ratios of retardation factors also reflect relative differences in average linear contaminant velocities. Throughout the comparison, sorption characteristics in terms of sorption kinetics and \( K_d \) values are kept constant in system A while they are varied in system B for each example (Table 1).

Kinetic rate constants are adjusted in order to allow for a comparison, sorption characteristics in terms of sorption kinetics and \( K_d \) values of systems with identical retardation factors for systems with different sorption kinetics. In these cases, the ‘natural’ rate of contaminant sorption in system A is assumed to be slower than in system B by factors of 2, 10 or 100. For all examples, typical aquifer characteristics leading to \((\rho/\theta)=7\) and an initial metal concentration of 4 mM are assumed arbitrarily.

Last, we will compare the ratios of retardation factors calculated in the hypothetical examples described above with ratios determined from experimental data in the literature. This will allow us to demonstrate the relevance of kinetic effects for the comparison of sorption and transport parameters based on previously reported metal sorption data.

### 3. Results and discussion

#### 3.1. Hypothetical examples of kinetic effects on \( K_d \) values and retardation factors

In the following, we will describe the effects of variations in pseudo-first order sorption kinetics and equilibrium distribution coefficients on \( X(t) \), the fraction of an equilibrium \( K_d \) value reached over time (Eq. (20)). For illustration purposes, we will also briefly discuss the influence of the same parameters on \( f(t) \), the fraction of the equilibrium surface concentration sorbed as a function of time. First, \( f(t) \) follows the same time-dependence in systems with the same pseudo-first order sorption kinetics (identical values of \( \tau \)) independent of the equilibrium \( K_d \) values reached (Fig. 1). On the other hand, these functions vary for systems with identical \( K_d \) values but different sorption kinetics. Furthermore, constant values of \( f(t) \) are reached approximately after five-times the characteristic time of the sorption reaction (5\( \tau \)). This is due to the direct link between \( f(t) \) and the contaminant surface concentration, and agrees with classical chemical engineering literature (Levenspiel, 1972).

In contrast to \( f(t) \), fractions of \( K_d \) values over time (\( X(t) \), Eq. (20)) are affected by the magnitude of equilibrium \( K_d \).

#### Table 1

Parameters used in calculations for hypothetical examples.

<table>
<thead>
<tr>
<th>Exam.</th>
<th>System A</th>
<th>System B</th>
<th>Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_f^a )</td>
<td>( k_f^b )</td>
<td>( K_d,A,-/K_d,B,- )</td>
</tr>
<tr>
<td></td>
<td>(day(^{-1}))</td>
<td>(day(^{-1}))</td>
<td>(1 kg(^{-1}))</td>
</tr>
<tr>
<td>Set a: same sorption kinetics in systems A and B: ( \tau_f^a=\tau_f^b )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.97E-01</td>
<td>2.82E-03</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>1.97E-01</td>
<td>2.82E-03</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>1.97E-01</td>
<td>2.82E-03</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>1.97E-01</td>
<td>2.82E-03</td>
<td>10</td>
</tr>
</tbody>
</table>

| Set b: sorption kinetics in system A is 2-times slower than in system B: \( \tau_f^a=2\tau_f^b \) | | | | | | |
| 1 | 1.97E-01 | 2.82E-03 | 10 | 5 | 1.65E-01 | 2.35E-01 | 0.1 | 2.5 | 100 | 2 |
| 2 | 1.97E-01 | 2.82E-03 | 10 | 5 | 3.50E-01 | 5.00E-02 | 1 | 2.5 | 10 | 2 |
| 3 | 1.97E-01 | 2.82E-03 | 10 | 5 | 3.94E-01 | 5.63E-03 | 10 | 2.5 | 1 | 2 |
| 4 | 1.97E-01 | 2.82E-03 | 10 | 5 | 3.99E-01 | 5.71E-04 | 100 | 2.5 | 0.1 | 2 |
| 5 | 1.97E-01 | 2.82E-03 | 10 | 5 | 4.00E-01 | 5.71E-05 | 1000 | 2.5 | 0.01 | 2 |

| Set c: sorption kinetics in system A is 10-times slower than in system B: \( \tau_f^a=10\tau_f^b \) | | | | | | |
| 1 | 1.97E-01 | 2.82E-03 | 10 | 5 | 8.24E-01 | 1.18E+01 | 0.1 | 0.5 | 100 | 10 |
| 2 | 1.97E-01 | 2.82E-03 | 10 | 5 | 1.75E+00 | 2.50E+00 | 1 | 0.5 | 10 | 10 |
| 3 | 1.97E-01 | 2.82E-03 | 10 | 5 | 1.97E+00 | 2.82E+00 | 10 | 0.5 | 1 | 10 |
| 4 | 1.97E-01 | 2.82E-03 | 10 | 5 | 2.00E+00 | 2.85E+00 | 100 | 0.5 | 0.1 | 10 |
| 5 | 1.97E-01 | 2.82E-03 | 10 | 5 | 2.00E+00 | 2.86E+00 | 1000 | 0.5 | 0.01 | 10 |

| Set d: sorption kinetics in system A is 100-times slower than in system B: \( \tau_f^a=100\tau_f^b \) | | | | | | |
| 1 | 1.97E-01 | 2.82E-03 | 10 | 5 | 8.24E-00 | 1.18E+01 | 0.1 | 0.05 | 100 | 100 |
| 2 | 1.97E-01 | 2.82E-03 | 10 | 5 | 1.75E+01 | 2.50E+00 | 1 | 0.05 | 10 | 100 |
| 3 | 1.97E-01 | 2.82E-03 | 10 | 5 | 1.97E+01 | 2.82E+00 | 10 | 0.05 | 1 | 100 |
| 4 | 1.97E-01 | 2.82E-03 | 10 | 5 | 2.00E+01 | 2.85E+00 | 100 | 0.05 | 0.1 | 100 |
| 5 | 1.97E-01 | 2.82E-03 | 10 | 5 | 2.00E+01 | 2.86E+00 | 1000 | 0.05 | 0.01 | 100 |

\( a \) \( k_f=K_d,\rho/\theta|k, k_1=1/(\theta fK_d+1) \) with \( (\rho/\theta)=7 \) (kg l\(^{-1}\)).

\( b \) \( \tau=1/(k_f+k_r) \).
Time-dependence of the fraction of the equilibrium surface concentration sorbed ($f(t)$) for various characteristic times of sorption reactions ($\tau$ in days) and equilibrium $K_d$ values (l kg$^{-1}$). Values of $f(t)$ were computed based on kinetic rate constants given in Table 1 (Sets a, b, c, exam. 1 and 5 each) for various pairs of $\tau$ and $K_{d,\infty}$ values.

Values not only if sorption kinetics are different but also if they are the same (Fig. 2). The time-frame that is needed to reach the same fraction of a $K_d$ value (e.g., 90%) is dependent on the equilibrium value of the distribution coefficient. Systems with larger distribution coefficients require longer time-frames of sorption equilibration to attain the same fraction of the equilibrium $K_d$ value. Furthermore, the ‘rule-of-thumb’ stating that constant values can be expected after a time-frame of $5\tau$ is not generally valid for $K_d$ values. Systems with high distribution coefficients can require substantially longer equilibration times, while systems with low distribution coefficients may attain constant $K_d$ values within this time-frame. The relationships depicted in Fig. 2 are plotted for systems with the same specific pseudo-first order sorption kinetics (same $\tau$). Due to the normalization of the time-axis based on $\tau$, these results are valid for any selected value of characteristic time, as long as $\tau$ is the same for all systems. A variation of the value of $\rho/\theta$ over the range of typical aquifer characteristics from 4 to 10 (kg l$^{-1}$) (Stumm, 1992) does not affect the shape of these curves or their position relative to each other. However, with increasing values of $\rho/\theta$ these curves are slightly shifted to the right (towards higher values of normalized sorption time).

Due to this time-dependence of $X(t)$, propagated errors may be introduced in the calculated ratios of $K_d$ values and retardation factors, when values of $X(t)$ are substantially different from each other and systems are compared under non-equilibrium conditions. Hence, if the same or very similar sorption kinetics are assumed for all systems, experimental sorption equilibration times should ideally be based on the time-frame that is needed to reach a constant $K_d$ value in the system with the highest sorption affinity. This would allow the minimization of potential errors due to kinetic limitations.

Last, four sets of examples were calculated to illustrate the effects of variations in sorption kinetics and in the ratios of $K_d$ values on the relative comparisons of retardation factors and contaminant velocities (Table 1, Fig. 3). Individual parts of Fig. 3a–d represent various degrees of differences in sorption kinetics between chemical systems A and B. For each kinetic condition, the ratio of equilibrium $K_d$ values in A and B is varied ranging from higher contaminant sorption affinities in system A than B ($K_{d,A}/K_{d,B} = 1$) to the same ($K_{d,A}/K_{d,B} = 1$), and lower relative sorption affinities ($K_{d,A}/K_{d,B} = 1$). Therefore, for values of $K_{d,A}/K_{d,B} = 1$, the contaminant velocity in system B is faster than in A; for values $< 1$ contaminant velocity in B is slower.

Time-axes in these graphs are normalized based on the characteristic time in system A ($\tau_A$), which is the system with slower sorption kinetics in all cases. This normalization ensures that full equilibrium conditions are reached within similar, normalized time-frames in all examples, which simplifies the comparison of results. The $y$-axes describe the factors by which contaminant retardation is changed in system A compared to system B. In other words, it shows the factors by which the relative contaminant velocity ($v_{B}/v_{A}$) is increased (for values $> 1$) or decreased (for values $< 1$) when chemical solution conditions are changed from system A to B. Dashed lines depict the ratios of retardation factors and contaminant velocities at full equilibrium conditions for the individual examples. This allows an evaluation of the potential over- or underestimation of chemical solution effects in the relative comparison of transport parameters during non-equilibrium conditions.

For the example set a) (Fig. 3a), the same pseudo-first order sorption kinetics are assumed in systems A and B. As derived mathematically, relative retardation factors and contaminant velocities are only independent of time in systems with identical distribution coefficients and sorption kinetics. For all other conditions, these ratios approach constant values within different time-frames, which are dependent on the ratio of their equilibrium $K_d$ values. A comparison of the effects of equilibrium $K_d$ values on $X(t)$ (Fig. 2) and on the ratios of retardation factors (Fig. 3a) suggests that the time-frame required to reach constant transport parameter ratios is largely determined by the sorption kinetics in the system with the higher equilibrium $K_d$ value. In cases where $K_{d,A}/K_{d,B} = 1$, the increase in contaminant velocity in system B relative to system A is underestimated unless full equilibrium has been reached; for systems with $K_{d,A}/K_{d,B} = 1$, the relative decrease in contaminant velocity in system B is underestimated under non-equilibrium conditions. Therefore, for systems with the same
pseudo-first order sorption kinetics, relative differences in contaminant retardation factors and velocities are always underestimated unless sorption equilibria have been reached.

For the following example sets (b–d), the sorption rates in system B are increased leading to 2-, 10- or 100-times faster sorption kinetics in system B compared to system A. As a consequence, the relative time-dependent behavior of these systems becomes more and more determined by the slow sorption kinetics in A. Furthermore, there are ‘variations’ possible in terms of the potential misinterpretation of relative changes in contaminant mobility over time. For example, for 10-times slower sorption kinetics in system A than in B \( (\tau_A = 10\tau_B) \) and \( K_{d,A,\infty}/K_{d,B,\infty} = 0.01 \), the contaminant velocity in system B is decreased by a factor of 100 compared to system A at full equilibrium conditions (Fig. 3c). For very short sorption equilibration times, however, this decrease appears to be smaller. This would result in an underestimation of the decrease in contaminant velocity in system B compared to system A. On the other hand, for longer sorption equilibration times, the decrease in contaminant velocity in system B appears to be higher than at full equilibrium conditions. Hence, the latter comparison would lead to an overestimation of the decrease in contaminant velocity in system B. Therefore, an over- or underestimation of relative changes in transport parameters is possible when systems with different sorption kinetics are compared under non-equilibrium conditions. The type of misinterpretation is dependent on the specific system characteristics in terms of equilibrium \( K_d \) values and sorption kinetics. Furthermore, it is probably difficult to anticipate these kinds of errors due to kinetic limitations without any specific knowledge of kinetic sorption characteristics in the systems of interest.

In most hypothetical examples, variations in the value of \( \rho/\theta \) in Eq. (21) over the range of typical aquifer characteristics from 4 to 10 (kg l\(^{-1}\)) \( (\text{Stumm, 1992}) \) will not affect these trends. As long as \( (\rho/\theta)K_d \gg 1 \), \( R_f(t) \sim \frac{R_f(t)}{R_{f,B}} \approx \{((\rho/\theta)K_{d,A}(t))/((\rho/\theta)K_{d,B}(t)) \} \) and the term \( (\rho/\theta) \) effectively cancels. In this case, this ratio is independent of aquifer characteristics in terms of bulk density and porosity. However, for very small \( K_d \) values, the extent of kinetic effects might be influenced by the specific values of \( (\rho/\theta) \), while the general trends remain the same. For example, a calculation of the ratio of equilibrium retardation factors for the hypothetical systems A and B assuming the same sorption kinetics (Table 1; set a, exam. 1) using values of \( (\rho/\theta) \) equal to 4, 7, and 10 determined \( R_f \) ratios of 29.3, 41.8 and 50.5 (dimensionless). In this example, this variation is due to the low distribution coefficient in system B \( (0.1 \text{ kg l}^{-1}) \). With \( K_{d,B,\infty} \) equal to 11 kg l\(^{-1}\) (set a, exam. 2), these ratios were calculated as 8.2, 8.88, and 9.18 for \( (\rho/\theta) \) values of 4, 7, and 10. For higher \( K_d \) values in this set of examples, no significant effects were observed.

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**Fig. 3.** Ratios of contaminant retardation factors and velocities describing sorption and mobility in systems A and B over time for a variety of ratios of equilibrium \( K_d \) values and kinetic conditions. The figures show (a) same contaminant sorption kinetics in both systems \( (\tau_A = \tau_B) \), or slower sorption kinetics in A than in B by factors of (b) 2 \( (\tau_A = 2\tau_B) \), (c) 10 \( (\tau_A = 10\tau_B) \) or (d) 100 \( (\tau_A = 100\tau_B) \). Dashed lines represent ratios reached at full equilibrium conditions. Time-axis has been normalized with \( \tau_A = 5 \text{ days} \), the longer characteristic sorption time of the two systems (Table 1). \( R_f \) ratios were calculated based on \( R_f(t) = 1 + 7K_d(t) \) (see Theoretical analysis in Section 2).
3.2. Comparison with literature data

In the following, we will present two sets of kinetic sorption data from the literature in order to (1) demonstrate the practical relevance of kinetic effects on the relative comparison of $K_d$ values and retardation factors; and (2) to compare reported experimental results with the hypothetical examples discussed above. For this purpose, we plot experimentally-determined contaminant distribution coefficients and ratios of contaminant retardation factors as a function of time. All ratios of retardation factors were computed with respect to the chemical system with the fastest sorption kinetics in order to demonstrate the largest possible kinetic errors. In the latter type of figure, we also provide calculated ratios of equilibrium $K_d$ values for the systems under evaluation in order to allow for a visual comparison of general trends between literature data and our hypothetical examples.

In the first data set (Pitois et al., 2008), the sorption kinetics of $8 \times 10^{-10}$ M europium(III) (Eu) to 0.5 g ml$^{-1}$ quartz sand was investigated in the absence and presence of Aldrich humic acid (HA) (HA=0, 20, 50, 100 mg l$^{-1}$; pH=6; I=0.1 M NaClO$_4$). In ligand-free systems, Eu(III) reaches complete sorption (>99%, as defined by the researchers (Pitois et al., 2008)) within a time-frame of 1 day (Fig. 4a). However, in the presence of HA, metal sorption is kinetically controlled over approximately 14 days. Due to this difference in sorption kinetics, the apparent Eu(III) $K_d$ values calculated for the individual systems are dependent on the selected sorption equilibration times. Furthermore, the relative decrease in the Eu(III) $K_d$ value, e.g., when compared between a ligand-free system and in the presence of 100 mg l$^{-1}$ HA, is a function of time. Eu(III) $K_d$ values show a 117-fold decrease due to the high ligand concentration after 1 day, but only 85-fold and 40-fold decreases after 5 and 28 days respectively. Therefore, the quantitative effects of organic ligands on Eu(III) sorption onto quartz could be substantially overestimated if insufficiently long sorption equilibration times were selected in experiments.

Furthermore, we calculated the ratio of Eu(III) retardation factors describing retardation in various ternary Eu(III)–HA–quartz systems (slow sorption kinetics) over metal retardation in the binary Eu(III)–quartz system (fastest sorption kinetics) as a function of time. This comparison of Eu(III) retardation factors and contaminant velocities shows a similar dependence on time as the comparison of Eu(III) $K_d$ values (Fig. 4b). For example, the presence of 100 mg l$^{-1}$ HA leads to either a 110-times or 40-times higher Eu(III) groundwater velocity depending on the selected experimental sorption time-frame (1-day versus 28-day sorption).
Therefore, the magnitude of increased Eu(III) mobility in the presence of organic ligands under sorption equilibrium conditions could be substantially overestimated if the specific kinetic behavior of this system was unknown or neglected.

The researchers (Pitois et al., 2008) did not provide values for the characteristic time (τ) of Eu(III) sorption reactions to quartz in the various systems. However, we can roughly estimate that τ is more than 10-times longer in ternary than in binary systems. Therefore, these changes in the ratios of retardation factors over time are possibly comparable to the behavior characterized in the hypothetical examples depicted in Fig. 3c or d. The latter, however, is only the case if the assumption of pseudo-first order sorption kinetics is valid for these systems.

In this data set, the lowest distribution coefficient was reported with 1.93 l kg⁻¹ for Eu(III) sorption in the presence of 100 ppm humic acid after 1 day. Based on this Kd value, a variation of ρ/θ between 4 and 10 kg l⁻¹ would not have any substantial impact.

In the second example (Fischer et al., 2007), the sorption behavior of 10⁻⁶ M manganese (Mn) to 2 g l⁻¹ goethite was investigated as a function of solution pH (e.g., pH = 5.4, 6.0, 6.4, 7.0; I = 0.01 M Ca(NO₃)₂) and time. Metal sorption in these systems is kinetically limited over approximately 3 to 28 days. Therefore, both the apparent Kd values as well as the ratio of retardation factors calculated for different pH values are time-dependent (Fig. 5). For example, the relative decrease in the Mn Kd value from pH = 7 to 5.4 seems to vary over more than an order of magnitude as a function of time (Fig. 5a). Depending on the selected time-point, the use of short-term sorption data would lead to an under- (1-day sorption) or overestimation (3-day sorption) of the decrease in Mn distribution coefficients due to these pH changes.

Furthermore, these variations in Kd values are also reflected in the relative changes of Mn retardation factors over time (Fig. 5b). For instance, when comparing Mn retardation between pH values of 5.4 (slow sorption) and 7 (fastest sorption), the relative differences in retardation factors and contaminant velocities can vary over more than two orders of magnitude depending on the sorption equilibration time. We estimate that changes in solution pH from pH = 7 to pH = 5.4 lead to a 5- to 10-fold increase in the characteristic time for Mn sorption onto goethite. We assume again that overall metal sorption reactions can be characterized by pseudo-first order sorption kinetics. Under these conditions, the trends determined from experimental data are comparable to the ratios of retardation factors and contaminant velocities calculated for hypothetical examples in Fig. 3c. As the lowest distribution coefficient in this data set was reported with 8.49 l kg⁻¹, a variation of ρ/θ between 4 and 10 kg l⁻¹ would not have any substantial influence on the results.

Fig. 5. Time-dependence of apparent Kd values and relative retardation factors (R ratios) for sorption of 10⁻⁶ M Mn to 2 g l⁻¹ goethite at various pH solution conditions (I = 0.01 M Ca(NO₃)₂). Complete Mn removal from solution at pH = 7 was calculated as 99.99% Mn sorbed. Rf ratios and average contaminant velocities (ui,pH = 7/ui,pH = x) were computed based on R(t) = 1 + 7Kd(t) (see Theoretical analysis in Section 2). All data compiled from the literature (Fischer et al., 2007).
Overall, experimental results reported in the literature confirm the importance of sorption kinetics for the relative comparison of transport parameters determined at various chemical solution conditions. In addition, they suggest that the kinetically-driven behavior, which was predicted by our mathematical analysis and demonstrated in hypothetical examples (Fig. 3), is relevant.

4. Summary and conclusions

We performed a theoretical analysis in order to characterize the influence of pseudo-first order sorption kinetics on the relative comparison of sorption and transport parameters, such as contaminant distribution coefficients \((K_d)\) and retardation factors assuming linear sorption behavior. This comparison refers to the sorption of a specific contaminant to a specific mineral phase in two systems with different solution conditions. The results of this analysis were illustrated in a series of hypothetical examples and compared to experimental data from the literature.

First, it was found that the time-frame that is needed to reach a steady-state \(K_d\) value is not only dependent on the specific sorption kinetics, but also on the equilibrium \(K_d\) value approached (Fig. 2). Therefore, the quantitative comparison of \(K_d\) values and retardation factors is always affected by the time-frames allowed for sorption equilibration as long as equilibrium conditions have not been reached. This is the case for parameter comparisons between chemical systems with the same or different sorption kinetics. Furthermore, the ‘rule-of-thumb’ stating that an equilibrium value can be expected within approximately 5-times the characteristic time of a reaction \((5\tau)\) does not generally apply to attaining constant \(K_d\) values. This rule is only valid for systems with fairly small equilibrium distribution coefficients.

In addition, potential errors due to kinetic limitations are dependent on the differences in sorption kinetics and equilibrium \(K_d\) values between the systems under consideration. For the same sorption kinetics in both systems, relative increases or decreases in contaminant velocities are always underestimated as long as sorption equilibria have not been reached in all systems. However, in the case of different sorption kinetics in the two systems, either an under- or overestimation of relative differences is possible. The latter is dependent on the specific differences in kinetic sorption characteristics between the systems, as well as on the selected sorption equilibration time.

While the influence of sorption kinetics on the comparison of \(K_d\) values seems obvious from a mathematical perspective, it has been widely ignored in experimental design and in the interpretation and comparison of \(K_d\) values and retardation factors. Therefore, for short-term experiments, observed changes in \(K_d\) values may be due to effects of chemical solution conditions, to differences in kinetic sorption behavior, or a combination of the two. Kinetic data are required in order to distinguish between these factors, and to avoid an over- or underestimation of solution chemical effects on contaminant sorption behavior at equilibrium conditions. Therefore, there is a strong need for the investigation of contaminant sorption kinetics, in particular as a function of varying solution conditions and over extended time-frames.

However, it may not be practical to perform batch kinetic experiments for all chemical solution conditions of interest. Nevertheless, appropriate experimental sorption equilibration times have to be selected to attempt at least a minimization of errors introduced by potential kinetic limitations. We can provide the following recommendations for the selection of experimental sorption equilibration times based on the results of the mathematical analysis presented above and under the assumptions of linear sorption behavior and pseudo-first order sorption kinetics:

1. In a first step, it needs to be evaluated if sorption kinetics are expected to be the same or different for the various chemical systems under investigation.
2. If sorption kinetics are assumed to be the same (or very similar), then a sample equilibration time should be selected that allows the system with the highest (anticipated) \(K_d\) value to be fully equilibrated in terms of its distribution coefficient. (Note that this time-frame could be considerably longer than \(5\tau\) for the overall sorption reaction.) Systems with lower equilibrium \(K_d\) values and very similar sorption kinetics will be equilibrated within the same or shorter time-frames. If a full equilibration in terms of constant \(K_d\) values has not been reached, then relative differences in contaminant velocities will be underestimated for the compared systems.
3. On the other hand, if different sorption kinetics are anticipated for the systems under investigation, then the system with the slowest sorption kinetics needs to be determined, either experimentally or based on chemical considerations. The experimental sorption equilibration time should then represent five-times the characteristic time \((5\tau)\) for the kinetics of the slowest overall sorption reaction. If systems of different sorption kinetics have not been fully equilibrated in terms of their \(K_d\) values, relative differences in contaminant velocities could be either under- or overestimated depending on the time-point selected for the comparison, and the specific combination of equilibrium \(K_d\) values and sorption rate constants.

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References


### Notation

- $f(t)$: Fraction of equilibrium surface concentration sorbed over time
- $K$: equilibrium constant for sorption reaction
- $K_{eq}(t)$: apparent, time-dependent distribution coefficient ($l$ kg$^{-1}$)
- $K_{d,A}(t)$, $K_{d,B}(t)$: apparent, time-dependent distribution coefficient in systems A and B ($l$ kg$^{-1}$)
- $K_{d}$: distribution coefficient at sorption equilibrium ($l$ kg$^{-1}$)
- $k_{f}$: forward rate constant ($kg(moldays)^{-1}$)
- $k_{r}$: reverse rate constant ($day^{-1}$)
- $k_{f,A}$, $k_{r,A}$: reverse rate constants in systems A and B ($day^{-1}$)
- $f(t)$: pseudo-first order forward rate constant ($day^{-1}$)
- $k_{r,A}$, $k_{r,B}$: pseudo-first order forward rate constants in systems A and B ($day^{-1}$)
- $M$: metal contaminant
- $[M]$: metal solution concentration ($mol l^{-1}$)
- $[M]_{s}$: metal solution concentration at time $t$ ($mol l^{-1}$)
- $[M]_{tot}$: total metal solution concentration ($mol l^{-1}$)
- $[M]_{s}$: metal solution concentration at time zero ($mol l^{-1}$)
- $[M]_{q}$: metal solution concentration at sorption equilibrium ($mol l^{-1}$)
- $r_{A}$, $r_{B}$: ratio of distribution coefficients at sorption equilibrium
- $t$: time-dependent ratio of distribution coefficients ($day^{-1}$)
- $R_{T}$: contaminant retardation factor
- $R_{T,A}(t)$, $R_{T,B}(t)$: time-dependent contaminant retardation factors in systems A and B

### Equations

- $S$: ‘free’ reactive surface site
- $S_{f}$: ‘free’ reactive site concentration at time $t$ ($mol l^{-1}$)
- $S_{f}$: ‘free’ reactive site concentration at sorption equilibrium ($mol l^{-1}$)
- $S_{M}$: metal-surface complex
- $S_{M}$: concentration of metal-surface complexes at time $t$ ($mol l^{-1}$)
- $S_{M}$: concentration of metal-surface complexes at time zero ($mol l^{-1}$)
- $S_{M}$: concentration of metal-surface complexes at sorption equilibrium ($mol l^{-1}$)
- $t$: time ($day$)
- $u$: average linear groundwater velocity ($cm s^{-1}$)
- $u_{t}$: average linear velocity of contaminant $i$ ($cm s^{-1}$)
- $u_{A}(t)$, $u_{B}(t)$: time-dependent average linear velocity of contaminant $i$ in systems A and B ($cm s^{-1}$)
- $X(t)$: time-dependent fraction of equilibrium $K_{d}$ value
- $\theta$: porosity ($kg l^{-1}$)
- $\rho$: bulk density ($kg l^{-1}$)
- $\tau$: characteristic time for sorption reaction in system A ($days$)
- $\tau_{B}$: characteristic time for sorption reaction in system B ($days$)