Sorption Kinetics of Chlorinated Hydrophobic Organic Chemicals

Part I: The Use of First-Order Kinetic Multi-Compartment Models**

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Abstract

This is the first of a two-part series describing the sorption kinetics of hydrophobic organic chemicals. This paper discusses the use of first-order kinetic compartment models in environmental studies, of subjects such as bioaccumulation and sorption. A comprehensive mathematical description and model calculations are presented. Differences between these models and the pharmacokinetic compartment models will be indicated, emphasis being given to the use of the former in sorption studies.

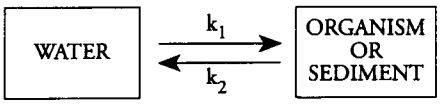
1 Introduction

The fate of organic micropollutants released into the aquatic environment is determined by a combination of physical and chemical processes such as volatilization, sorption in soils and sediments, accumulation in aquatic organisms and chemal and biological degradation. First-order kinetic compartment models are often used to describe the processes separately, and particularly the kinetics of the processes.
The simplest kinetic model to describe the accumulation of chemicals in aquatic organisms or the sorption of chemicals in soils and sediements is the model where the organism or the sediment is represented as one homogeneous compartment. However, in several studies it has been shown that this model is too simple.
Accumulation studies and particularly elimination studies suggest the use of two fish-compartment models for hydrophobic organic chemicals [1, 2]. Several papers give a description of one- and two-compartment accumulation models [1, 3 – 5]. However, since the mathematics of the models are given for limited experimental conditions, a more extended mathematical description is often required.
Sorption and desorption data for organic chemicals also appear to be more complicated than is assumed in a one-sediment compartment model [e.g. 6 – 11]. Two-sediment compartment models have been described in several studies [10, 12 – 14]. However, to simplify the mathematical description of these models, important assumptions are required.
From sorption or bioaccumulation experiments kinetic parameters have to be obtained by inverse modelling. Data sets of these experiments, however, only yield temporal trends of the chemical's concentration in water and whole fish or whole sediment. In the case of two sediment or two fish-compartments, no information is available about the (internal distribution) concentration in the individual compartments. Therefore, regular techniques to assess or to calculate the exchange rate constants between the compartments, as is used for instance in pharmacokinetic studies, are not applicable. To allow one to obtain kinetic parameters for data sets of more-compartment processes in which two compartments can not be distinguished, a numerical method is developed. The method is applied to the results of sorption-desorption data, but is also applicable to bioaccumulation or transformation of more compartment processes.
In the present paper the use of first-order kinetic compartment models in environmental studies is investigated, emphasis being on the use of such models in sorption studies. The mathematics of the models for the specific situation in accumulation and sorption studies are given, together with a comprehensive description of calculations.

2 First-Order Kinetic Compartment Models

2.1 One-Compartment Model

In the one-compartment model organisms or sediment are described as one homogeneous compartment. The exchange of the chemical between the organism or sediment and the water compartment is then described by first-order kinetics.



Here, k_1 and k_2 are first-order rate constants (h^{-1}), and the concentration of the chemical in the water and in the organism or the sediment is given in $\mu g/L$. However, k_1 is actually a pseudo-first-order rate constant which describes the mass of a chemical removed from the water over time. A change in the ratio of organism or sediment/water will change k_1. One can convert this k_1 to a first-order rate constant so that it becomes system independent (k_1^*) by dividing it by the organism/water or sediment/water ratio. The rate constant k_1^* has then the dimension of $L.kg^{-1}.h^{-1}$, which corresponds to the chemical concentration in the organism or the sediment expressed in $\mu g/kg$.

When the concentration of the chemical in the water is zero, and there is thus no uptake of the chemical from the water into the sediment (or organism), the decrease in concentration in the sediment or organism (C) can be given by:

$$dC/dt = -k_2.C \quad (1)$$

and after integration:

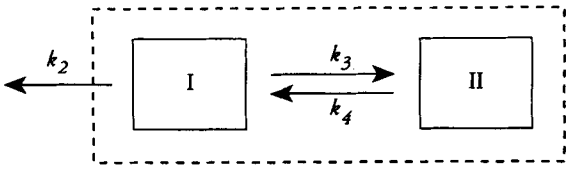
$$C = C_{(t=0)} .e^{-k_2.t} \quad (2)$$

where t is the time (h) and $C_{(t=0)}$ the concentration of the chemical in the sediment or in the organism at $t = 0$. The latter equation shows that the decrease in chemical concentration is an exponential decrease; the excretion rate constant k_2 can be estimated by fitting the decrease in chemical concentration to equation 2.

However, to describe the kinetics of the accumulation or the sorption process, the simple one-fish or one-sediment compartment model often turns out to be inadequate. In fact this calls for a model with two (or more) fish or sediment compartments. Such models can be developed by modifying the kinetic models that are used in pharmacokinetics to describe the excretion of pharmaca by an organism after a single dose has been administered or, a more complicated situation, when the pharmacon was administered continuously (intravenous infusion) [e.g. 15 – 17].

2.2 Two-Compartment Models in Environmental Studies

As far as the model description is concerned, accumulation or sorption is comparable to the pharmacokinetic situation of continuous administration. In accumulation or sorption experiments, fish or sediment have been exposed to the chemical for an extended period before excretion or desorption starts. However, a serious problem arises when pharmacokinetic models are used in accumulation or sorption studies. The mathematical description of the pharmacokinetic model is given for cases where chemical concentrations are measured in one of the compartments. However, in accumulation and sorption studies concentrations of the chemicals are measured in the complete organism or sediment rather than in part of it. A schematic representation for these specific situations is given below, where compartment I and compartment II represent fish or sediment compartments, and complete fish or sediment is indicated by the dotted line:



The decrease in chemical concentration in compartment I and II can be theoretically given by:

$$dC_I/dt = -(k_2 + k_3).C_I + k_4.C_{II} \quad (3\ a)$$

$$dC_{II}/dt = k_3.C_I - k_4.C_{II} \quad (3\ b)$$

where C_I and C_{II} are the chemical concentrations in compartment I and compartment II, and k_3 and k_4 are first-order rate constants. Solving these two differential equations yields for the first and the second compartment respectively, solutions of the form [18]:

$$C_I = A^I.e^{-at} + B^I.e^{-bt} \quad (4\ a)$$

$$C_{II} = A^{II}.e^{-at} + B^{II}.e^{-bt} \quad (4\ b)$$

where the parameters A', B', A'', B'', a and b are complicated functions of the rate constants (k_2, k_3 and k_4).

However, the decrease in the concentration of the chemical in the whole fish or sediment should be described by the sum of the concentrations of the chemical in compartments I and II. The chemical concentrations in the first and second compartment (C_I and C_{II}) are referenced to the total mass, so $C_{I+II} = C_I + C_{II}$.

$$C_{I+II} = A.e^{-at} + B.e^{-bt} \quad (5)$$

where $A = A' + A''$ and $B = B' + B''$. Values for the parameters A, B, a and b are obtained by fitting to this equation the experimental concentration of the chemical in the fish or sediment. Rate constants k_2, k_3 and k_4 can then be calculated from these estimates. However, the relationships between the rate constants and the parameters will be different from those associated with equations 4 a or 4 b. This is due to the specific conditions of the accumulation and sorption experiments: *i)* compartment II is not empty at the beginning of the excretion/desorption period and *ii)* the chemical concentration is measured in the two compartments together.

Compartment models that are described in chemical reaction kinetics [19, 20], cannot be used in environmental studies either. Mathematical descriptions of these kinetic models are the same as those of the pharmacokinetic models, because the same assumptions are made to simplify calculations. These assumptions are possible because at the start of a chemical reaction there is only the original compound present and no reaction products have yet been formed. Therefore in terms of compartments, the second compartment can be assumed to be empty at the start of the reaction. Furthermore, the rate of the reaction is monitored by following the formation of one of the reaction products or by following the disappearance of the original compound. In terms of compartment models this means that the chemical concentration is measured in one single compartment.

2.3 Calculations

In calculating rate constants according to the above mentioned method, i.e. calculating rate constants based on the parameters which result from the curve fitting of the experimental data (→ *Fig. 1*), one encounters two problems: *i)* By fitting the experimental data it is assumed that the parameters of the exponential equation are independent, however they are not, for they are all complicated functions of the same rate constants. *ii)* To calculate the rate constants, one needs not only to have the estimates of the parameters but also to know the chemical concentration at the beginning of the experiment (→ *Appendix*). Since in most cases this is also an experimental data point, its influence on the resulting calculations of the rate constant is disproportionally high compared to the influence of the parameters. The latter are the result of the use of all data points together in curve fitting.

An alternative way of calculating rate constants is to use the experimental data together with the set of differential equations corresponding to the kinetic model concerned. The rate constants estimated in this way can then be used to calculate the parameters of the exponential equations which describe the experimental data. This route is also indicated in **Figure 1.** This method ist worked out in more detail in the Appendix.

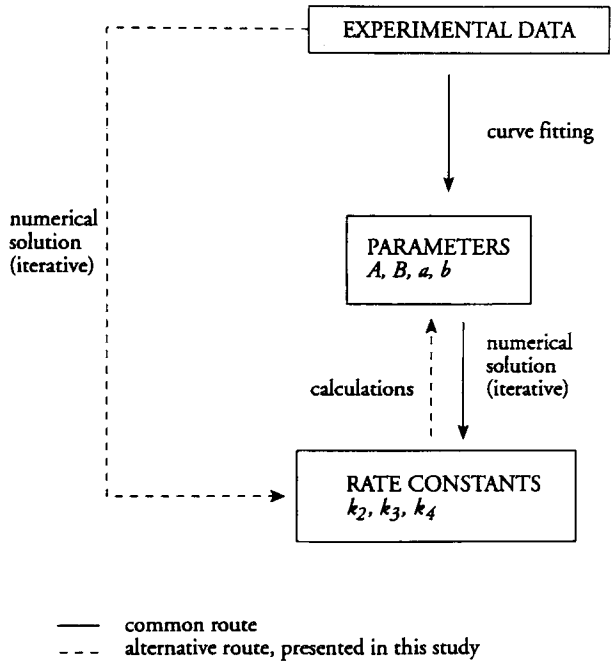
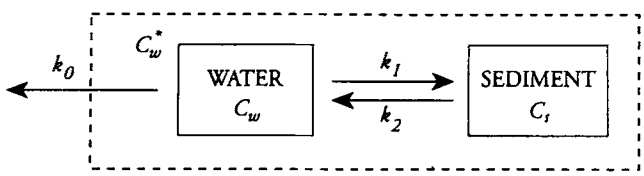


Fig. 1: Calculating rate constants from experimental data

3 Sorption Studies

3.1 One-Sediment Compartment Model

In sediment studies the use of compartment models is even more complicated. In determining the dissolved and sorbed concentrations separately one encounters difficulties because of the problems of separating sediment and water [21, 22]. This implies that in desorption studies, the concentrations of the chemicals have to be determined in the whole sediment suspension rather than separately in sediment and water. For desorption studies where the disappearance of chemicals from a sediment suspension is being investigated, the process can be represented by:



This one-sediment compartment model must be regarded as a *two*-compartment kinetic model.
In this model it is assumed that only the dissolved chemical is removed from the sediment suspension, the removal being described by the rate constant k_0 (h^{-1}). This rate constant is dependent on the efficiency of the experimental method used to remove the dissolved chemical from the suspension, and is thus a system-dependent rate constant [23]. Values for k_0, belonging to a set of experimental conditions (e.g. temperature, volume of water), can be determined separately in an experiment without sediment.
In the desorption experiments the chemical concentration is determined in the whole sediment suspension. This concentration (C_w^*, μg/L) is the sum of the concentrations of the dissolved and sorbed chemicals:

$$C_w^* = C_w + C_s.S \qquad (6)$$

where C_w (μg/L) is the dissolved concentration of the chemical in the water, C_s is the concentration of the chemical in the sediment (μg/kg) and S is the sediment/water ratio (kg/L).
In the period of desorption the decrease in chemical concentration in the sediment suspension will be biphasic, because two compartments are involved (water and sediment). This decrease is described by a two-exponential equation (see also equation 5):

$$C_w^* = P.e^{-pt} + Q.e^{-qt} \qquad (7)$$

Changes in the concentration of the chemicals in the water and the sediment compartment are given by the differential equations:

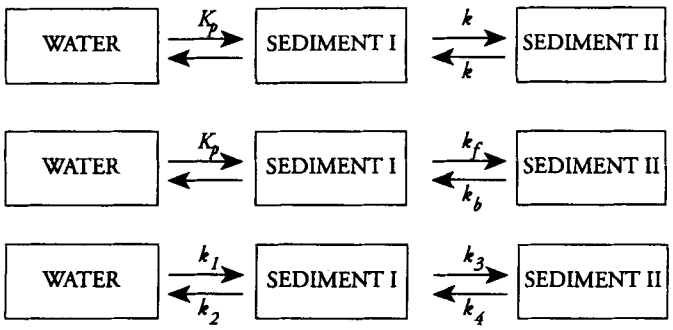
$$dC_w/dt = -(k_0 + k_1).C_w + k_2.C_s.S \qquad (8\ a)$$

$$dC_s.S/dt = k_1.C_w - k_2.C_s.S \qquad (8\ b)$$

3.2 Simplified Two-Sediment Compartment Models

A triphasic decrease in chemical concentration in the sediment suspension corresponds to a *three*-compartment kinetic model with *two* sediment compartments. In the last decade different first-order kinetic two-sediment compartment models have been used to describe sorption *(→ Fig. 2)*. In this figure only two sediment compartments in series are shown, because that is the one which is reported the most frequently. However, analogous assumptions and/or simplifications can be made for the sediment compartments in parallel.

In the two-sediment compartment model, introduced by KARICKHOFF [10, 12], two assumptions are made which limit the mathematical complexity. Firstly, an instantaneous equilibrium is assumed between sediment compartment I and water. The advantage of this is that only one parameter is required, namely the sorption partition coefficient, to describe the chemical exchange between these compartments. Secondly, the chemical movement into and out of the second compartment is assumed to be described with the same first-order rate constant (k).
The bicontinuum model introduced by BRUSSEAU and coworkers [13, 14] is different in that the movement of the chemical in and out sediment compartment II is described with two different rate constants (k_f and k_b). In this model too an instantaneous equilibrium is assumed between the first sediment compartment and the water.



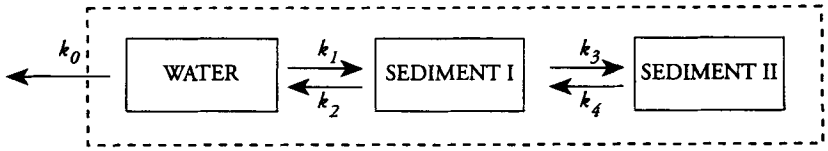
K_p = sorption partition coefficient; k, k_f, k_b, k_1, k_2, k_3, k_4: first-order rate constants

Fig. 2: Two-sediment compartment models to simulate sorption kinetics

3.3 Two-Sediment Compartment Model

The two-sediment compartment model presented in the present study is an extended version of these two-sediment compartment models. No instantaneous equilibrium or equal "in" and "out" rate constants for sediment compartment II has been assumed in advance and exchanges between compartments are all described with different rate constants for the forward and backward direction. Afterwards, i.e. after calculations of the rate constants, the assumptions in the alternative simplified models may turn out to be justified. However, this may differ from experiment to experiment, because the nature of the chemical and the nature of the sediment influences the sorption process and the sorption kinetics.

The two-sediment compartment model (series version) of the present study can be represented by:



The total concentration of the chemical in the sediment suspension (C_w^*, μg/L) is then given by:

$$C_w^* = C_w + C_{sI}.S + C_{sII}.S \qquad (9)$$

where C_{sI} and C_{sII} are the concentrations of the chemical in the first and the second compartment respectively, referenced to the total sediment mass (μg/kg). A three-exponential equation is required to describe adequately the triphasic decrease in chemical concentration in the sediment suspension:

$$C_w^* = P.e^{-pt} + Q.e^{-qt} + R.e^{-rt} \qquad (10)$$

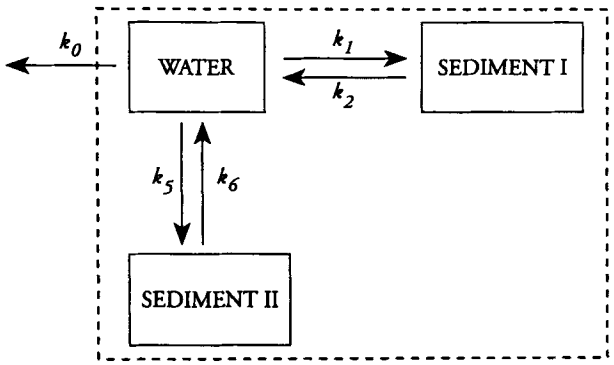
The three equations that describe the change in concentration in the three compartments, water, sediment I and sediment II, are given respectively by:

$$dC_w/dt = -(k_0+k_1).C_w + k_2.C_{sI}.S \qquad (11\ a)$$

$$dC_{sI}.S/dt = k_1.C_w - (k_2+k_3).C_{sI}.S + k_4.C_{sII}.S \qquad (11\ b)$$

$$dC_{sII}.S/dt = k_3.C_{SI}.S - k_4C._{SII}.S \qquad (11\ c)$$

Theoretically, an alternative version of a two-sediment compartment model can be constructed in which no exchange of the chemical is possible between the two sediment compartments.



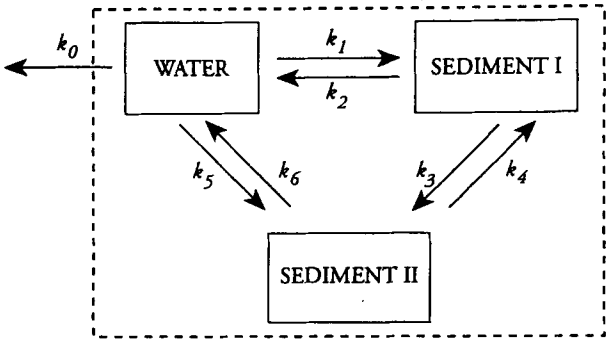
The differential equations accompanying the above scheme are:

$$dC_w/dt = -(k_0+k_1+k_5).C_w + k_2.C_{sI}.S + k_6C_{sII}.S \qquad (12\ a)$$

$$dC_{sI}.S/dt = k_1.C_w - k_2.C_{sI}.S \qquad (12\ b)$$

$$dC_{sII}.S/dt = k_5.C_w - k_6.C_{sII}.S \qquad (12\ c)$$

A third version of two-sediment compartment model can be constructed by combining the two previous versions. This version describes the exchange of the chemicals between the two sediment compartments as well as between the sediment compartments and the water.



k_5 and k_6 are first-order rate constants. The accompanying differential equations are given by:

$$dC_w/dt = -(k_0+k_1+k_5).C_w + k_2.C_{sI}.S + k_6C_{sII}.S \quad (13\ a)$$

$$dC_{sI}.S/dt = k_1.C_w - (k_2+k_3).C_{sI}.S + k_4.C_{sII}.S \quad (13\ b)$$

$$dC_{sII}.S/dt = k_5.C_w + k_3.C_{sI}.S - (k_4+k_6).C_{sII}.S \quad (13\ c)$$

It can be shown that all three versions cannot be distinguished solely on the basis of the decrease in chemical concentrations in the sediment suspension [24]. Thi decrease is triphasic according to all three versions and can be described by a three-exponential decay. However, estimates of the rate constants will be different, because of the different sets of differential equations. These sets, together with the experimentally determined concentrations of the chemicals in the sediment suspension, can be used to derive the rate constants *(→ Appendix)*. However, for the last version of the two-sediment compartment model in fact it is mathematically impossible to calculate the rate constants independently, because this model involves too many rate constants.

4 Conclusions

First-order kinetic compartment models as described in the pharmacokinetics cannot be applied automatically to environmental studies. The mathematics required for sorption and accumulation studies is more complicated, due to specific experimental conditions.

The two-sediment compartment model presented in the present study is an extended version of two-sediment compartment models that have already been used in sorption studies. The latter incorporate one or more assumptions in order to limit computational difficulties. These assumptions are avoided in the present model.

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[24] Mathematical demonstration is available on request

6 Appendix

This appendix explains how the rate constants can be computed. For brevity, the discussion is restricted to the three-compartment model with two sediment compartments in series (equations 11a,b,c). The computational steps for the other models discussed in this paper run along the same lines; the reader is left to fill in the details.

1.1 The explanation becomes more routine if the problem is formulated in matrix notation.
The set of differential equations corresponding to the three-compartment kinetic model with two sediment compartments in series (equations (11a,b,c)) can be given in matrix form:

$$\begin{bmatrix} \frac{d}{dt} C_w \\ \frac{d}{dt} C_{sI} \cdot S \\ \frac{d}{dt} C_{sII} \cdot S \end{bmatrix} = \begin{bmatrix} -(k_0 + k_1) & k_2 & 0 \\ k_1 & -(k_2 + k_3) & k_4 \\ 0 & k_3 & -k_4 \end{bmatrix} \begin{bmatrix} C_w \\ C_{sI} \cdot S \\ C_{sII} \cdot S \end{bmatrix}, \quad (1.1)$$

or in a more condensed form

$$\vec{y}^{I}(t) = (K + K_0)\vec{y}(t) \quad \text{for all} \quad t \geq 0, \quad (1.2)$$

where $\vec{y}(t)$ represents the concentrations of the chemicals in the various compartments after t hours of desorption time:

$$\vec{y} = \begin{bmatrix} C_w \\ C_{sI} \cdot S \\ C_{sII} \cdot S \end{bmatrix} \quad (1.3)$$

and K and K_0 are matrices of rate constants:

$$K := \begin{bmatrix} -k_1 & k_2 & 0 \\ k_1 & -(k_2+k_3) & k_4 \\ 0 & k_3 & -k_4 \end{bmatrix} \quad \text{and} \quad K_0 := \begin{bmatrix} -k_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \quad (1.4)$$

Here, the total concentration of the chemical suspension after t hours of desorption time is denoted by $y(t)$ (see equation 9):

$$y(t) = C_w^*(t) = C_w(t) + C_{sI}(t) \cdot S + C_{sII}(t) \cdot S. \quad (1.5)$$

y is a three-exponential function:

$$y(t) = Pe^{-pt} + Qe^{-qt} + Re^{-rt}. \quad (1.6)$$

By taking measurements, one obtains measured values for a number of function values $y(t_1), \ldots, y(t_n)$. Here n is the number of measurements performed, and t_i are the points of time at which measurements were taken.
The function y depends only on the rate constants $k_0, \ldots, k_4$, and the concentrations C_{w0}, C_{sI0}, C_{sII0} at the beginning of the desorption period in the various compartments. The value of the rate constant k_0 is known, as it can be determined in a separate experiment without sediment. This leaves seven unknowns $k_1, \ldots, k_4$, C_{w0}, C_{sI0}, C_{sII0} that together determine the function y. The six parameters P, Q, R, p, q, r in (1.6) can be estimated by fitting a three-exponential function through the measured values $y(t_i)$. Unfortunately, these six parameters cannot determine the seven unknowns uniquely. Apparently, in order to be able to compute the rate constants $k_1, \ldots, k_4$, one needs some extra information.

This can be found by taking the sorption uptake period into account. The concentrations of the chemical in the various compartments during this sorption uptake period of T hours can also be described by differential equations. In matrix notation, the change in concentration then can be described by

$$\begin{bmatrix} \frac{d}{dt} C_w \\ \frac{d}{dt} C_{sI} \cdot S \\ \frac{d}{dt} C_{SII} \cdot S \end{bmatrix} = \begin{bmatrix} -k_1 & k_2 & 0 \\ k_1 & -(k_2+k_3) & k_4 \\ 0 & k_3 & -k_4 \end{bmatrix} \begin{bmatrix} C_w \\ C_{sI} \cdot S \\ C_{sII} \cdot S \end{bmatrix}, \quad (1.7)$$

or in a more condensed form

$$\vec{\chi}^{I}(t) = K\vec{\chi}(t) \quad (1.8)$$

where $\vec{\chi}(t)$ represents the concentrations of the chemicals at time t in the various compartments during the sorption uptake period. The rate constants $k_1, \ldots, k_4$ in the sorption uptake period are identical to the ones in the desorption period. The length T of the sorption uptake period is known precisely. In each of the compartments, the concentration of the chemical at the end of the sorption uptake period is equal to the concentration at the beginning of the desorption period:

$$\vec{y}(0) = \vec{\chi}(T). \quad (1.9)$$

Apparently, since T and k_0 are known, the function values $y(t)$ are uniquely determined by the four rate constants $k_1, \ldots, k_4$ and the concentration χ_0 of the chemical in the water at the beginning of the sorption uptake period (the initial concentration in the sediment compartments is zero)[1]:

$$\vec{\chi}(0) = \begin{bmatrix} C_w(0) \\ C_{sI}(0) \cdot S \\ C_{sII}(0) \cdot S \end{bmatrix} = \begin{bmatrix} \chi_0 \\ 0 \\ 0 \end{bmatrix} \quad (1.10)$$

It is a routine matter to compute $\vec{\chi}(T)$ and any function value $y(t)$ if one not only knows T, t and k_0 but one also has values for $k_1, \ldots, k_4$ and χ_0: the computation involves standard manipulations with the eigenvalues and eigenvectors[2] of the matrices K and $K + K_0$ (computational details can be found in section 1.10 or, e.g. [1], pp. 127 – 144). Summarizing, this leads to the following situation:

[1] In the two-compartment situation the four parameters P, Q, p, q that describe the two-exponential function (see equation 7) are uniquely determined by the known rate constant k_0, two unknown rate constants k_1, k_2, and the two unknown initial concentrations C_{w0}, C_{s0}. Therefore, one may be able to compute k_1 and k_2 if the parameters P, Q, p, q have been estimated. However, one may minimize the propagation of the errors, introduced by the measurements, by basing the computations on as many measurement values as are available. Therefore, also in this two-compartment situation, it is preferable to take the sorption uptake period into account. Moreover, the approach described above and the subsequent way of computing applies undiscriminately to all models discussed in this paper.

[2] In the case of matrices of size 3 × 3, one can express the eigenvalues and eigenvectors in terms of the rate constants $k_0, \ldots, k_4$. These expressions are rather nasty (and are not available for larger matrices). However, standard numerical computer programs yield accurate numerical values for the eigenvalues and eigenvectors for matrices of any size for which numerical values are given for all matrix entries. The program MATLAB (The MathWorks, Inc., South Natick, MA 01760, U.S.A.) was used in all the computations.

1.2 There is a sequence $0 = t_1 \leq t_2 \leq \ldots \leq t_n$ of points of time (hours since the beginning of the desorption period) at which the measurements are performed. There are known values for the rate constant k_0 and the length of time T of the sorption uptake period. As described above, for any possible sequence $(k_1, \ldots, k_4)$ of rate constants and any possible value of the initial concentration χ_0, the total concentration $y(t_i)$ of the chemical in the suspension can be computed at any point t_i of time of measurement.

In experimental data sets, neither the exact values $k_j^\bullet$, $\chi_0^\bullet$ for the rate constants k_j and the initial concentration χ_0, nor the exact values $y^\bullet(t_i)$ of the total concentration $y(t_i)$ are available. Only experimental values χ_0^* for χ_0 and y_i^* for $y(t_i)$ are available from which an estimation of the exact values $k_j^\bullet$ has to be made. As explained above, for these estimated k_j-values y-values can be computed. The y-values, estimated in this way should be optimal, i.e. the estimated values $\bar{k}_j$ for k_j and $\bar{\chi}_0$ for χ_0 should be such that the corresponding y-values $\bar{y}(t_i)$ are the best approximations of the experimental data y_i^* and χ_0^*. This leads to the following problem.

1.3 The problem: The change in the concentration of the chemical in the various compartments is assumed to be described by the differential equation (1.2) for the exact sequence $k_1^\bullet, k_2^\bullet, k_3^\bullet, k_4^\bullet$ of values of rate constants k_1, k_2, k_3, k_4 and the exact value $\chi_0^\bullet$ of the initial concentration χ_0. These exact values are not known nor are the exact values $y^\bullet(t_i)$ of the corresponding function $y^\bullet$ with $y^\bullet = y$. However, values y_i^* were measured that differed from the exact values $y^\bullet(t_i)$ by the measuring errors $y_i^* - y^\bullet(t_i)$.
From these measured values y_i^*, an optimal estimation $\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4$ of the sequence $k_1^\bullet, k_2^\bullet, k_3^\bullet, k_4^\bullet$ of exact values[3] and an estimation of the standard deviation of these $\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4$ (see 1.5) have to be obtained.
It is emphasized that the exact value $\chi_0^\bullet$ is not known: even to obtain the initial concentration the measured values y_i^* have to be used. Since there is no loss of chemical from the system during the sorption uptake period, the total concentration χ_0 at the beginning of the sorption uptake period is equal to the total concentration at the end of this sorption uptake period. Therefore, by (1.9), χ_0 is also the *total* concentration $y(0)$ at the beginning of the desorption period: $y(0) = \chi_0$. So, in order to obtain $\chi_0^\bullet$ theoretically only y_1^* is needed; however, as observed in section 2.3, the choice $\chi_0^\bullet = y_1^*$ would mean a disproportional influence of y_1^* on the rate constants compared to the influence of the other y_i^*.
In the sections 1.4 and 1.5 it is clarified under what assumptions and in what sense the obtained k-values $\bar{k}_j$ are optimal. In section 1.6 it is explained how to estimate the standard deviation in the values $\bar{k}_j$ and $\bar{\chi}_0$ once these values are known. These optimal values are computed iteratively. For reason of simplicity some notation is introduced, which is used in section 1.7, in which the iterative method to compute $\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \bar{\chi}_0$ is described. The subsequent sections 1.8 and 1.9 contain comments and refinements on this method. Finally, in section 1.10, a detailed description of the computation of the values $y(t)$ is presented. Concerning the measurements, the following assumption is made:

1.4 Assumption: The errors in the function values y_i^* are uncorrelated, and, in a relative sense, have equal variances σ^2; to be precise: the variances matrix of the relative error vector, which is the vector with coordinates $\frac{y^\bullet(t_i) - y_i^*}{y_i^*}$, is equal to $\sigma^2 I$, where I is the identity matrix.
The errors in the function values $y^\bullet(t_i)$ cannot only be caused by the inhomogenity of the sediment, but also by chemical analysis which gives relative errors with a distribution as in the assumption. Since the error introduced by the sediment is unknown, there are no arguments for adapting the assumption.

1.5 The best estimation: Note that the sequence $(y(t_1), y(t_2), \ldots, y(t_n))$ of concentration values at the subsequential points t_i of measurement can be seen as the value of a (computable) function depending on $(k_1, \ldots, k_4, \chi_0)$. For ease of describtion, this function is denoted by Φ:

$$\Phi\,(k_1, k_2, k_3, k_4, \chi_0) = (y(t_1), \ldots, y(t_n)). \tag{1.11}$$

In order to handle more elegantly the fact that the values y_i^* have equal variances in a relative sense, one must first slightly modify this function Φ. Consider the function $\tilde{\Phi}$ that assigns to any $(k_1, \ldots, k_4, \chi_0)$ the scaled sequence $(\frac{y(t_1)}{y_1^*}, \ldots, (\frac{y(t_n)}{y_n^*})$ of total concentration values:

$$\tilde{\Phi}\,(k_1, k_2, k_3, k_4, \chi_0) = (\frac{y(t_1)}{y_1^*}, \frac{y(t_2)}{y_2^*}, \ldots, \frac{y(t_n)}{y_n^*}). \tag{1.12}$$

The optimal estimation $(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \chi_0)$ of the sequence $(k_1^\bullet, k_2^\bullet, k_3^\bullet, k_4^\bullet, \chi_0^\bullet)$ of exact values is the sequence $k_1, k_2, k_3, k_4, \chi_0$ that minimizes[4]

$$\sum_{j=1}^{n}\left(\frac{y(t_i) - y_i^*}{y_i^*}\right)^2 = \| \tilde{\Phi}(k_1, k_2, k_3, k_4, \chi_0) - 1 \|^2, \tag{1.13}$$

where **1** denotes the sequence $(1,1, \ldots, 1)$ of n ones. This sequence $(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \chi_0)$ is also called the minimum least-squares solution to the problem

$$\Phi(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \chi_0) = (1,1, \ldots, 1). \tag{1.14}$$

The estimator $(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \chi_0)$ is the best one in the following sense. If assumption 1.4 holds, in first order, on account of the Gauss-Markov theorem (cf. [3]), $(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \bar{\chi}_0)$ is the best unbiased estimator of $(k_1^\bullet, k_2^\bullet, k_3^\bullet, k_4^\bullet, \chi_0^\bullet)$: it has minimum variance.
In order to estimate the standard deviation of the values $\bar{k}_i$, and $\bar{\chi}_0$ the variance σ^2 is needed. Unfortunately its value is unknown. In the computations its value is estimated by

$$\chi^2 := \frac{1}{n-5} \sum_{j=1}^{n}\left(\frac{\bar{y}(t_i) - y_i^*}{y_i^*}\right)^2, \tag{1.15}$$

where $\bar{y}$ is the function y corresponding to $(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4, \bar{\chi}_0)$: in first order, the residual mean square is an unbiased estimator of σ^2 (cf. [3], section 3.7).

1.6 The standard deviation: For ease of notation, put **k** instead of (k_1, k_2, k_3, k_4). Let $J_\Phi(\mathbf{k}, \chi_0)$ be the Jacobi matrix of Φ in $(\mathbf{k}, \chi_0)$:

$J_\Phi(\mathbf{k}, \chi_0)$ is an $n \times 5$-matrix with coefficients $\frac{\delta y(t_i)}{\delta k_j}(\mathbf{k}, \chi_0)$ in $(j-$th column $(j = 1, \ldots, 4)$ and coefficients $\frac{\delta y(t_i)}{\delta \chi_0}(\mathbf{k}, \chi_0)$ in the last column. Similarly, $J_{\tilde{\Phi}}(\mathbf{k}, \chi_0)$ is the Jakobi matrix of $\tilde{\Phi}$ in $(\mathbf{k}, \chi_0)$. Note that $J_{\tilde{\Phi}}(\mathbf{k}, \chi_0) = W^{-1} J_\Phi(\mathbf{k}, \chi_0)$, where $W = \mathrm{diag}\,(y_1^*, \ldots, y_n^*)$ is the diagonal matrix with the measured values on the diagonal.
Then, in first order,

$$\chi^2(\bar{J}^T\bar{J})^{-1}; \qquad \text{where } \bar{J} := J_\Phi(\bar{\mathbf{k}}, \bar{\chi}_0). \tag{1.16}$$

is an unbiased estimator of the variance matrix of $(\bar{\mathbf{k}}, \bar{\chi}_0)$ (cf. [3], section 3.8). An estimation of the standard deviation of $\bar{k}_i$ is the square root of the i-th diagonal element of $\chi^2(\bar{J}^T\bar{J})^{-1}$ and an estimation of the standard deviation of $\bar{\chi}_0$ is the square root of the right lower diagonal element of this matrix (cf. [3], section 3.8).

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[3] The computational strategy to be described presently also yields an estimation $\bar{\chi}_0$ of the exact initial value $\chi_0^\bullet$.

[4] $\| (\chi_1, \ldots, \chi_n) \|$ is, by definition, equal to the Euclidean distance $\sqrt{\chi_1^2 + \ldots + \chi_n^2}$

[5] Errors on k_0 and T contribute to the standard deviation of $\bar{k}_i$ as well. In the actual computations, these contributions were taken into account. For brevity, however, these computational details are not discussed here.

1.7 **An iterative solution method:** If $(\bar{k}, \bar{\chi}_0)$ is the solution of the least-squares problem (1.14), with $\bar{k}=(\bar{k}_1, \bar{k}_2, \bar{k}_3, \bar{k}_4)$, then $(\bar{k}, \bar{\chi}_0)$, is the exact solution of a so-called normal equation (cf. [2], § 10.2)

$$J_{\tilde{\Phi}}(k, \chi_0)^T (\tilde{\Phi}(k, \chi_0) - 1) = 0. \quad (1.17)$$

An attempt is made to approximate the solution $(\bar{k}, \bar{\chi}_0)$ of the equation (1.17) iteratively by a GN (Gauss-Newton type of) process (also called a linearization method; cf. [2], § 10.3).
Suppose $(k^{(j)}, \chi_0^{(j)})$ is an approximation of the true solution $(\bar{k}, \bar{\chi}_0)$. Then, a new and hopefully better approximation $(k^{(j+1)}, \chi_0^{(j+1)})$ is obtained as follows. Perform one GN step in order to compute the solution of the problem

$$J_j^T(\tilde{\Phi}(k, \bar{\chi}_0) - 1) = 0, \text{ where } J_j := J_{\tilde{\Phi}}(k^{(j)}, \chi_0^{(j)}): \quad (1.18)$$

with

$$r^{(j)} := \tilde{\Phi}(k^{(j)}, \chi_0^{(j)}) - 1 \text{ and } \Delta^{(j)} := (J_j^T J_j)^{-1} J_j^T r^{(j)}), \quad (1.19)$$

let

$$k^{(j+1)}, \chi_0^{(j+1)}) = (k^{(j)}, \chi_0^{(j)}) + \Delta^{(j)}. \quad (1.20)$$

If the sequence $((k^{(j)}, \chi_0^{(j)}))$ converges, then it converges to a sequence of values in which ϕ attains a local minimum, where

$$\phi(k, \chi_0) := \|\tilde{\Phi}(k, \chi_0) - 1\|^2: \quad (1.21)$$

ϕ attains a local minimum in any solution of the normal equation (1.17) and vice versa. However, the best estimation is the sequence of values at which ϕ attains its global minimum. If ϕ attains a local minimum in not more than one sequence of values, then the limit of $((k^{(j)}, \chi_0^{(j)}))$ is precisely $(\bar{k}, \bar{\chi}_0)$.

1.8 **Starting and stopping the process:** As is well known, the success of any iterative process greatly depends on the choice of the starting value. There is no exclusive strategy. In almost all of the experiments the first trial in the "trial and error strategy" produced a converging sequence.
The iteration was stopped when the value

$$\| J_{\tilde{\Phi}}(k^{(j)}, \chi_0^{(j)})^T (\tilde{\Phi}(k^{(j)}, \chi_0^{(j)}) - 1)\|$$

was sufficiently small ($\leq 10^{-12}$). The last value $(k^{(j)}, \chi_0^{(j)})$ was taken as an approximation for $(\bar{k}, \bar{\chi}_0)$.
ϕ attains (approximately) a local minimum in the last iterate $(k^{(j)}, \chi_0^{(j)})$. In order to collect some evidence that the computed minimum is a global one, the computations were carried out with other starting values as well. This led to the same results. Moreover, the method of computing an estimation of the standard deviation, as explained in section 1.6, is also applicable to non-global minimum values. This leads inevitably to larger values for the errors.

1.9 **Modifications:** Only positive solutions k_i, χ_0 of the minimisation problem (1.13) are of interest. In order to prevent the GN process from converging to some non-positive values, $\Delta^{(j)}$ in (1.19) is interpreted as a search direction. Instead of (1.20),

$$(k^{(j+1)}, \chi_0^{(j+1)}) = (k^{(j)}, \chi_0^{(j)}) + \alpha_j \Delta^{(j)}, \quad (1.22)$$

is taken, where α_j is an appropriate scalar, a so-called damping parameter. In the standard situation $\alpha_j = 1$. If, however, in a certain step the choice $\alpha_j = 1$ leads to an approximation of which one or more of the coordinates are non-positive, a smaller positive α_j is taken such that the new approximation $(k^{(j+1)}, \chi_0^{(j+1)})$ has only positive coordinates. In some of the experiments convergence was obstructed by this positiveness restriction. In this situation, a relaxation of the positiveness requirement turned out to be useful: if, with $\alpha_j = 1$, some of the coordinates are less than $-\epsilon$ for some appropriate ϵ, $0 \leq \epsilon \ll 1$ then a smaller positive α_j is taken such that the new approximation has coordinates $> -\epsilon$.
Also in cases where the process does not seem to converge, namely in the cases where in a certain step the ϕ values did not reduce (say, $\phi(k^{(j+1)}, \chi_0^{(j+1)}) > 1.1\, \phi(k^{(j)}, \chi_0^{(j)})$), a value for α_j smaller than 1 is taken (see also [2], p. 269).
In literature, one uses not only the GN search direction, but also a search direction produced by a cheaper steepest descent step and combinations of these two (this strategy is known as Marquardt's compromise, cf. [2], p. 272). This modified search direction is more likely to reduce the ϕ-values than the GN search direction, i.e. the "steepest descent approach" gives a reduction in the ϕ values, also in cases where the GN approach fails to reduce. However, concerning the present problems and experimental data, in the cases where the GN approach gave a significant reduction in the ϕ-value in one step, this reduction was about 10^4 times better than the reduction by a steepest descent step. Also in cases where in one GN step there was no reduction of the ϕ-value, it turned out to be more efficient to proceed with the next step using the seemingly worse GN iterate. The "bad" GN steps lead to a new, better starting position for fast convergence, while the steepest descent process lingered a great number (as much as 10^4) of steps near the old, bad starting position.

1.10 **The computation of Φ-values and the Jacobi matrices:** For any $(k_1, k_2, k_3, k_4, \chi_0)$, the function $\Phi(k_1, k_2, k_3, k_4, \chi_0)$ is computed as follows. The solution $\vec{y}$ of the differential equation (1.2) is of the form

$$\vec{y}(t) = \alpha\vec{u}\, e^{-pt} + \beta\vec{v}\, e^{-qt} + \gamma\vec{w}\, e^{-rt} \quad \text{for all } t \geq 0,$$

where α, β, γ are some appropriate real scalars and $\vec{u}, \vec{v}, \vec{w}$ are linearly independent eigenvectors of $K + K_0$ with respective eigenvalues $-p$, $-q$ and $-r$. Once $\vec{y}$ is known any of the function values $y(t)$ in (1.5) or $y(t_i)$ in (1.12) can easily be computed, because: $P = \alpha(u_1 + u_2 + u_3)$, with u_1, u_2, u_3 the coordinates of $\vec{u}$, etc. The scalars α, β, γ, are determined by the requirement $\vec{y}(0) = \vec{\chi}(T)$.
Therefore, in order to compute the $y(t_i)$ values, proceed as follows. Compute lineraly independent eigenvectors $\vec{u}, \vec{v}, \vec{w}$ of $K + K_0$ and their respective eigenvalues $-p$, $-q$ and $-r$. In order to compute the real scalars α, β, γ, define the 3×3-matrix Y whose columns are the eigenvectors $\vec{u}, \vec{v}, \vec{w}$:

$$Y = (\vec{u} \mid \vec{v} \mid \vec{w}).$$

Note that

$$\vec{y}(0) = Y \begin{bmatrix} \alpha \\ \beta \\ \gamma \end{bmatrix} = \vec{\chi}(T)$$

and solve α, β, γ from this last linear equation. Clearly, in order to get numerical values for α, β and γ one needs to know the vetor $\vec{\chi}(T)$. However, the computation of $\vec{\chi}(T)$ runs along the same lines, uses the eigenvalues and eigenvectors of K and the known initial value $\vec{\chi}(0) = (\chi_0, 0, 0)^T$.
In order to compute the Jacobi matrices, the derivatives were replaced by finite differences.

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