

Transport models for desorption from natural soils packed in flushed columns

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Abstract. This paper addresses an experimental and theoretical study of sorbed contaminant removal from a column (or reactor) by flushing. This removal may take place by either volatilization or rinsing, and nonlinear sorption is accounted for by employing a Freundlich relationship. A one-dimensional nonequilibrium transport model is proposed which describes the unsteady mass transfer between flushing medium and soil phases in the column, using a linear chemical transfer model. The moving boundary problem is transferred, and a perturbation method is employed to obtain an approximate solution of the governing equations for a small Merkel number Me (this dimensionless number comprises the product of fluid residence time and the mass transfer coefficient). The solution reveals the effect of the various parameters, such as the Freundlich parameter n , on the contaminant transport in fluid phase and decay in solid phase. Applying the model to various experimental data results in values for the overall mass transfer coefficients, which are useful for engineering computations. Furthermore, the model enables the prediction of the initial soil contamination level as well as the parameter n solely from the measured exit contaminant concentrations in the flushing fluid. A thorough comparison of this prediction with the measured soil concentration (prior to the experiments) yields good agreement.

1. Introduction

In order to optimize real-scale soil remediation processes, conceptual models are in use and in development. As some soil parameters are very hard or nearly impossible to assess theoretically, often bench-scale experiments are performed to investigate the feasibility of a cleaning technique. For these experiments, columns are usually used; the columns are flushed in the axial direction. Relevant experimental conditions, such as flushing velocity, flushing medium, additives, etc., can be varied, and their effect can be evaluated.

Current transport models often start from nonequilibrium between contaminant in the soil and flushing fluid. As a result of this nonequilibrium, contaminant is desorbed from the soil, transferred to the flushing fluid, and removed by convective transport. In an early publication, *Lapidus and Amundson* [1952] proposed a nonequilibrium transport model and analytical solutions in the case of a linear sorption isotherm. In a subsequent paper, *Oddson et al.* [1970] presented analytical solutions assuming negligible diffusion/dispersion but retaining the start-up phase, that is, considering the wetting front. *Van Genuchten et al.* [1974] considered nonlinear sorption using a Freundlich adsorption isotherm and solved the governing equations numerically. Assuming traveling wave solutions, *Van der Zee* [1990] and, more recently, *Simon et al.* [1997] obtained analytical expressions for special cases whereby the sorption isotherm and initial and entry concentration of the fluid obey some specific conditions. Both studies also contain an extensive discussion of foregoing publications.

To the author's knowledge, no analytical models and solutions are available that account simultaneously for (1) non-

equilibrium between soil and fluid phases, (2) start-up phase, (3) desorption of the contaminant, using a Freundlich isotherm, and (4) convective transport and decay of soil contamination concentration. These features are typical for flushing and remediation of soil in practice. For engineering end purposes it is of major importance to derive basic models and obtain compact analytical solutions that (1) reveal the principle prevailing phenomena of the process, (2) permit a straightforward fit with experimental data, and (3) validate more advanced numerical models. Accordingly, such an analysis has been executed and is presented here in detail.

First, a one-dimensional transient model is derived which describes the principle phenomena in a flushed column (or reactor) stacked with soil. The model accounts for the filling of the column with flushing fluid and desorption of contaminant from the soil, using a nonlinear Freundlich isotherm. Mass transfer from soil to fluid is considered to be induced by a concentration gradient in soil and fluid phases. A mass balance of contaminant in the soil phase yields an expression for the contaminant decay in the soil. For the flushing medium a mass balance yields the increase of the contaminant concentration in the direction of flow, whereby diffusion/mechanical dispersion is taken to be negligibly small in comparison with advection. During remediation of real soils, mass transfer processes are usually extremely slow, especially in comparison to the imposed fluid velocity and related residence time of the fluid in the soil. On the basis of this feature of the small Merkel number Me , approximate solutions of the governing equations are obtained using a perturbation technique. This limiting case is opposite to the other limit of equilibrium between the phases, which is often employed in contaminant transport models.

Analytical expressions are obtained for the contaminant concentration in the flushing medium at the exit of the column.

This is a property which can be measured and is known from practical flushing experiments. Accordingly, here the model is applied to experiments with natural soils. The application yields mass transfer coefficients for the removal during stripping (evaporation of contaminant) and during rinsing (dissolution of contaminant) of soils containing chlorinated hydrocarbons.

2. Transport Models

In this section a contaminant transport model is derived on the basis of nonequilibrium between the phases in the soil and nonlinear Freundlich sorption. For the flushing medium, neglecting diffusion/dispersion, a differential mass balance of transported contaminant gives

$$\phi \frac{\partial c_f}{\partial t} + u_f \frac{\partial c_f}{\partial x} = k_t \left[\left(\frac{C_s H^n}{K_d} \right)^{1/n} - c_f \right]. \quad (1)$$

In this equation the first term accounts for accumulation. Molecular diffusion and mechanical dispersion are neglected as the process is advection dominated.

The decay of contaminant, sorbed at the soil, by desorption and mass transfer to flushing medium is governed by

$$(1 - \phi) \rho_s \frac{\partial C_s}{\partial t} = -k_t \left[\left(\frac{C_s H^n}{K_d} \right)^{1/n} - c_f \right]. \quad (2)$$

During the flushing of the first pore volume, (1) and (2) hold in the region ($0 \leq x \leq \chi(t)$), where $\chi(t)$ represents the front (a moving boundary) behind which the soil is saturated with flushing fluid. From an overall mass balance the front position follows as

$$\chi(t) = (u_f t) / \phi. \quad (3)$$

It is also possible to determine the time Y needed for the flushing medium to attain a given position x in the soil:

$$Y(x) = x \phi / u_f. \quad (4)$$

With this equation one can derive the time τ required to fill a column with length L with flushing fluid:

$$\tau = L \phi / u_f. \quad (5)$$

Note that the ratio t/τ governs the number of flushed pore volume.

The boundary conditions pertaining to (1) and (2) read

$$c_f(x = 0, t) = 0, \quad (6)$$

$$C_s(x = \chi(t), t) = C_{si}. \quad (7)$$

Equation (6) accounts for the clean flushing medium at the entrance of the column; equation (7) reflects the initial contamination level of the soil when the flushing is started. Note that the present transient model accounts for the decay of contaminant concentration in the soil, resulting in a diminishing drive for mass transfer. The model assumes that no free contaminant phase is present in the soil. If a free contaminant had been present, a simplified model could have been applied that starts from a constant contaminant concentration in the soil phase. This concentration would be proportional to the vapor pressure of the pure contaminant if the soil is stripped, or to the solubility of the contaminant if the soil is rinsed by a liquid.

Here the common chemical engineering assumption is em-

ployed that the mass transfer between sorbed, liquid, and vapor contaminant is represented by the difference between equilibrium and actual concentration, where k_t is an overall mass transfer coefficient. This approach is reflected by the right-hand sides of (1) and (2). Though the mass transfer coefficient could be assessed theoretically, in practice, it is measured as a lump parameter as it depends on the soil composition, the flushing conditions, and so on.

The overall mass transfer coefficient can be thought of as being composed of several mass transfer coefficients. For instance, if one considers stripping of the soil, that is, the flushing medium is a vapor, there will be a transfer of mass between sorbed contaminant, stagnant (immobile) liquid (i.e., moisture or condensate), and vapor phase. The mass transfer between liquid-vapor interface and vapor can then be described as

$$\dot{m} = k_f (H c_{wf} - c_f). \quad (8)$$

In this equation, k_f represents the mass transfer coefficient between stagnant liquid and vapor phase, and c_{wf} and c_f represent the concentrations of the contaminant at liquid-vapor interface and in vapor phase, respectively. H reflects the dimensionless Henry's law coefficient:

$$H = [P_c(T_f) M_c] / RT_f S, \quad (9)$$

wherein S denotes the solubility of the contaminant in the liquid phase and P_c denotes the saturation pressure of the contaminant pertaining to the fluid temperature.

The mass transfer through the stagnant liquid reads

$$\dot{m} = k_w (c_{ws} - c_{wf}), \quad (10)$$

wherein c_{ws} constitutes the contaminant concentration at solid-liquid interface. The mass transfer between contaminant sorbed to the soil and dissolved in the stagnant liquid follows from

$$\dot{m} = k_s [(C_s / K_d)^{1/n} - c_{ws}]. \quad (11)$$

In this equation, C_s represents the mass of contaminant per dry mass soil, and K_d represents the distribution ratio. The present model accounts for nonlinear sorption by employing a Freundlich absorption isotherm. For $n = 1$ the commonly used linear sorption isotherm is obtained.

In order to express the mass transfer in terms of C_s and c_f , which can be measured, (8), (10), and (11) are combined, yielding the right-hand sides of (1) and (2). The total mass transfer coefficient k_t for stripping is thus expressed as

$$k_t = [(H/k_w) + (H/k_s) + (1/k_f)]^{-1}. \quad (12)$$

It has been assumed in deriving (12) that the soil is flushed by a vapor. One can readily see that no contaminant is transported in the case where equilibrium prevails, that is, when $C_s = K_d c_w''$ and $H c_w = c_f$; see (1) and (2).

On the other hand, when the rinsing of the column by a liquid (e.g., water) is considered, (1)–(12) are still valid and applicable. The mass transfer takes place from solid to solid-stagnant liquid interface and from this interface to mobile rinsing fluid. The mass transfer coefficient then reads

$$k_t = [(1/k_s) + (1/k_f)]^{-1}, \quad (13)$$

and the right-hand sides of (1) and (2) remain the same (with H set equal to unity). Hence (1) and (2) are generally applicable to both stripping and rinsing of soils.

Equations (1), (2), (6), and (7) represent a moving boundary problem ($t \geq 0$, $0 \leq x \leq \chi(t)$). These equations are transformed into

$$\partial c_f / \partial X = Me(c_s - c_f), \quad (14)$$

$$\frac{\partial c_s^n}{\partial T} = n \left(\frac{C_{si} H^n}{K_d} \right)^{(n-1)/n} (c_f - c_s), \quad (15)$$

$$c_f(X = 0, T) = 0, \quad (16)$$

$$c_s(X, T = 0) = \left(\frac{C_{si} H^n}{K_d} \right)^{1/n}, \quad (17)$$

with, as dimensionless coordinate,

$$X = x/L, \quad (18)$$

as transformed time,

$$T = \frac{k_r H C_{si}^{(1-n)/n}}{K_d^{1/n} (1 - \phi) \rho_s n} (t - Y(x)), \quad (19)$$

as soil concentration,

$$c_s = \left(\frac{C_s H^n}{K_d} \right)^{1/n}, \quad (20)$$

and, as Merkel number,

$$Me = (k_r L) / u_f. \quad (21)$$

This number is also often referred to as the Damkohler number when k_r represents a reaction rate constant. In order to obtain compact and practically useful solutions, an asymptotic analysis, following *Van Dyke* [1975], will be executed.

3. Asymptotic Analysis

The Merkel number may be thought of as the ratio of mass transfer rate to flushing velocity. For the experiments performed (and most practical situations) this number is much smaller than unity. Using asymptotic techniques [*Van Dyke*, 1975], approximate analytical solutions of the governing equations are derived for small Me .

Substituting the perturbation expansions

$$c_s = c_{s0} + \varepsilon c_{s1} + O(\varepsilon^2) \quad (22)$$

$$c_f = c_{f0} + \varepsilon c_{f1} + O(\varepsilon^2) \quad (23)$$

with

$$\varepsilon = Me \quad (24)$$

and applying

$$(c_{s0} + \varepsilon c_{s1} + O(\varepsilon^2))^n = c_{s0}^n + \varepsilon n c_{s1} c_{s0}^{n-1} + O(\varepsilon^2) \quad (25)$$

into equations (14)–(17), equating the coefficients of equal power of ε yields as the zero-order equations

$$(\partial c_{f0}) / \partial X = 0, \quad (26)$$

$$\frac{\partial c_{s0}^n}{\partial T} = n \left(\frac{C_{si} H^n}{K_d} \right)^{(n-1)/n} (c_{f0} - c_{s0}), \quad (27)$$

with, as boundary conditions,

$$c_{f0}(X = 0, T) = 0, \quad (28)$$

$$c_{s0}(X, T = 0) = \left(\frac{C_{si} H^n}{K_d} \right)^{1/n}. \quad (29)$$

The following are obtained as first-order equations:

$$\partial c_{f1} / \partial X = c_{s0} - c_{f0}, \quad (30)$$

$$\frac{\partial c_{s1} c_{s0}^{(n-1)}}{\partial T} = \left(\frac{C_{si} H^n}{K_d} \right)^{(n-1)/n} (c_{f1} - c_{s1}), \quad (31)$$

with boundary conditions

$$c_{f1}(X = 0, T) = 0, \quad (32)$$

$$c_{s1}(X, T = 0) = 0. \quad (33)$$

To solve equations (26)–(33), distinction has to be made between the cases $n = 1$ and $n \neq 1$.

For $n = 1$ (linear sorption) the solution of zero-order equations (26)–(29) reads

$$c_{f0} = 0, \quad (34)$$

$$c_{s0} = [(C_{si} H) / K_d] e^{-T}. \quad (35)$$

Subsequently, solving the first-order equations (30)–(33) yields

$$c_{f1} = [(C_{si} H) / K_d] X e^{-T}, \quad (36)$$

$$c_{s1} = [(C_{si} H) / K_d] T X e^{-T}. \quad (37)$$

Next, (26)–(33) are solved for $n \neq 1$ (nonlinear sorption). The solution of zero-order equations (26)–(29) then reads

$$c_{f0} = 0, \quad (38)$$

$$c_{s0} = \left(\frac{C_{si} H^n}{K_d} \right)^{1/n} [(1 - n)T + 1]^{1/(n-1)}. \quad (39)$$

Solving the first-order equations (30)–(33) yields

$$c_{f1} = \left(\frac{C_{si} H^n}{K_d} \right)^{1/n} X [(1 - n)T + 1]^{1/(n-1)}, \quad (40)$$

$$c_{s1} = \frac{1}{n-1} \left(\frac{C_{si} H^n}{K_d} \right)^{1/n} X \{ [(1 - n)T + 1]^{1/(n-1)} - [(1 - n)T + 1]^{n/(n-1)} \}. \quad (41)$$

Summarizing, for $n = 1$ the first-order approximation of the contamination concentration is obtained by combining (23), (24), (34), and (36):

$$c_f(X, T) = Me [(C_{si} H) / (K_d)] X e^{-T}. \quad (42)$$

For $n \neq 1$ the first-order approximation is obtained by combining (23), (24), (38), and (40):

$$c_f(X, T) = Me \left(\frac{C_{si} H^n}{K_d} \right)^{1/n} X [(1 - n)T + 1]^{1/(n-1)}. \quad (43)$$

Equations (42) and (43) reveal that at each position in the column the concentration runs down similarly as a function of time. Furthermore, in the present analysis of small Me , according to (42) and (43), the contaminant concentration in the vapor phase at the exit, $X = 1$ ($x = L$) at the instant the entering fluid has completely saturated the column ($t = \tau$), reads

$$c_f(x = L, t = \tau) = Me \left(\frac{C_{si} H^n}{K_d} \right)^{1/n} \quad (44)$$

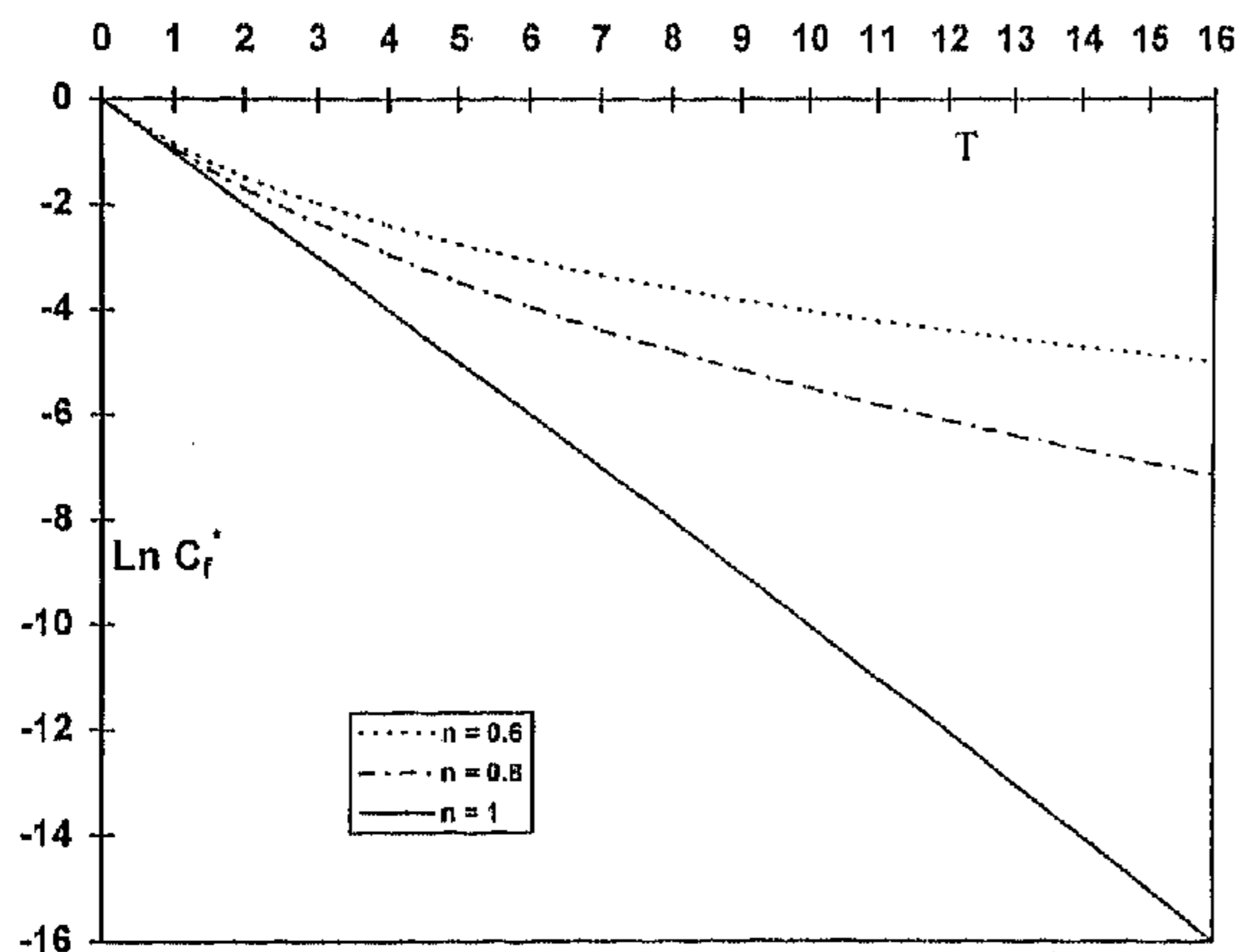


Figure 1. $\text{Ln } c_f^*$ versus T for $n = 1, 0.8,$ and 0.6 .

During the filling of the column, equilibrium prevails between fluid already present in the column and soil. Accordingly, the exit concentration during the flushing of the first pore volume reads

$$c_f(x = L, 0 \leq t < \tau) = \left(\frac{C_{si} H^n}{K_d} \right)^{1/n}. \quad (45)$$

This exit concentration would also prevail for $t \geq \tau$ in the case where equilibrium is assumed between flushing medium and soil. Accordingly, (44) and (45) represent the two limiting cases of small Me (rate limitation) and infinitely large Me (local equilibrium assumption), respectively. One can see that these extreme cases yield exit concentrations that differ by a factor of Me .

As stated above, the concentration development versus time is equal at each position in the column. Furthermore, the concentration in the fluid (and contaminant level in the soil) decrease in time. Accordingly, $c_f^*(T)$, defined as

$$c_f^*(T) = \frac{c_f(X, T)}{Me X \left(\frac{C_{si} H^n}{K_d} \right)^{1/n}}, \quad (46)$$

introduced. By definition, $c_f^*(T)$ is a function of T only. In the case of $n = 1$ from (42) and (46) it follows that

$$c_f^*(T) = e^{-T}, \quad (47)$$

and for $n \neq 1$, (43) and (46) yield

$$c_f^*(T) = [(1 - n)T + 1]^{1/(n-1)}. \quad (48)$$

Note that in the limit of n tending to unity, (48) tends to (47), indeed, as expected.

In Figure 1, (47) and (48) are set out graphically. The value of $c_f^*(T)$ is equal to unity at $T = 0$ and decreases for increasing T . Figure 1 shows the deviation from exponential behavior as n deviates from unity, which is also referred to as tailing. It can readily be concluded that to reduce the exit concentration by a factor of 20 ($\text{Ln}(c_f^*) \approx -3$), it takes twice as much time in the case $n = 0.6$ than in the case $n = 1$ ($T = 6$ versus $T = 3$). For reducing the exit concentration by a factor of 150 ($\text{Ln}(c_f^*) \approx -5$), more than three times as much time is needed in the case $n = 0.6$ than in the case $n = 1$ ($T = 16$ versus $T = 5$). These examples illustrate the substantial effect of nonlinear sorption on contaminant decay.

The presented analytical solutions permit the derivation of overall mass transfer coefficients from experimental data. These overall mass transfer coefficients, in turn, can be used for assessing cleaning times. In sections 5 and 6 the solutions are applied to some practical experiments and measurements.

During most experiments the exit concentration is determined by collecting the fluid at the exit during a certain time interval, followed by analyzing the collected sample, which represents an average value. In section 4 a quantification is presented of the error involved with assigning the measured (mean) concentration to the time when half of the collection has taken place.

4. Practical Application of the Model

In this section the error involved with averaging the analytical solution over a time interval $t_s \leq t \leq t_e$ is examined. First, it should be noted that during some flushing experiments, u_f is not always constant. However, in the case of u_f being a function of time (and hence also Me), (14)–(17), as well as the present asymptotic analysis, are not altered. So, (42) and (43) are still applicable, it being understood, however, that u_f is a function of time now. So, here u_f is allowed to be a function of time, whereas all other parameters, such as k_f , are assumed to be constant.

Substituting (4), (5), (18), (19), and (21) into (42) yields, in the case $n = 1$, as concentration at the exit ($x = L$) of the column for $t > \tau$:

$$c_f(x = L, t > \tau) = c_{fi} e^{-\lambda(t-\tau)}, \quad (49)$$

with c_{fi} being the exit contaminant concentration in the fluid at $t = \tau$,

$$c_{fi} = (k_f H C_{si} L) / (K_d u_f), \quad (50)$$

and, as time constant,

$$\lambda = (k_f H) / [K_d (1 - \phi) \rho_s], \quad (51)$$

The mean concentration in the fluid which is collected between t_s and t_e , and mean flushing velocity, thus follow for $n = 1$ as

$$\bar{c}_f = \frac{1}{\bar{u}_f (t_s - t_e)} \int_{t_s}^{t_e} u_f c_{fi} e^{-\lambda(t-\tau)} dt, \quad (52)$$

with mean velocity

$$\bar{u}_f = \frac{1}{(t_s - t_e)} \int_{t_s}^{t_e} u_f dt. \quad (53)$$

Substituting (50) into (52) and integrating yields

$$\bar{c}_f = \frac{1}{\bar{u}_f (t_s - t_e)} \frac{k_f H C_{si} L}{\lambda K_d} (e^{-\lambda(t_s-\tau)} - e^{-\lambda(t_e-\tau)}). \quad (54)$$

Introducing

$$\bar{t} = (t_s + t_e) / 2, \quad (55)$$

$$\varepsilon = \lambda(t_e - t_s) / 2, \quad (56)$$

and substituting into (54) yields

$$\bar{c}_f \bar{u}_f(\bar{t}) = c_{fi}^* e^{-\lambda(\bar{t}-\tau)} [1 + \frac{1}{6} \varepsilon^2 + O(\varepsilon^4)], \quad (57)$$

$$c_{fi}^* = (k_f H C_{si} L) / K_d. \quad (58)$$

For $n \neq 1$ it follows from (4), (5), (18), (19), (21), and (43) that at $x = L$ and for $t > \tau$,

$$c_f(x = L, t > \tau) = [(1 - n)\lambda(t - \tau) + c_{fi}^{n-1}]^{1/(n-1)}, \quad (59)$$

with

$$c_{fi} = \left(\frac{k_i^n H^n C_{si} L^n}{K_d u_f^n} \right)^{1/n}, \quad (60)$$

and

$$\lambda = \frac{k_i^n H^n L^{n-1}}{K_d(1 - \phi)\rho_s u_f^{n-1} n}. \quad (61)$$

The measured concentration in each bottle which is filled between t_s and t_e , and mean flushing velocity, follow from (59) as

$$\bar{c}_f = \frac{1}{\bar{u}_f(t_s - t_e)} \int_{t_s}^{t_e} u_f [(1 - n)\lambda(t - \tau) + c_{fi}^{n-1}]^{1/(n-1)} dt, \quad (62)$$

whereby \bar{u}_f follows from (53). Substituting (60) and (61) into (62) and integrating yields

$$\bar{c}_f = \frac{\lambda^{* - 1}}{\bar{u}_f(t_s - t_e)} \left\{ [(1 - n)\lambda^*(t_e - \tau) + c_{fi}^{*n-1}]^{n/(n-1)} - [(1 - n)\lambda^*(t_s - \tau) + c_{fi}^{*n-1}]^{n/(n-1)} \right\}, \quad (63)$$

whereby

$$c_{fi}^* = \left(\frac{k_i^n H^n C_{si} L^n}{K_d} \right)^{1/n}, \quad (64)$$

$$\lambda^* = \frac{k_i^n H^n L^{n-1}}{K_d(1 - \phi)\rho_s n}. \quad (65)$$

Inserting (55) and

$$\varepsilon = \left[\frac{1}{(1 - n)(\bar{t} - \tau) + \frac{c_{fi}^{*n-1}}{\lambda^*}} \right] \left(\frac{t_e - t_s}{2} \right), \quad (66)$$

yields

$$\bar{c}_f \bar{u}_f(\bar{t}) = [(1 - n)\lambda^*(\bar{t} - \tau) + c_{fi}^{*n-1}]^{1/(n-1)} \cdot \left[1 + \frac{2 - n}{6} \varepsilon^2 + O(\varepsilon^4) \right]. \quad (67)$$

Note that c_{fi}^{*n-1}/λ^* , appearing in (66), is equal to c_{fi}^{n-1}/λ ; see (60), (61), (64), and (65).

In this section the error involved with using (49) and (59) for cases where the exit concentration is averaged over a period of time and with nonconstant fluid flow is specified, which is the case when the exit fluid is collected. From (57) and (67) one can conclude this to be allowed if $\varepsilon \ll 1$. Moreover, the error involved is of the order ε^2 (and not ε), which is a fortunate consequence of assigning the mean mixed concentration to the arithmetic mean of starting and ending time of sampling time (equation (55)).

5. Application of the Model to HCH Stripping

In previous sections, analytical expressions were derived for the concentration of the contaminant in the (collected) flushing medium. In this section the derived solutions are applied to the stripping of 1,2,3,4,5,6-hexachlorocyclohexane (chemical

Table 1. The 1,2,3,4,5,6- $C_6Cl_6H_6$ (HCH) Concentration in Hexane and Water Condensate During Hexane and Steam Stripping

Bottle	\bar{t} , s	\bar{c}_b , $kg\ m^{-3}$
<i>Hexane Stage</i>		
1	1.620×10^3	1.856×10^{-3}
2	4.920×10^3	0.860×10^{-3}
3	8.160×10^3	0.453×10^{-3}
4	11.58×10^3	0.347×10^{-3}
5	14.52×10^3	0.328×10^{-3}
6	16.38×10^3	0.223×10^{-3}
7	18.48×10^3	0.110×10^{-3}
8	20.88×10^3	0.099×10^{-3}
<i>Steam Stage</i>		
10	34.50×10^3	0.029×10^{-3}
11	49.62×10^3	0.018×10^{-3}

Data from experiment C of Brouwers [1996].

formula $C_6Cl_6H_6$, abbreviation HCH). In a previous paper, two-stage stripping experiments of natural soil contaminated with mercury and predominantly β -HCH have been reported in more detail [Brouwers, 1996]. During this process the soil is first flushed with an organic solvent in vapor form. In the second stage, steam is passed through the soil in order to remove the solvent and remaining contaminant. Experiment C, which was intensively monitored, is used as a reference and is briefly summarized here.

The treated soil, total mass of 0.85 kg, was stacked in a glass column (inner cross-sectional area $A = 2.043 \times 10^{-3} m^2$), and the length L of the packed soil was about 0.25 m. About 85% of this weight consisted of dry soil, and 15% consisted of native soil moisture. With the mass of dry soil (0.723 kg) and the total occupied volume ($AL = 511 cm^3$), a soil bulk density $(1 - \phi)\rho_s$ of $1414 kg\ m^{-3}$ is obtained. Invoking a soil density ρ_s of $2625 kg\ m^{-3}$ yields a porosity ϕ of 0.46 and a pore volume of $235 cm^3$. The dry mass consisted of about 3% organic matter, 12% silt and clay (particles $< 63 \mu m$), and 85% sand (particles $> 63 \mu m$). Chemical soil analyses prior to the experiment yielded on average $5.14 (\pm 0.35)$ mg of HCH per kilogram dry weight (dw). About 95% of this HCH comprised the β isomer.

The stripping vapors were injected at the bottom, passed through the column, and led away from the exit at the top to a condenser. The condensate, containing the contaminants, was collected in 1-L bottles for analysis after the experiment. The entry pressure at the bottom amounts to about 1.15 bar absolute. Hexane was employed as organic solvent in the first stage and steam was employed as flushing medium in the second stage. In all, 8.5 L of liquid hexane were flushed in 6.5 hours, and, subsequently, 2.5 L of water were flushed in 9.5 hours. Both the hexane and steam flushing velocities were very constant in time. Moreover, the flushing time (hours) was much larger than the start-up time (minutes), so τ can be neglected. In Table 1 the measured HCH concentrations in the bottles are listed versus the elapsed time. The measured concentration \bar{c}_b is the mean concentration of the flushing fluid during the filling of one bottle. This measured concentration is assigned to the elapsed time, denoted by \bar{t} , half of the bottle is filled. In Figure 2 the measured data is graphically represented.

The measured concentration in the condensate collected in the bottle is related to the exit concentration in the fluid (vapor) phase via

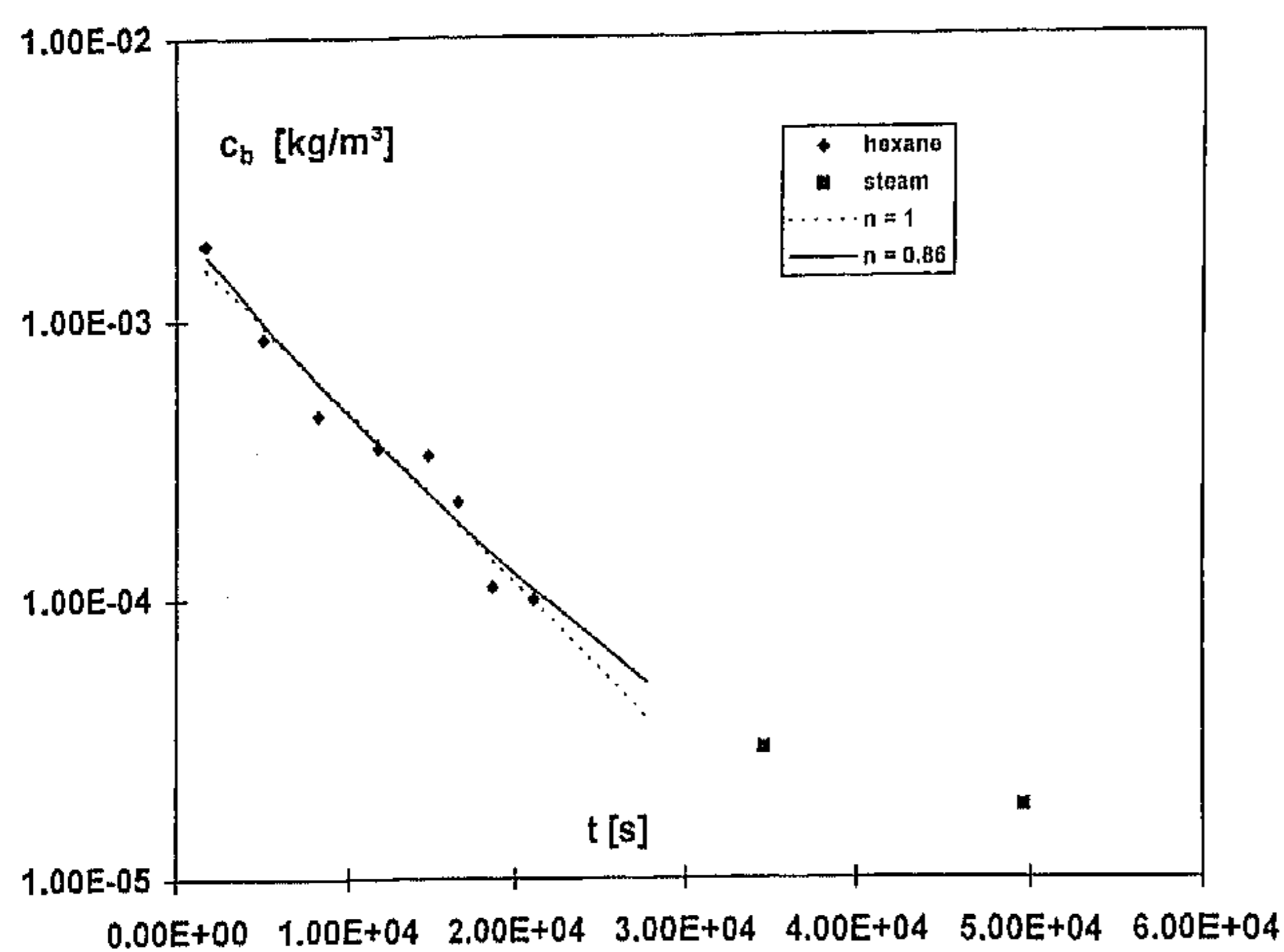


Figure 2. The 1,2,3,4,5,6- $C_6Cl_6H_6$ (HCH) concentration in the bottles during hexane and steam stripping (experiment C) [Brouwers, 1996].

$$\bar{c}_b(\bar{t}) = (\rho_b/\rho_f)\bar{c}_f(\bar{t}). \quad (68)$$

The superficial vapor velocity u_f of the flushing medium is related to the condensate flow via

$$\bar{u}_b(\bar{t}) = (\rho_f/\rho_b)\bar{u}_f(\bar{t}), \quad (69)$$

where the mean superficial condensate velocity \bar{u}_b , and, likewise, \bar{u}_f , is based on the cross-sectional area of the tube. The parameter \bar{u}_b follows directly from the time needed to fill a 1-L bottle and the cross-sectional area of the test tube. From (68) and (69) it follows that the velocity and density of the vapor in the packed bed cancel out if one replaces $\bar{u}_f\bar{c}_f(\bar{t})$ with $\bar{u}_b\bar{c}_b(\bar{t})$. To apply the model, it is irrelevant whether the flushing medium is in vapor or liquid phase. The model is completely written in terms of the effluent which is collected in the bottles and subsequently analyzed. The effluent flow is easy to measure during the filling of the bottles (likewise the contaminant concentration of the condensate in the bottles). As the velocity is constant ($u_b = \bar{u}_b$) and the same for all bottles, (57) in rewritten form is used:

$$\bar{c}_b(\bar{t}) = c_{bi}e^{-\lambda\bar{t}}, \quad (70)$$

where c_{bi} follows from

$$c_{bi} = (k_i H C_{si} L) / (K_d u_b), \quad (71)$$

λ follows from (51), and the ε^2 term is neglected. Equation (70) was also used by Brouwers [1996], who used the HCH concentration of the first three bottles from Table 1. From the time and concentration pertaining to bottles 1 and 3, c_{bi} and λ were computed with the help of (70), yielding $\lambda = 2.156 \times 10^{-4} \text{ s}^{-1}$ and $c_{bi} = 2.63 \text{ mg L}^{-1}$. This concentration is the value of the intersection of the line through points 1 and 3 with the vertical axis of Figure 2. From the derived value of λ , the overall mass transfer coefficient Hk_i/K_d can be obtained with (51), as the bulk density is known (1414 kg m^{-3}). From this value, $\lambda = 2.156 \times 10^{-4} \text{ s}^{-1}$, and (51) it followed that $Hk_i/K_d = 0.305 \text{ kg m}^{-3} \text{ s}^{-1}$ during the hexane stage. Moreover, using (56), it followed that $1/6 \varepsilon^2$ equals 1.5%, so that its neglect can be justified a posteriori.

Next, the reliability of the model was investigated with the help of the measured values c_{bi} , Hk_i/K_d , u_b , and L and (71).

The mean hexane velocity u_b follows from the volume flow (1 L/55 min) during the filling of the three bottles and the cross-sectional area (20.43 cm^2) as $1.48 \times 10^{-4} \text{ m s}^{-1}$. With these data one is in a position to assess the initial HCH mass fraction C_{si} , which can be compared with C_{si} measured before the experiment. Substituting all relevant values into (71) resulted in $C_{si} = 5.10 \text{ mg kg}^{-1} \text{ dw}$. This initial HCH fraction was in excellent agreement with the values obtained from analysis of the soil prior to the experiment (4.79 – $5.49 \text{ mg kg}^{-1} \text{ dw}$).

With the measured HCH concentrations in bottles 10 and 11 (see Figure 2), which were filled with water during the steam stripping stage, the overall mass transfer coefficient during the steam-stripping stage was determined. In Table 1 the measured HCH concentrations are tabulated. With these values and (70), c_{bi} and λ are computed as $0.861 \times 10^{-1} \text{ mg L}^{-1}$ and $0.316 \times 10^{-4} \text{ s}^{-1}$, respectively. Analogous to the procedure followed with hexane, an overall mass transfer coefficient $Hk_i/K_d = 0.445 \times 10^{-1} \text{ kg m}^{-3} \text{ s}^{-1}$ was derived for the steam stage. Using (56), it followed for this fitting that $1/6 \varepsilon^2$ equals 0.8%, so that its neglect was justifiable indeed.

Here, c_{bi} and λ are assessed again for the hexane stage, but now use is made from the concentrations measured in bottles 1 up to and including 8, using regression. The curve fitting results in $c_{bi} = 1.93 \text{ mg L}^{-1}$ and $\lambda = 1.426 \times 10^{-4} \text{ s}^{-1}$. From this value of $\lambda = 1.426 \times 10^{-4} \text{ s}^{-1}$ and (51), it follows that $Hk_i/K_d = 0.202 \text{ kg m}^{-3} \text{ s}^{-1}$ for the hexane stripping. This value is about 30% smaller than the value of Hk_i/K_d obtained with the first three bottles only. The volume flow (8.5 L/6.5 h) (and $A = 20.43 \text{ cm}^2$) results in an average u_b of $1.78 \times 10^{-4} \text{ m s}^{-1}$. With the help of the known values c_{bi} , Hk_i/K_d , u_b , and L and (71), $C_{si} = 6.80 \text{ mg kg}^{-1} \text{ dw}$. So, when use is made of the measured concentrations in all eight bottles, the mass transfer coefficient is slightly lower, and the verification still results in a good prediction of C_{si} . In Figure 2 the fitted line is included. One can readily see that though the curve coincides with the experimental data fairly well, the data are not correlated by a straight line. For this fitting, (56) revealed that $1/6 \varepsilon^2$ equals 0.6%, and hence it can be neglected as well.

So far, sorption has been assumed to be a linear isotherm, and hence $n = 1$ has been imposed implicitly. Using the results of previous sections, one is also in a position to apply the solution which starts from the Freundlich isotherm with n as a free parameter. To this end, (67), with neglect of the ε^2 term on the right-hand side, is used to express the fluid concentration in the bottle as

$$\bar{c}_b(\bar{t}) = [(1 - n)\lambda\bar{t} + c_{bi}^{n-1}]^{1/(n-1)}, \quad (72)$$

with

$$c_{bi} = \left(\frac{k_i^n H^n C_{si} L^n}{K_d u_b^n} \right)^{1/n} \quad (73)$$

and

$$\lambda = \frac{k_i^n H^n L^{n-1}}{K_d (1 - \phi) \rho_s u_b^{n-1} n}, \quad (74)$$

whereby use has been made of (60), (61), (64), and (65) so that τ can be neglected and so that u_f and u_b are constant. Equation (72) contains three parameters, namely, $(1 - n)\lambda$, c_{bi}^{n-1} , and $1/(n - 1)$, which are obtained by curve fitting of (72) using \bar{c}_b and \bar{t} pertaining to bottles 1 to 8, listed in Table 1. As method, a nonlinear Levenberg-Marquardt least squares routine from

Shaw and Tigg [1994] has been employed. The data fitting yields $1/(n - 1) = -7.35$ (or $n = 0.86$), $c_{bi}^{n-1} = 2.29$ (kg m^{-3}) $^{n-1}$, and $(1 - n)\lambda = 5.63 \cdot 10^{-5}$ (kg m^{-3}) $^{n-1}/\text{s}$. In Figure 2 this fitted curve is also depicted. It can be seen that this curve fits the experimental data better than the straight line pertaining to $n = 1$.

From the fitted values of n , $(1 - n)\lambda$, and hence λ , now the overall mass transfer coefficient $H^n k_t^n / K_d$ can be obtained with (74), as u_b (1.78×10^{-4} m s^{-1}), L (0.25 m), and $(1 - \phi)\rho_s$ (1414 kg m^{-3}) are known. Substituting said values yields $Hk_t / K_d^{1/n} = 1.42$ $\text{kg m}^{-3} \text{s}^{-1}$. With the help of the known values c_{bi}^{n-1} , n , $H^n k_t^n / K_d$, u_b , and L and (73), it follows that $C_{si} = 8.90$ mg kg^{-1} dw. Moreover, using (66), it followed that $(2 - n)/6\varepsilon^2$ equals 0.02%, so that neglecting the ε^2 term of (67) was allowed.

The value obtained for C_{si} is in good agreement with the C_{si} obtained from chemical analyses of the soil, namely, $C_{si} = 5.14$ mg kg^{-1} dw. Moreover, the fitted $n = 0.86$ agrees with the measured nonlinear isotherms of β -HCH in the literature [Mills and Biggar, 1969; Wahid and Sethunathan, 1979].

So, using the linear and/or nonlinear model, one is able to assess, solely from the measured exit concentrations of the flushing fluid, both the initial soil contamination level and the adsorption intensity parameter n . These predictions confirm the experimental accuracy achieved and the analytical solutions used. One can use either the limited information gathered with the first bottles after the start of the process or all information acquired with the analysis of all bottles filled during the entire process.

6. Application of the Model to Dichloroethylene Rinsing

In this section the derived model is applied to rinsing experiments of natural soils contaminated with 1,2 *cis*-dichloroethylene ($\text{C}_2\text{Cl}_2\text{H}_2$) reported by J. C. M. De Wit (private communication, 1996). At three locations of a contaminated site, three undisturbed soil samples were taken two times at depths rang-

Table 2. Soil Compositions and 1,2 *cis*-Dichloroethylene Contamination Levels, and Results of Model Application and Curve Fitting

	Tube I	Tube II	Tube III
<i>Soil Analyses</i>			
Dry weight (dw), %	73	75	84
Organic fraction f_o , %	9	7	5
Silt and clay fraction, %	82	70	86
Sand fraction, %	9	23	9
C_{si} , mg kg^{-1} dw	23.6	50.1	24.8
<i>Computed Soil Properties</i>			
ρ_s , kg m^{-3}	2538	2563	2588
ϕ , %	48	46	33
τ , days	1.53	1.96	1.43
<i>Results of Model Fit</i>			
$1/(n - 1)$	-3.22	-2.32	-17.96
c_{bi}^{n-1} , ($\text{kg m}^{-2} \text{s}^{-1}$) $^{n-1}$	182	307	2.73
$(1 - n)\lambda^*$, (kg m^{-2}) $^{n-1} \text{s}^{-n}$	3.06×10^{-4}	7.29×10^{-3}	1.49×10^{-7}
n	0.69	0.57	0.94
c_{bi}^* , $\text{kg m}^{-2} \text{s}^{-1}$	5.28×10^{-8}	1.69×10^{-6}	1.37×10^{-8}
λ^* , (kg m^{-2}) $^{n-1} \text{s}^{-n}$	9.84×10^{-4}	1.69×10^{-2}	2.68×10^{-6}
$k_t / K_d^{1/n}$, $\text{kg m}^{-3} \text{s}^{-1}$	5.86×10^{-1}	50.74	3.03×10^{-3}
C_{si} , mg kg^{-1} dw	24.3	89.5	20.5

Table 3. The 1,2 *cis*- $\text{C}_2\text{Cl}_2\text{H}_2$ Concentration in Bags and Mean Flushing Velocity During Rinsing of Tube I

Bag	t_s , days	t_e , days	\bar{t} , days	\bar{u}_b , mm h^{-1}	\bar{c}_b , mg L^{-1}
1	3	4	3.5	12.5	7.000
2	6	11	8.5	4.14	4.200
3	11	13	12	6.66	2.100
4	13	18	15.5	3.57	1.500
5	21	25	23	4.06	0.430
6	55	60	57.5	3.12	0.053

Data from J. C. M. De Witt (personal communication, 1996).

ing from 12 to 13 m below ground level by using sampling tubes. One tube of each couple was used for analysis, while the other tube was rinsed. The physical and chemical composition of the soils in the tubes which were analyzed are summarized in Table 2.

The three treated tubes were vertically placed and at both ends sealed with flanges. Demineralized water was passed through the column from top to bottom and led from the exit to sealed vacuum teflon bags. The soil in the core sample has a length of 44 cm, and the inner diameter of the core is 6.7 cm. Hence, the inner cross-sectional area is 3.526×10^{-3} m^2 , and the inner volume of the tube is 1.551×10^{-3} m^3 . The tubes were flushed with water which was collected in bags of about 1 L each. From the water collected in some bags the dichloroethylene concentration was determined. In Tables 3–5 the concentrations and the mean flushing rate pertaining to the analyzed bags of tubes I, II, and III, respectively, are summarized. Here, water is flushed through the column and collected, without any phase change, so that the velocity in the column u_f corresponds to the velocity with which the bag is filled, u_b . Similarly, the concentration at the exit of the column, $c_f(x = L)$, corresponds to the concentration of the fluid that enters the bag, c_b .

In contrast to the previous section, the flushing velocity is not constant (see Tables 3–5), and τ , that is, the time needed to flush the first pore volume, is not negligible in comparison to the time taken to fill the first bags. From (67) it follows that in the case of a time dependent flow rate, the measured mean exit concentration should be weighed with the mean flow velocity during the filling of that particular bag.

In order to determine the pore volume and required saturation time, first the density of the soil is computed via

$$\rho_s = (1 - f_o)\rho_m + f_o\rho_o \quad (75)$$

The porosity of the soil sample now follows from

Table 4. The 1,2 *cis*- $\text{C}_2\text{Cl}_2\text{H}_2$ Concentration in Bags and Mean Flushing Velocity During Rinsing of Tube II

Bag	t_s , days	t_e , days	\bar{t} , days	\bar{u}_b , mm h^{-1}	\bar{c}_b , mg L^{-1}
1	3	5	4	6.13	18.000
2	5	11	8	3.23	9.200
3	11	13	12	6.35	1.200
4	13	18	15.5	3.23	0.410
5	21	27	24	2.35	0.150
6	53	55	54	8.20	0.025

Data from J. C. M. De Wit (personal communication, 1996).

Table 5. The 1,2 *cis*-C₂Cl₂H₂ Concentration in Bags and Mean Flushing Velocity During Flushing Velocity of Tube III

Bag	t_s , days	t_e , days	\bar{t} , days	\bar{u}_b , mm h ⁻¹	\bar{c}_b , mg L ⁻¹
1	5	11	8	3.91	8.000
2	11	13	12	7.11	3.700
3	13	18	15.5	3.77	3.000
4	18	21	19.5	5.50	2.300
5	25	28	26.5	4.96	1.600
6	54	57	55.5	4.00	0.220

Data from J. C. M. De Wit (personal communication, 1996).

$$\phi = 1 - \frac{\rho_w dw}{\rho_s(1 - dw) + \rho_w dw} \quad (76)$$

Specific density of organic matter ρ_o , mineral (silt, clay, and sand) fraction ρ_m , and water ρ_w is taken as 1400, 2650, and 1000 kg m⁻³, respectively. The computed ρ_s and ϕ are included in Table 2. With the help of the mean flush velocity at the start of each experiment, ϕ and the core sample's volume and cross-sectional area τ are computed, which are also included in Table 2. The bag that contains fluid from the first pore volume is not analyzed, as this fluid is in equilibrium with the soil (Tables 2–5 and section 3).

Subsequently, (64), (65), and (67) are applied to the experimental data of Tables 3–5 and Figures 3–5. As the experiments concerned rinsing, here k_t is governed by (13) and H equals unity. Using the Levenberg-Marquardt least squares routine of *Shaw and Tigg* [1994], values of $1/(n - 1)$, $(1 - n)\lambda^*$ and c_{bi}^{*n-1} are assessed, which are summarized in Table 2. Next, n , λ^* , and c_{bi}^* are computed; these results are also listed in Table 2. With the help of these fitted parameters and invoking $L = 0.44$ m and the values for $(1 - \phi)\rho_s$, the values of $k/K_d^{1/n}$ and C_{si} are computed and included in Table 2 as well. Finally, the maximum value of $(2 - n)/6 \varepsilon^2$ was assessed for the three fittings. For tubes I and III the property was highest for the first bag and amounted to 0.72 and 1.06%, respectively. For tube II the maximum $(2 - n)/6 \varepsilon^2$ is found for bag 2 and amounts to 28%, which is substantially higher than all values computed up to here. This value illustrates that

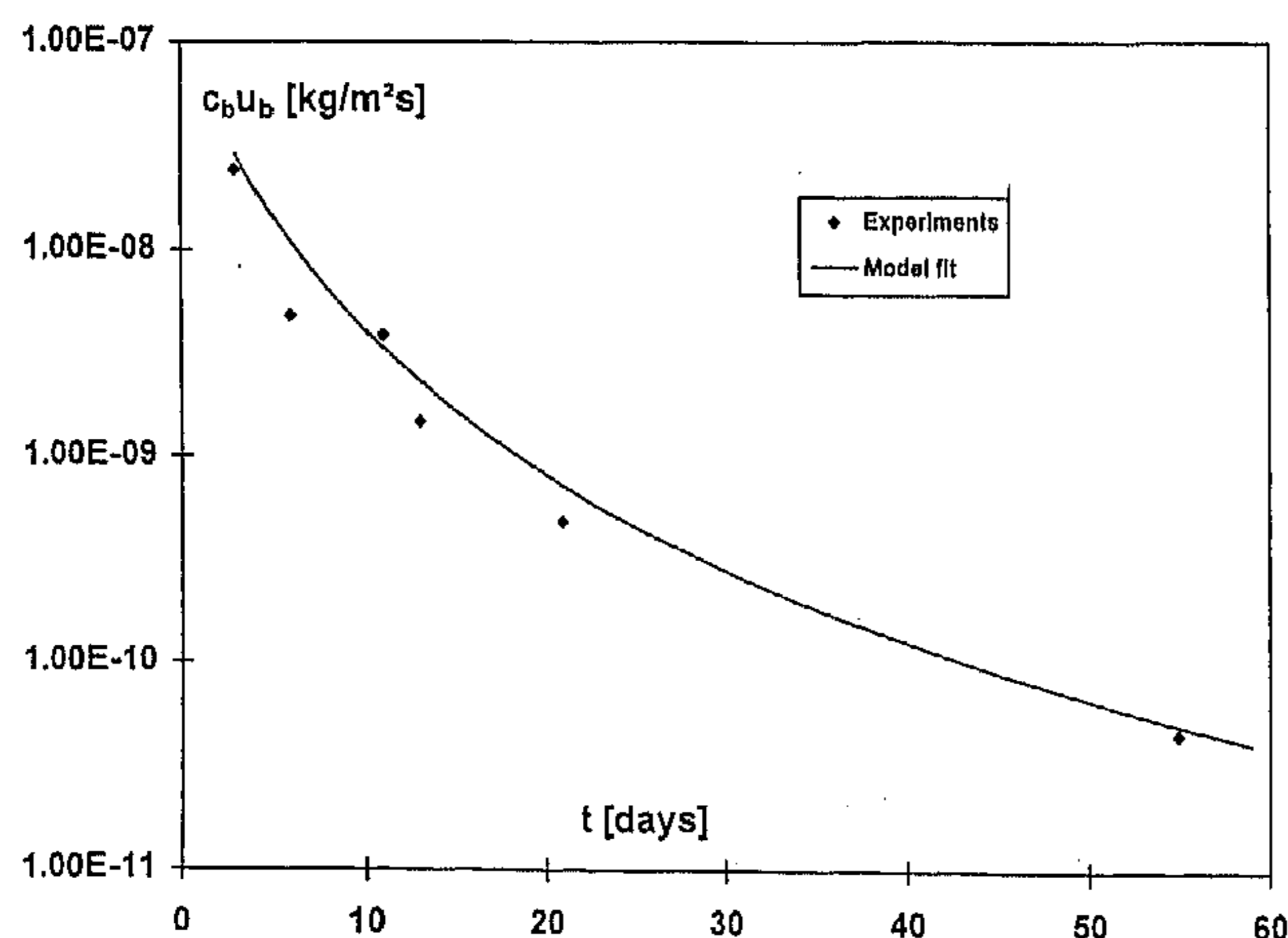


Figure 3. The 1,2 *cis*-C₂Cl₂H₂ concentration in bags and mean flushing velocity during rinsing of tube I (J. C. M. De Wit, private communication, 1996).

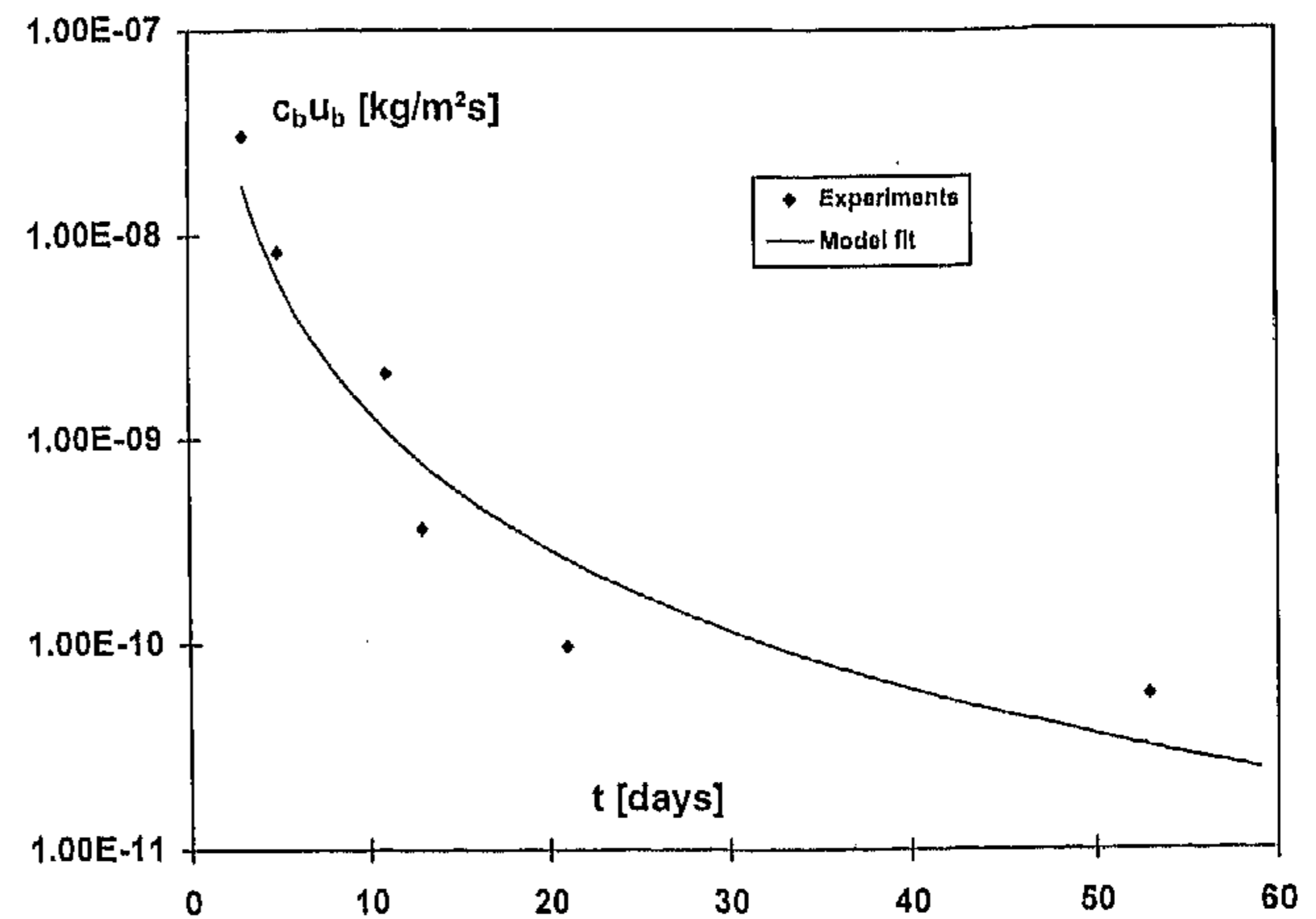


Figure 4. The 1,2 *cis*-C₂Cl₂H₂ concentration in bags and mean flushing velocity during rinsing of tube II (J. C. M. De Wit, private communication, 1996).

one always should bear in mind that there is an error involved with employing mean mixed exit concentrations that follow from a certain sampling time, which should therefore be as brief as possible.

From Table 2 it follows that n ranges from 0.57 to 0.94. These values of n are expected. As no sorption experiments concerning 1,2 *cis*-dichloroethylene are known to the author, for comparison, trichloroethylene data provided by *Kraemer et al.* [1994] and *Werth and Reinhard* [1997] are used. The first authors found for various sand mixtures values of n (referred to as $1/n$) ranging from 0.85 (± 0.27) to 0.92 (± 0.04), whereby C_s ranged from 0.001 to 10 mg/kg dw. *Werth and Reinhard* [1997] reported for various soils values of n ranging from 0.27 (± 0.02) to 0.71 (± 0.13) for C_s ranging from 0.1 to 100 mg kg⁻¹ dw. All measured values of n are in line with the values for 1,2 *cis*-dichloroethylene determined here, both in magnitude and in spreading.

In Table 2 it follows that the initial soil contamination level C_{si} obtained with the model and curve fit corresponds well to the values following from chemical analyses, especially for tubes I and II. In all cases the predicted values differ at most

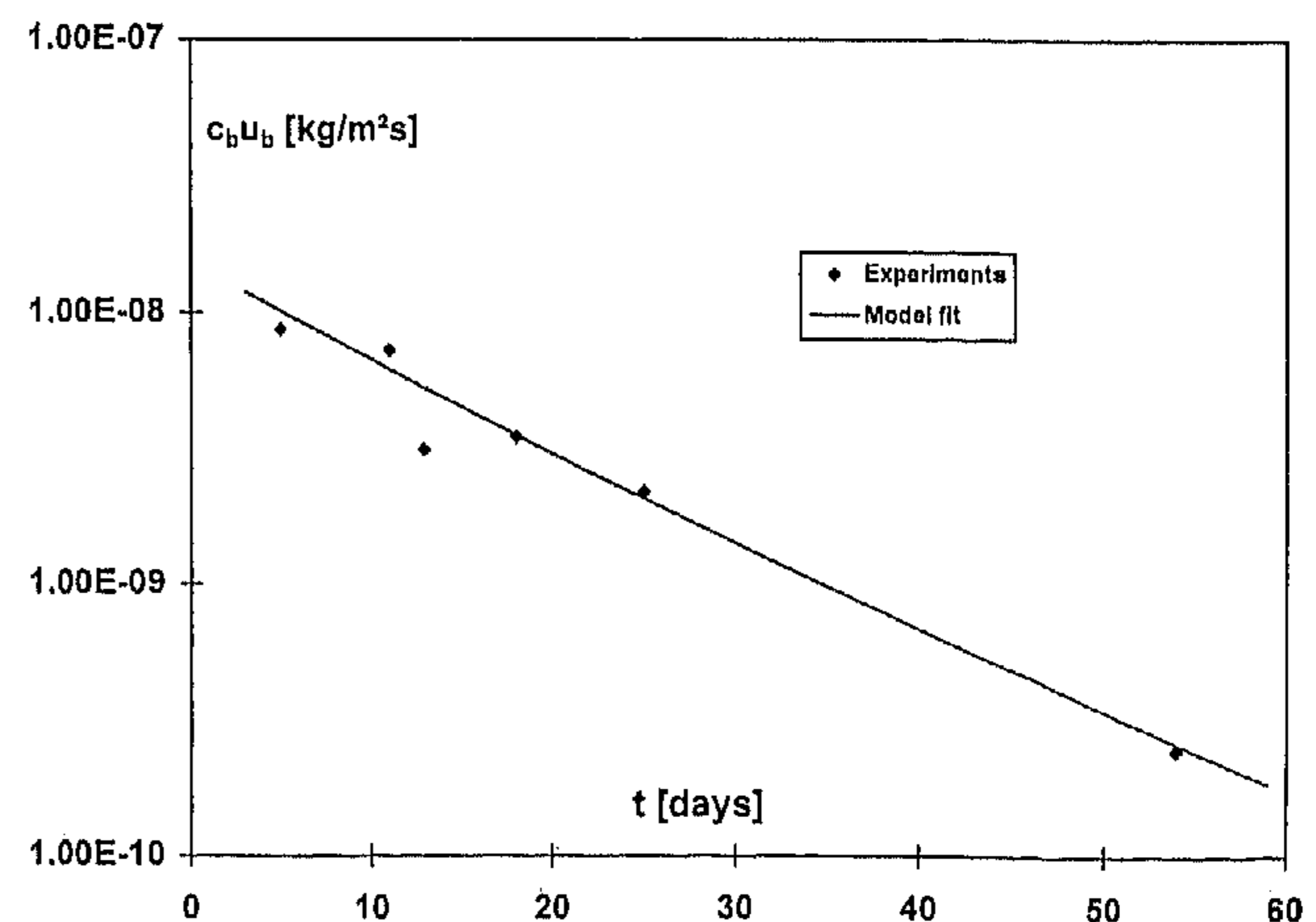


Figure 5. The 1,2 *cis*-C₂Cl₂H₂ concentration in bags and mean flushing velocity during rinsing of tube III (J. C. M. De Wit, private communication, 1996).

50% from the directly measured values, which is very satisfactory if one realizes the uncertainties involved with chemical analyses of water and soil and the employed approximate solutions.

In Figures 3–5 the data and the fitted curves are presented graphically. In these logarithmic graphs one can readily see the deviation from exponential decay in contaminant concentration versus time, suggesting nonlinear desorption effects, especially for tubes I and II. One can, furthermore, observe the fair agreement between fitted curve and experimental data.

7. Conclusions

In the present study a one-dimensional model is presented that describes the transport of contaminants in a column or reactor flushed with a fluid. The model accounts for nonlinear sorption using a Freundlich relationship, chemical nonequilibrium between soil and fluid phases, and convective contaminant transport in the fluid phase. Moreover, the model accounts for the start-up phase, that is, the time τ needed to flush the first pore volume of the column.

The resulting moving boundary problem can be transformed into a system of partial differential equations by employing a suitable coordinate transformation. Analytical approximate solutions are obtained by using perturbation techniques. This approach yields solutions for the contamination concentration both in soil and fluid in cases where the process is mass transfer controlled (Me is small). The pertaining solution represents the opposite limit of the other limit frequently made, namely, that of local equilibrium between the phases.

The analytical solutions clearly show the effect of nonlinear sorption on contaminant removal. Particularly, in case of a sorption parameter $n < 1$, the resulting deviation from exponential decay ("tailing") is illustrated by Figure 1. Furthermore, it follows that the soil contamination runs down versus time in each position in the column identically. For $n = 1$ it runs down exponentially; for $n \neq 1$ it behaves as $((1 - n)(t - \tau) + 1)^{1/(n-1)}$.

For many experiments the exit concentration is determined by collecting fluid during a given sampling time. Accordingly, the model is used to obtain expressions for cases where fluid is collected and an average concentration is actually measured. Moreover, the model is extended to the cases where the flushing velocity is not constant during an experiment. This analysis yields expressions which reflect that the measured mean exit concentration should be weighed by the mean velocity during collecting (equations (57) and (67)), as well as conditions which reflect "how short" a sampling time should be in order to render ε sufficiently small (equations (56) and (66)).

Subsequently, the resulting expressions are applied to stripping and rinsing experiments executed with natural soils contaminated with chlorinated hydrocarbons. Applying the model to the measured fluid contaminant concentration collected at the exit of the column yields mass transfer coefficients. Furthermore, the model permits the prediction of both the initial contamination level in the soil and the sorption intensity parameter n , which are found to correspond well with the expected values. The comparison of model and experiment yields good agreement, confirming the usefulness and reliability of the presented model.

Notation

A	cross-sectional area of the test tube [m^2].
C_s	mass of contaminant per dry mass of soil.
C_{si}	initial mass of contaminant per dry mass of soil.
c_b	contaminant concentration in fluid in bottle/bag [kg m^{-3}].
c_{bi}	initial contaminant concentration in fluid in bottle/bag (equation (71) if $n = 1$ and equation (73) if $n \neq 1$) [kg m^{-3}].
c_f	contaminant concentration in fluid in column [kg m^{-3}].
c_f^*	dimensionless contaminant concentration in column (equation (48)).
c_{fi}	initial contaminant concentration in fluid in bottle/bag (equation (50) if $n = 1$ and equation (60) if $n \neq 1$) [kg m^{-3}].
c_{fi}^*	modified initial contaminant concentration in fluid in bottle/bag (equation (58) if $n = 1$ and equation (64) if $n \neq 1$) [kg m^{-3}].
c_{wf}	contaminant concentration in stagnant liquid phase at interface with vapor [kg m^{-3}].
c_{ws}	contaminant concentration in stagnant liquid phase at interface with soil [kg m^{-3}].
c_s	contaminant concentration per dry mass of soil (equation (20)).
dw	dry weight (mass) fraction of soil.
f_o	organic (mass) fraction of soil.
H	dimensionless Henry's law coefficient (equation (9)).
K_d	soil sorption capacity [$\text{kg}^{-n} \text{m}^{3n}$].
k_f	mass transfer coefficient to flushing fluid [s^{-1}].
k_s	mass transfer coefficient for soil and stagnant liquid [s^{-1}].
k_t	total mass transfer coefficient (equations (12) or (13)) [s^{-1}].
k_w	mass transfer coefficient through stagnant liquid [s^{-1}].
L	length of column packed with contaminated soil [m].
M_c	mass of 1 kmol of contaminant [kg].
Me	Merkel number (equation (21)).
\dot{m}	mass flux [$\text{kg m}^{-3} \text{s}^{-1}$].
n	sorption intensity parameter.
P_c	vapor pressure of contaminant [Pa].
R	gas constant [$\text{J K}^{-1} \text{kmol}^{-1}$].
S	contaminant solubility [kg m^{-3}].
T	transformed time (equation (19)) [s].
T_f	fluid temperature [K].
t	time [s].
\bar{t}	mean time to fill bottle/bag (equation (55)) [s].
t_e	ending time of bottle/bag filling [s].
t_s	starting time of bottle/bag filling [s].
u_b	superficial fluid velocity in column related to velocity in bottle/bag [m s^{-1}].
u_f	superficial fluid velocity in column [m s^{-1}].
X	dimensionless coordinate (equation (18)).
x	coordinate [m].
ε	perturbation quantity (equation (24), (56), or (66)).
λ	time constant (equation (51) if $n = 1$ and equation (61) if $n \neq 1$) [$\text{kg}^{n-1} \text{m}^{3-3n} \text{s}^{-1}$].
λ^*	modified time constant (equation (65)) [$\text{kg}^{n-1} \text{m}^{2-2n} \text{s}^{-n}$].
ρ_b	fluid density in bottle/bag [kg m^{-3}].
ρ_f	fluid density in column [kg m^{-3}].
ρ_m	mineral fraction density [kg m^{-3}].
ρ_o	organic matter density [kg m^{-3}].
ρ_s	soil density [kg m^{-3}].

- τ time needed to saturate the column (equation (5)) [s].
 ϕ porosity.
 χ front position of flushing fluid [m].
 Y time needed to saturate the column at a given position [s].

Superscript – mean mixed.

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