Environmental Modelling & Software 13 (1998) 139–149

Environmental
Modelling & Software

Analytical solutions of the convection–dispersion equation applied to transport of pesticides in soil columns

J.I. Freijer [a,*], E.J.M. Veling [b], S.M. Hassanizadeh [b]

[a] National Institute of Public Health and the Environment, P.O. Box 1, 3720 BA, Bilthoven, The Netherlands
[b] Delft University of Technology, Faculty of Civil Engineering and Geosciences, Section for Hydrology and Ecology, P.O. Box 5048, 2600 GA, Delft, The Netherlands

Received 18 September 1997; accepted 31 December 1997

Abstract

Mathematical solutions are presented to describe leaching and degradation of pesticides in a specific type of column experiment, which is frequently required for the official registration of pesticides. In the column experiment in question a 2 cm layer of soil containing a known amount of the pesticide is placed on top of a soil column with a length of 28 cm. Water is added to the layer on top of the column for a certain period at a constant rate, while allowing free drainage at the bottom of the column. This induces leaching of the compound from the top layer. The mathematical solutions presented allow interpretation of the experiment in terms of the half-life and the sorption coefficient of the compound from the measured amount in the leachate and the amount remaining in the column after leaching. Example calculations are carried out for the German and US leaching scenarios, which are currently used in admission procedures for new and existing pesticides. It is concluded that, for a standard soil with an organic carbon content of 0.01 kg kg^{-1}, the German BBA guidelines are suitable to estimate half-lives (T_{50}) and sorption coefficients (K_{oc}), for compounds with $T_{50} < 20$ days and $K_{oc} < 0.06$ m^3 kg^{-1}. An alternative leaching scenario, as described in the US–EPA guidelines seems to be useful to estimate T_{50} in the range 10–250 days and K_{oc} in the range 0.05–0.20 m^3 kg^{-1}. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Environmental fate; Leaching experiments; Mathematical modelling; Organic contaminants

Software availability

Name of software:	TRASUM
Developer and contact address:	
Fortran version:	E.J.M. Veling, Delft University of Technology, Faculty of Civil Engineering and Geosciences, Section for Hydrology and Ecology, P.O. Box 5048, 2600 GA Delft, The Netherlands E-mail: ed.veling@ct.tudelft.nl
Pascal version:	J.I. Freijer, National Institute of Public Health and the Environment, P.O. Box 1, 3720 BA, Bilthoven, The Netherlands E-mail: jan.freijer@rivm.nl
Year first available:	1998
Hardware required:	IBM PC Intel 386 or better with at least 640 KB RAM and 10 MB free harddisk space
Software required:	MS–DOS 3.3 or later; for displaying diagrams included in this paper: XY for DOS (Van Heerden and Tiktak, 1994).
Program language:	Borland Turbo Pascal v5.0 or later (2192 lines); Fortran 77 (2178 lines).
Program size:	51 KB (Pascal version).
Availability and cost:	Code and executable available on request, free of charge.

* Corresponding author. e-mail: jan.freijer@rivm.nl

1364-8152/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S1364-8152(98)00016-4

1. Introduction

In recent years, concern about pollution of soil and groundwater by pesticides and their metabolites has grown. In order to protect the environment, admission procedures have been put in operation to evaluate the environmental behavior of new and existing pesticides for agricultural applications. Currently, national authorities in several countries prescribe experimental tests to assess the transformation and leaching potential of pesticides (Brouwer et al., 1994). One of the tests required to quantify movement of these products is a column experiment as described in the German BBA guidelines (BBA, 1986).

Column experiments are frequently used to gain quantitative information on the movement and transformation of pesticides in soil (e.g. Kruger et al., 1993; Pignatello et al., 1993; Brouwer et al., 1994). In most of these experiments water containing the dissolved compound of interest is added to the soil column, while free elution is allowed at the bottom of the column. Analytical solutions of the dispersion–convection equation for this type of boundary conditions are available to describe the movement and degradation of the solute (Van Genuchten and Alves, 1982; Van Genuchten and Wierenga, 1986; Veling, 1993; Toride et al., 1995).

In some of the column experiments required for admission of new and existing pesticides (EPA, 1978; BBA, 1986) instead of applying a solution to the column, the soil with the pesticide is placed on top of a soil column. Then, water devoid of the compound is added at a constant rate, which induces leaching of the pesticide from the top layer and its redistribution through the soil column. In this type of transport problem different boundary conditions are pertinent. The aim of this paper is to compare various analytical solutions for the above transport problem. The solutions differ in (i) the specification of the upper boundary condition and the initial condition and (ii) the consideration of finite and semi-infinite domain of analysis. Also, the possibilities to estimate two basic properties of pesticides, the sorption coefficient and the half-life from the results of the column experiments, are evaluated. A sensitivity analysis is performed to determine how the residual fraction in the column after leaching and the leachate fraction relate to the half-life and the sorption coefficient of the compound studied. The sensitivity analysis is performed for the leaching scenarios mentioned in the German and the US–EPA (EPA, 1978) guidelines.

2. Description of the column experiment

In the above-mentioned column experiment (BBA, 1986), a well-mixed soil/pesticide mixture is prepared with a known total concentration. This mixture is placed as a layer with a thickness of 2 cm on top of a column packed with the same soil. The pristine soil column must have a length of 28 cm and a diameter of 5 cm. The thin layer is thus quite small compared with the column length. The soil in the column is saturated with water prior to placing the soil layer on the column. Water is supplied at the top with a constant known rate, which induces transport of the pesticide from the upper layer containing the pesticide. The BBA (1986) recommends a leaching period of 2 days at a Darcy flux of 0.10 m d^{-1}. Alternatively, the US–EPA (EPA, 1978) suggests, for aged residues of pesticides, a leaching period of 45 days at a Darcy flux of 0.0125 m d^{-1}. Although the latter scenario is intended for aged residues, it can also be applied to fresh soil/pesticide mixtures. At the bottom of the column free drainage is allowed. In the packed soil and the thin layer, the pesticide is redistributed over the solid and liquid phases, and degraded by microorganisms, which causes the concentration to change in time and space. During the experiment, the effluent is collected and analysed. After a certain period of leaching, the experiment is stopped and the soil column is sectioned into a number of layers, which are then analysed separately. Although detailed (multiple effluent fractions, and soil sections) analyses are desirable, in practice analyses are often limited to the total effluent and the total amount in the column after leaching.

3. Model development

The processes considered in modelling the column leaching experiment are one-dimensional advection and dispersion through the liquid phase, sorption to the solid phase, and biological degradation. The governing equation describing the mass balance in the column is:

$$\frac{\partial X}{\partial t} = -\frac{\partial J_s}{\partial z} - kX \quad (1)$$

where X (kg m^{-3}) is the total concentration, t (d) is time, z (m) is distance, and k (d^{-1}) is the degradation rate constant. This rate constant is related to the half-life of the compound by

$$T_{50} = \ln(2)/k \quad (2)$$

The total transport flux J_s (kg m^{-2} d^{-1}) is the sum of advective and dispersive transport:

$$J_s = v\theta C - D\theta \frac{\partial C}{\partial z} \quad (3)$$

where v (m d^{-1}) is the pore water velocity, θ (m^3 m^{-3}) the water content, and C (kg m^{-3}) the resident concentration in the liquid phase. The dispersion coefficient, D (m^2 d^{-1}), includes diffusion and hydrodynamic dispersion:

$$D = D_0\kappa + \alpha v \tag{4}$$

where D_0 (m^2 d^{-1}) is the diffusion coefficient in water, κ a soil matrix factor, and α (m) the dispersion length. The total concentration is equal to the sum of the solid phase and liquid phase concentration:

$$X = \theta C + \rho Y \tag{5}$$

where Y (kg kg^{-1}) is the solid phase concentration, and ρ (kg m^{-3}) the dry bulk density. It is assumed that pesticide in the solid phase and the liquid phase are in equilibrium in accordance with a linear isotherm:

$$Y = K_{oc}f_{oc}C \tag{6}$$

where K_{oc} (m^3 kg^{-1}) is the sorption coefficient referenced to the organic matter, and f_{oc} (kg kg^{-1}) the organic matter content. Combination of Eqs. (1)–(6) yields:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - RkC \tag{7}$$

with the retardation factor, R, equal to

$$R = 1 + \rho f_{oc}K_{oc}/\theta \tag{8}$$

In arriving at Eq. (7), the following assumptions have been made: (i) the water content, flow velocity, and dispersion coefficient are constant; (ii) advection and dispersion occur only in a vertical direction; (iii) the retardation factor is independent of the concentration; (iv) transformations in the liquid and solid phases of the soil occur at the same rate.

3.1. Initial and boundary conditions

Two different possibilities exist for the formulation of the initial and boundary conditions pertaining to Eq. (7).

3.1.1. Case 1

The top layer that initially contains the pesticide is considered to be part of the column, and its presence is incorporated into the initial conditions. The modelling domain is from $z = -l$ to $z = \infty$. The initial conditions are:

$$C(z,0) = C_0, \quad -l < z \leqslant 0 \tag{9}$$

$$C(z,0) = 0, \quad 0 < z < \infty \tag{10}$$

where C_0 (kg m^{-3}) is the initial concentration and l (m) is the thickness of the top layer added to the soil column. Two boundary conditions are needed. In the definition of the upper boundary condition it is assumed that the water added at the top of the column is free of the pesticide. Furthermore, it is assumed that there is no concentration gradient at infinite depth. Accordingly, the boundary conditions are given as:

$$vC(-l,t) - D\frac{\partial C}{\partial z}(-l,t) = 0, \quad t \geqslant 0 \tag{11}$$

$$\frac{\partial C}{\partial z}(\infty,t) = 0, \quad t \geqslant 0 \tag{12}$$

Similar initial and boundary conditions have been considered by Lindstrom and Boersma (1971); Jury et al. (1990); Toride et al. (1993).

3.1.2. Case 2

In this alternative set of boundary conditions the thickness of the layer of the soil containing the pesticide must be thin compared with the total length of the column. The thin soil layer is considered to be outside the modelling domain (Freijer et al., 1995). The upper boundary condition is determined by the processes occurring in the thin layer that initially contains the pesticide. Assuming that the top layer is well mixed and is relatively thin, the upper boundary condition in case 2 is specified as:

$$lR\frac{\partial C}{\partial t}(0,t) = D\frac{\partial C}{\partial z}(0,t) - vC(0,t) - lRkC(0,t), \quad t \geqslant 0 \tag{13}$$

In order to complete this special boundary condition, it is necessary to specify the initial value of the pesticide concentration in the thin layer containing the pesticide:

$$C(0,0) = C_0 \tag{14}$$

In case 2, two different domains are considered: a semi-infinite (2a) and a finite (2b) domain. The initial condition for the semi-infinite domain (case 2a) is identical to that in Eq. (10), as is the lower boundary condition, which is given in Eq. (12). For the finite domain (case 2b) the initial condition reads:

$$C(z,0) = 0, \quad 0 < z < L \tag{15}$$

The lower boundary condition for case 2b is given as:

$$\frac{\partial C}{\partial z}(L,t) = 0, \quad t \geqslant 0 \tag{16}$$

3.2. Solutions of the governing equation

The governing differential Eq. (7) is solved by means of the Laplace transform technique for both semi-infinite and finite domains. The method of separation of variables (Walter, 1973) is an alternative solution method, which was used to verify the results of the solutions obtained with the Laplace transform technique (case 2b). First, the following set of dimensionless variables is introduced.

$$\zeta = vz/D \tag{17}$$

$$\tau = v^2t/(RD) \tag{18}$$

$$\epsilon = kRD/v^2 \tag{19}$$

$$\lambda = lv/D \tag{20}$$

and the Peclet number

$$p = Lv/D \tag{21}$$

Then for the various cases discussed above the following three solutions are obtained:

3.2.1. Case 1, semi-infinite domain

The solution in case 1 is given by

$$C(\zeta,\tau) = \frac{1}{2} C_0\exp(-\epsilon\tau)\{P + \exp(\zeta + \lambda)Q\} \tag{22}$$

with

$$P = \mathrm{erfc}\left[\frac{\zeta - \tau}{2\sqrt{\tau}}\right] - \mathrm{erfc}\left[\frac{\zeta + \lambda - \tau}{2\sqrt{\tau}}\right] \tag{23}$$

$$\begin{aligned} Q = {} & (1 + \tau + \zeta + \lambda)\mathrm{erfc}\left[\frac{\tau + \zeta + \lambda}{2\sqrt{\tau}}\right] \\ & - \frac{2\sqrt{\tau}}{\sqrt{\pi}}\exp\left[\frac{-(\tau + \zeta + \lambda)^2}{4\tau}\right] \\ & - (1 + \tau + \zeta + 2\lambda)\mathrm{erfc}\left[\frac{\tau + \zeta + 2\lambda}{2\sqrt{\tau}}\right] \\ & + \frac{2\sqrt{\tau}}{\sqrt{\pi}}\exp\left[\frac{-(\tau + \zeta + 2\lambda)^2}{4\tau}\right] \end{aligned} \tag{24}$$

The solution in Eq. (22) is identical to the limit of the Henry coefficient, $k_H \rightarrow 0$ in the solution of the convection–dispersion equation for three-phase transport given by Jury et al. (1990).

3.2.2. Case 2a, semi-infinite domain

In case 2a, for $\lambda \neq 1$ the solution is

$$C(\zeta,\tau) = C_0\exp(-\epsilon\tau)(P + Q) \tag{25}$$

with

$$P = \frac{\lambda - 2}{2(\lambda - 1)}\exp\left[\frac{-\tau(\lambda - 1)}{\lambda^2}\right] \exp[\zeta/\lambda]\mathrm{erfc}\left[\frac{\zeta - \tau}{2\sqrt{\tau}} + \frac{1}{\lambda}\sqrt{\tau}\right] \tag{26}$$

$$Q = \frac{\lambda}{2(\lambda - 1)}\exp(\zeta)\mathrm{erfc}\left[\frac{\zeta + \tau}{2\sqrt{\tau}}\right] \tag{27}$$

For $\lambda = 1$ the solution reads

$$C(\zeta,\tau) = C_0\exp(-\epsilon\tau)(P - Q) \tag{28}$$

with

$$P = (1 + \frac{1}{2}\zeta + \frac{1}{2}\tau)\exp(\zeta)\mathrm{erfc}\left(\frac{\zeta + \tau}{2\sqrt{\tau}}\right) \tag{29}$$

$$Q = \frac{\sqrt{\tau}}{\sqrt{\pi}}\exp\left[\frac{-(\zeta - \tau)^2}{4\tau}\right] \tag{30}$$

3.2.3. Case 2b, finite domain

For a finite modelling domain the solution is

$$C(\zeta,\tau) = \lambda C_0\exp(\frac{1}{2}\zeta)\exp(-\epsilon\tau - \frac{1}{4}\tau)\sum_{i=0}^{\infty} T_i \tag{31}$$

where

$$\begin{cases} T_0 = \exp(U_0^2\tau)\dfrac{-2U_0}{N_0}\{U_0\cosh[U_0(p - \zeta)] + \dfrac{1}{2}\sinh[U_0(p - \zeta)]\} & \text{, for } \lambda > 2 \\ T_0 = 0 & \text{, for } 0 < \lambda \leqslant 2 \end{cases} \tag{32}$$

where

$$\begin{aligned} N_0 = \Bigg[& \frac{-\frac{1}{8}\{-4\lambda(\lambda + 2)U_0^2 + (\lambda - 4)(\lambda - 2)\}}{\sqrt{-\lambda^2U_0^2 + \frac{1}{4}(\lambda - 2)^2}} \\ & - p(-U_0^2 + \frac{1}{4})\sqrt{-\lambda^2U_0^2 + \frac{1}{4}(\lambda - 2)^2}\Bigg] \end{aligned} \tag{33}$$

$$\mathrm{sign}\{1 - (\lambda + 2)(-U_0^2 + \frac{1}{4})\}$$

U_0 is the solution of ($U_0 > 0$)

$$\tanh(U_0 p) = -U_0 \frac{\lambda + (U_0^2 - \frac{1}{4})^{-1}}{\frac{1}{2}\lambda + 1 + \frac{1}{2}(U_0^2 - \frac{1}{4})^{-1}} \quad (34)$$

For $i > 0$, the terms T_i are given by

$$T_i = \exp(-U_i^2\tau)\frac{2U_i}{N_i}\{U_i\cos[U_i(p-\zeta)] + \frac{1}{2}\sin[U_i(p-\zeta)]\} \quad (35)$$

and the N_i terms are

$$N_i = \left[\frac{-\frac{1}{8}\{4\lambda(\lambda+2)U_i^2 + (\lambda-4)(\lambda-2)\}}{\sqrt{\lambda^2 U_i^2 + \frac{1}{4}(\lambda-2)^2}} - p(U_i^2 + \frac{1}{4})\sqrt{\lambda^2 U_i^2 + \frac{1}{4}(\lambda-2)^2}\right] \quad (36)$$

$$\text{sign}[\cos(U_i\, p)\{1 - (\lambda+2)(U_i^2 + \frac{1}{4})\}]$$

in which U_i are solutions of ($U_i > 0$)

$$\tan(U_i\, p) = -U_i \frac{\lambda - (U_i^2 + \frac{1}{4})^{-1}}{\frac{1}{2}\lambda + 1 - \frac{1}{2}(U_i^2 + \frac{1}{4})^{-1}} \quad (37)$$

In the following sections, the differences in outcomes of the above given solutions are analysed in relation to the boundary conditions (Sections 4 and 5). The impact of the boundary conditions are examined by comparing calculations of the resident concentration as a function of depth and time. For these calculations a standard parameter set, given in Table 1 is used. The calculations are performed for various values of the top-layer thickness, l. Finally, Section 6 discusses a possible application of the model to interpret column experiments in terms of half-life and sorption coefficient of the pesticide.

Table 1
Values of parameters comprising the base in calculations of Fig. 1 and Fig. 2

Parameter	Figure 1	Figure 2	Units
l	Variable	0.02	m
K_{oc}	0.100	0.100	$m^3\ kg^{-1}$
T_{50}	100	100	d
θ	0.40	0.40	$m^3\ m^{-3}$
$v\theta$	0.0125	0.0125	$m\ d^{-1}$
D_0	4×10^{-5}	4×10^{-5}	$m^2\ d^{-1}$
α	0.005	Variable	m
f_{oc}	0.01	0.01	$kg\ kg^{-1}$
ρ	1400	1400	$kg\ m^{-3}$
κ	0.34	0.34	

4. Comparison of the solutions in case 1 and case 2 for the semi-infinite domain

The solutions in cases 1 and 2 for a semi-infinite domain are given in Eqs. (22) and (25), respectively. The most important difference between the two solutions is caused by the assumption on the distribution of the compound in the top layer. In case 1 the compound is subjected to Eq. (7) for $-l < z \leq 0$, whereas in case 2 this layer is subjected to Eq. (13). The differences in outcomes depend strongly on the thickness, l, of the top layer. If we let $l \rightarrow 0$, both solutions degenerate to the solution for an instantaneous pulse (Veling, 1993), which employs the following upper boundary condition

$$C(0,t) - \frac{D}{v}\frac{\partial C}{\partial z}(0,t) = \frac{m}{\theta v A}\delta(t),\ t \geqslant 0 \quad (38)$$

where m is the total amount of compound injected (kg), A is the cross-sectional area of the column, (m^2), and $\delta(t)$ is the Dirac-delta distribution. The solution for the above-mentioned upper boundary condition reads:

$$C(\zeta,\tau) = C_0^* \exp(-\epsilon\tau) \left\{\frac{1}{\sqrt{\pi\tau}}\exp\left[\frac{-(\zeta-\tau)^2}{4\tau}\right] - \frac{1}{2}\exp(\zeta)\text{erfc}\left[\frac{\zeta+\tau}{2\sqrt{\tau}}\right]\right\} \quad (39)$$

with

$$C_0^* = \frac{mv}{\theta ARD} \quad (40)$$

Fig. 1 displays the concentration as a function of depth at two instances of time, for four different layer thicknesses. Parameter specifications of these calculations are given in Table 1. The figure demonstrates that with decreasing values of l the solutions converge. At low values, $l = 1$ and $l = 2$ cm, the results resemble each other quite well. However, when increasing the value of l the outcomes diverge. The assumption that the upper layer is well mixed causes an upstream tailing, as can be seen in the lower right panel of Fig. 1. It can thus be concluded that for low values of l the case 1 and case 2 upper boundary conditions are equally suited to describe leaching of pesticide from the upper layer and its subsequent displacement through the column.

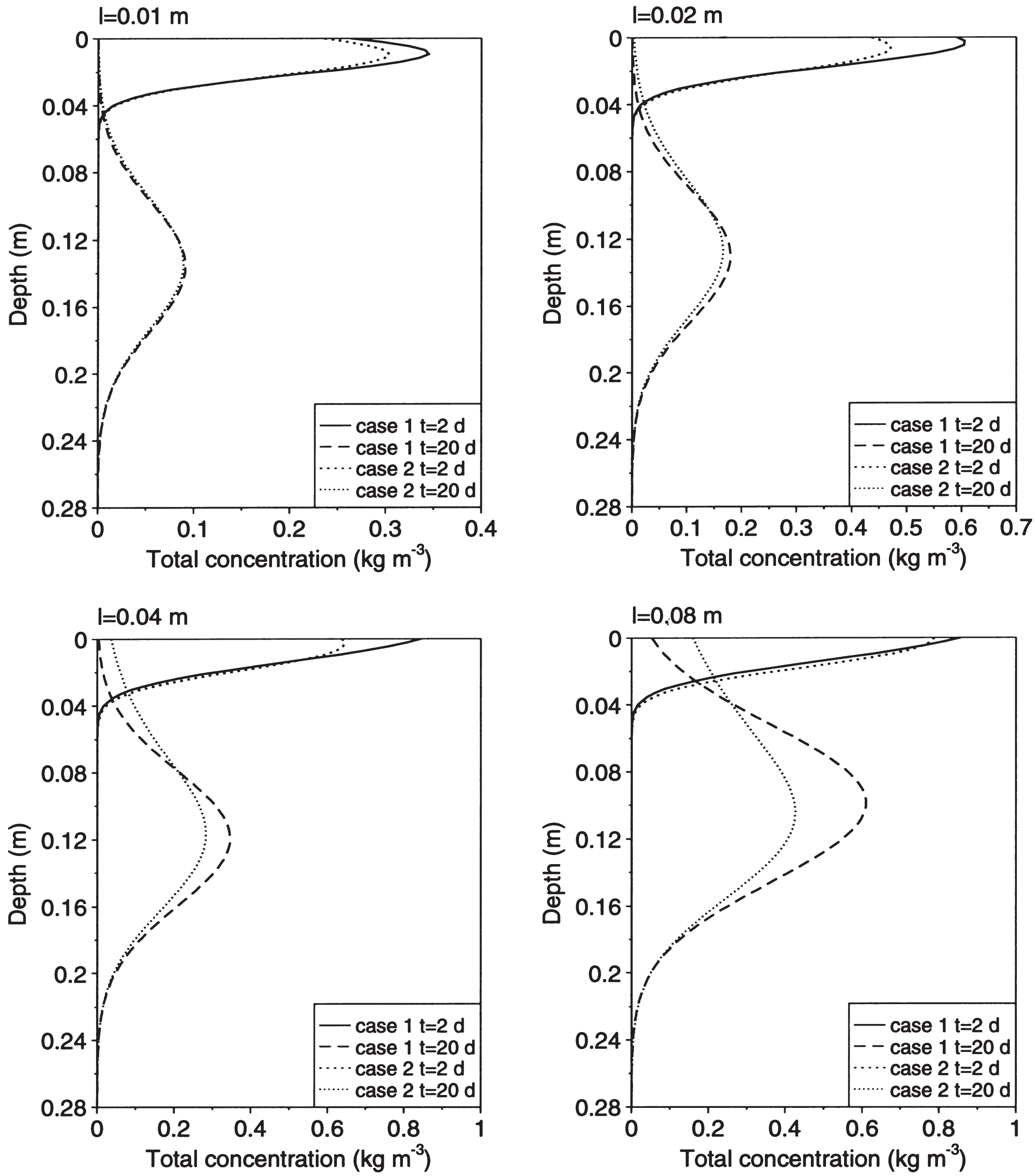

Fig. 1. Total concentration as a function of depth at two instances of time based on the solutions for case 1 and case 2a with four different top layer thickness values (l = 0.01, 0.02, 0.04 and 0.08 m).

5. Comparison of solutions in case 2 for finite and semi-infinite domains

The difference in outcomes that can be expected when comparing case 2a and case 2b is related to the effect of the concentration gradient of the outflowing pore water at the end of the column. The solution in Eq. (31) is based on the assumption that at the column outflow end the concentration gradient is zero, whereas, the solution in Eq. (25) is based on the assumption that a zero concentration gradient occurs at an infinite exit distance, thus implying a concentration gradient higher than zero at the end of the column. Which one of the two is the most realistic condition to model solute transport in a column remains a dilemma as pointed out by Parlange et al. (1992). Several authors have paid attention to the observation that the solutions for finite and infinite exit distances agree closely for Peclet numbers of $p > 4$ (Van

Genuchten and Parker, 1984; Parlange et al., 1992). In Parlange et al. (1992) an in-depth explanation is given for this observation, by relating the Peclet number to an explicit outlet condition. At high Peclet numbers the usage of the semi-infinite solution is to be preferred above that for a finite value of L, because the series solution given in Eq. (31) converges too slowly to provide accurate results.

In the current transport problem the column length is 0.28 m, which shows that for dispersion lengths of $\alpha <$ 0.07 m the Peclet number exceeds four. Because in the column studies considered here dispersion lengths are always much smaller than 0.07 m, the solution for a semi-infinite domain can safely be employed to approximate a finite column. In Fig. 2 the concentration is displayed as a function of depth using the solution for cases 2a and 2b within a range of dispersion lengths close to $\alpha = 0.07$ m. Other parameter specifications for these calculations are given in Table 1. The results clearly demonstrate that there is a non-zero concentration gradient at the end of the column for the semi-infinite solution, which increases with increasing dispersion length, and accordingly with decreasing Peclet number. Nevertheless, the difference between the two solutions remains marginal.

6. Estimation of half-life and sorption coefficient

Basically, properties of pesticides, such as T_{50} and K_{oc}, can be obtained from column experiments by parameter optimization. Several techniques are available to estimate the parameters using iterative procedures in which $C(x,t)$ functions are fitted to time series of concentration measurements by tuning the parameter values (Toride et al., 1995). These techniques require data in the form of concentration of pesticide along the column length or in the leachate as a function of time. However, such measurements are often not carried out in routine column experiments for the registration of pesticides. More commonly, in the experiments in question, the total amount remaining in the column or in sections of the column after leaching, and the total amount of compound present in the leachate at the end of the leaching period are measured (BBA, 1986; Brouwer et al., 1994). Since these measurements represent amounts in discrete layers and time intervals, the following integrals are of interest: the total amount of pesticide in the top layer,

$$\int_{-l}^{0} X(z',t)dz' \tag{41}$$

the total amount of pesticide remaining in the column,

$$\int_{0}^{z} X(z',t)dz' \tag{42}$$

and the integrated total transport flux,

$$\int_{0}^{t} J_s(z,t')dt' \tag{43}$$

In evaluating these integrals, we use the results of case 2a. The total amount in the top layer as a function of time is given by:

$$\int_{-l}^{0} X(z',t)dz' = \theta RC(0,t)l \tag{44}$$

Using the dimensionless variables defined in Eqs. (17) and (18), the integral in Eq. (42) can be written as:

$$\int_{0}^{z} X(z',t)dz' = \frac{\theta RD}{v}\int_{0}^{\zeta} C(\zeta',\tau)d\zeta' \tag{45}$$

If the flux-averaged concentration is defined as (Kreft and Zuber, 1978)

$$C^F = C - \frac{D}{v}\frac{\partial C}{\partial z} \tag{46}$$

then the integral in Eq. (43) can be written in terms of flux-averaged concentration

$$\int_{0}^{t} J_s(z,t')dt' = \frac{\theta RD}{v}\int_{0}^{\tau} C^F(\zeta,\tau')d\tau' \tag{47}$$

The values of the integrals at the right hand side of Eqs. (45) and (47) can be found by partial integration. Thus, the integral in Eq. (45) is:

$$\int_{0}^{\zeta} C(\zeta',\tau)d\zeta' = C_0\exp(-\epsilon\tau)(O + P + Q) \tag{48}$$

with, for $\lambda \neq 1$,

$$O = \frac{1}{2}\exp\left[\frac{-(\lambda-1)\tau}{\lambda^2}\right]\left[\lambda\exp\left(\frac{\zeta}{\lambda}\right)\mathrm{erfc}\left(\frac{\zeta-\tau}{2\sqrt{\tau}} + \frac{1}{\lambda}\sqrt{\tau}\right) - \lambda\mathrm{erfc}\left(\frac{-\sqrt{\tau}}{2} + \frac{\sqrt{\tau}}{\lambda}\right)\right] \tag{49}$$

$$P = \frac{1}{2}\lambda\mathrm{erfc}\left(\frac{-\sqrt{\tau}}{2}\right) - \frac{1}{2}\lambda\mathrm{erfc}\left(\frac{\zeta-\tau}{2\sqrt{\tau}}\right) \tag{50}$$

$$Q = \frac{-1}{(\lambda-1)}\left(O - \frac{\lambda}{2}\exp(\zeta)\mathrm{erfc}\left[\frac{\zeta+\tau}{2\sqrt{\tau}}\right] + \frac{\lambda}{2}\mathrm{erfc}\left[\frac{\sqrt{\tau}}{2}\right]\right) \tag{51}$$

For $\lambda = 1$, O, P, and Q are

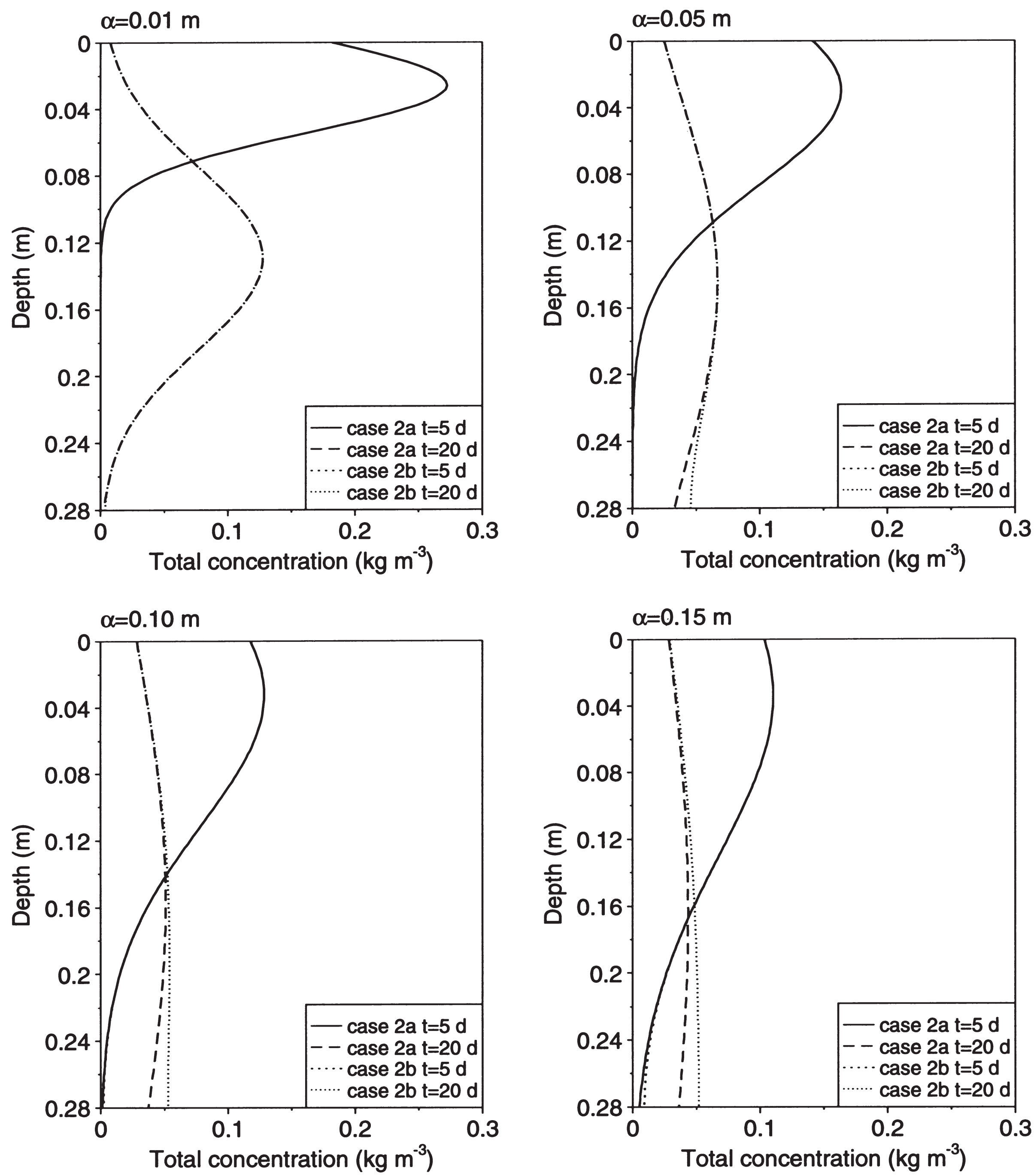

Fig. 2. Total concentration as a function of depth at two instances of time based on the solutions for case 2a (semi-infinite domain) and case 2b (finite domain; $L = 0.28$) for different dispersion length values ($\alpha = 0.01$, 0.05, 0.10 and 0.15 m).

$$O = (\frac{1}{2} + \frac{1}{2}\zeta + \frac{1}{2}\tau)\exp(\zeta)\mathrm{erfc}\left(\frac{\zeta + \tau}{2\sqrt{\tau}}\right) - \frac{1}{2}\mathrm{erfc}\left(\frac{\zeta - \tau}{2\sqrt{\tau}}\right) \quad (52)$$

$$P = -\left(\frac{1}{2} + \frac{1}{2}\tau\right)\mathrm{erfc}\left(\frac{\sqrt{\tau}}{2}\right) + \frac{1}{2}\mathrm{erfc}\left(\frac{-\sqrt{\tau}}{2}\right) \quad (53)$$

$$Q = \sqrt{\frac{\tau}{\pi}}\left(\exp\left[\frac{-\tau}{4}\right] - \exp\left[\frac{-(\zeta - \tau)^2}{4\tau}\right]\right) \quad (54)$$

The integral in Eq. (47) is

$$\int_0^\tau C^F(\zeta,\tau')d\tau' = C_0\left[\frac{\lambda - 2}{2\lambda}O - \frac{1}{\sqrt{1 + 4\epsilon}}(P - Q)\right] \quad (55)$$

with

$$O = \exp(-\epsilon\tau)\exp\left[\frac{-(\lambda-1)\tau}{\lambda^2}\right]\exp\left[\frac{\zeta}{\lambda}\right]$$
$$\mathrm{erfc}\left[\frac{\zeta-\tau}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\lambda}\right]\frac{-\lambda^2}{\epsilon\lambda^2+\lambda-1}+$$
$$\frac{\lambda^2}{2(\epsilon\lambda^2+\lambda-1)}\left[P\left(1+\frac{2-\lambda}{\lambda\sqrt{1+4\epsilon}}\right)\right.$$
$$\left.+\,Q\left(1-\frac{2-\lambda}{\lambda\sqrt{1+4\epsilon}}\right)\right] \quad (56)$$

$$P = \exp\left[\frac{\zeta}{2}+\frac{\zeta}{2}\sqrt{1+4\epsilon}\right]\mathrm{erfc}\left[\frac{1}{2}\sqrt{1+4\epsilon}\sqrt{\tau}+\frac{\zeta}{2\sqrt{\tau}}\right] \quad (57)$$

$$Q = \exp\left[\frac{\zeta}{2}-\frac{\zeta}{2}\sqrt{1+4\epsilon}\right]\mathrm{erfc}\left[-\frac{1}{2}\sqrt{1+4\epsilon}\sqrt{\tau}+\frac{\zeta}{2\sqrt{\tau}}\right] \quad (58)$$

Provided that all theoretical assumptions are valid, the above integrals can now be used to calculate the apparent relationship between the half-life, T_{50}, and the sorption coefficient, K_{oc}, and a simple combination of two measured entities. For example, the fraction of the initial dose that leached after a certain period, and the fraction that remains in the column can be considered.

The apparent relationship is obtained by calculating the fraction that remains in the column after leaching (% residual), and the fraction that has leached (% leached) for a number of different combinations of half-life and sorption coefficient. Other parameter values are kept constant in these calculations. Two different standard parameter sets are used, one representing an experiment following the German BBA guidelines, and one following the US–EPA guidelines (Table 2). The parameters that are kept constant include soil properties, such as organic matter content, bulk density, matrix factor, and dispersion length. In principal, all of the parameters given in Table 2 can be determined from independent experiments. The most uncertain parameter in Table 2 is probably the dispersion length. In general, the dispersion length is related to the heterogeneity of the flow field of the solute. Under laboratory conditions with uniform packed soils and a constant uniform injection of the solute, a relatively uniform flow field can be obtained, yielding low dispersion lengths (Oostrom et al., 1992). Oostrom et al. (1992) report values ranging from 1.4×10^{-4} to 3.1×10^{-2} m. In our calculations we have assigned a rather high value (5.0×10^{-3} m) for the dispersion length (Table 2). This is because the German guidelines (BBA, 1986) do not specifically state that a constant flow velocity has to be maintained. It is therefore plausible that in many experiments some variation in water velocity occurs due to non-uniformity and time-variation in the addition of water to the column. In the current calculations the variation in water velocity can be accounted for by assuming a relatively high dispersion length.

The results of the calculations can be displayed in nomograms, such as given in Fig. 3 (BBA) and Fig. 4

Table 2
Values of parameters comprising the base in calculations of Fig. 3 and Fig. 4.

Parameter	Figure 3	Figure 4	Units
l	0.02	0.02	m
z	0.28	0.28	m
t	2	45	d
θ	0.40	0.40	$m^3\ m^{-3}$
$v\theta$	0.1	0.0125	$m\ d^{-1}$
D_0	4×10^{-5}	4×10^{-5}	$m^2\ d^{-1}$
α	0.005	0.005	m
f_{oc}	0.01	0.01	$kg\ kg^{-1}$
ρ	1400	1400	$kg\ m^{-3}$
κ	0.34	0.34	

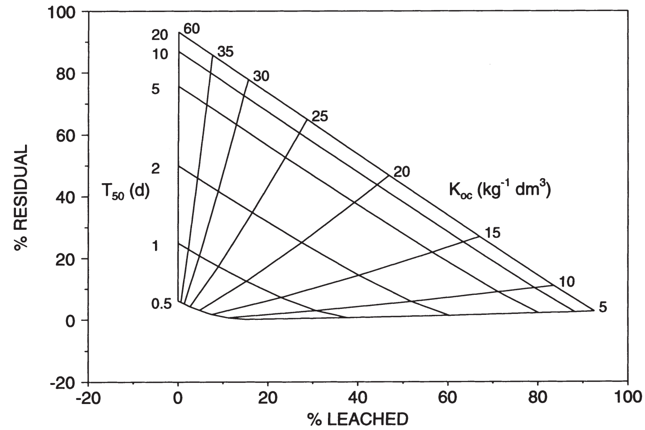

Fig. 3. Nomogram relating K_{oc} and T_{50} with leached fraction and residual fraction according to the German BBA leaching scenario.

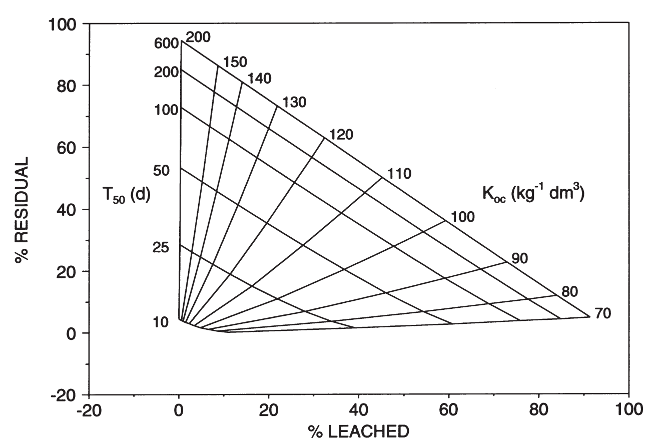

Fig. 4. Nomogram relating K_{oc} and T_{50} with leached fraction and residual fraction according to the US–EPA leaching scenario.

(US–EPA). In these graphs, the depth and time integrals are scaled to the initial amount of pesticide in the top layer and displayed on the *x* and *y* axes, whereas the input parameters are given as isolines. Figs. 3 and 4 demonstrate that each combination of half-life and sorption coefficient is uniquely related to a residual fraction and a leached fraction. For example in Fig. 3, for a pesticide with a half-life of 2 days and a sorption coefficient of 0.030 $m^3\ kg^{-1}$, under the German leaching scenario the residual fraction is 42% and the leached fraction is 9%.

The nomograms displayed in Figs. 3 and 4 show the range of parameter values that can theoretically be derived from the leaching scenarios described by the BBA and the US–EPA. In this respect, the two experiments yield information on completely different combinations of half-life and sorption coefficient. In the German experiments leaching is carried out for only 2 days, but at high water flow velocities, which sets the upper parameter horizon of T_{50} to approximately 20 days, and that of K_{oc} to 0.06 $m^3\ kg^{-1}$. The leaching period is insufficiently long to be useful for compounds with long half-lives, and the added water (0.2 m) is not enough to leach relatively immobile compounds. The longer duration of the US–EPA guidelines, and the higher amount of water added to the column (0.56 m), set the useful range of K_{oc} to 0.06–0.20 $m^3\ kg^{-1}$, and that of T_{50} to 10–250 days.

It is also possible to evaluate the effect of measurement errors on the estimation of T_{50} and K_{oc}. For example, instead of working with exact values of fractions leached and fractions remaining in the columns, a rectangle can be drawn in the nomogram. The rectangle is centered around the measured values, and its sides are determined by the measurement errors. The K_{oc} isoline that intersects with the upper left corner of this rectangle yields the maximum K_{oc} value, while the isoline that intersects with the lower right corner gives the minimum K_{oc} value. Similarly, the T_{50} isoline that intersects with the upper right corner of the area gives the maximum T_{50} values, and the isoline that intersects with the lower left corner yields the minimum T_{50} value. For example, consider two measurements and their measurement error: fraction leached = 35 ± 5% and fraction residual = 45 ± 5% in the US–EPA experiment (Fig. 4). Using the above method yields the following estimates: $T_{50} \in [85,500]$ d, and $K_{oc} \in [0.109,0.118]$ $m^3\ kg^{-1}$.

7. Conclusion

Analytical solutions for transport of pesticides through a soil column with an initial pesticide concentration in the top layer were developed using three different combinations of initial and boundary conditions. It was demonstrated that the three solutions yield comparable results. We selected one of the solutions for the evaluation of time and depth integrals. The integrals were used to interpret the results of pesticide leaching experiments in terms of half-life and sorption coefficient of the pesticides. These compound-specific parameters can be estimated from the measurement of pesticides in the leachate and in the residuals in the column after leaching. Example calculations were carried out for the BBA and US–EPA leaching scenarios, which are currently used in admission procedures for new and existing pesticides. It can be concluded that the two scenarios yield information on completely different ranges of half-life and sorption coefficient.

Acknowledgements

This study has been performed in the framework of project 715801 at the National Institute of Public Health and the Environment, Bilthoven, The Netherlands in cooperation with the Winand Staring Center, Wageningen, The Netherlands. The authors wish to thank A.M.A. van der Linden, J.J.T.I. Boesten, and M. Leistra for fruitful discussions and support.

References

BBA, 1986. Seepage behaviour of plant protection products. Guidelines for the official testing of plant protection products. Part IV 4–2. Braunschweig, Germany.

Brouwer, W.W.M., Boesten, J.J.T.I., Linders, J.B.H.J., Van Der Linden, A.M.A., 1994. The behaviour of pesticides in soil: Dutch guidelines for laboratory studies and their evaluation. Pesticide Outlook 5, 23–28.

EPA, 1978. Proposed guidelines for registering pesticides in the United States. Chapter (b) of Section 163.62–9. Federal Register 43(132), 29719.

Freijer, J.I., Broerse, S.Q., Hassanizadeh, S.M., Van der Linden, A.M.A., Veling E.J.M., 1995. Column leaching experiments for aged residues of pesticides: interpretation and criteria. Report no. 715801004. National Institute of Public Health and the Environment, Bilthoven, The Netherlands.

Jury, W.A., Russo, D., Streile, G., El Abd, H., 1990. Evaluation of volatilization by organic chemicals residing below the soil surface. Water Resourc. Res. 26, 13–20.

Kreft, A., Zuber, A., 1978. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. Chem. Engin. Sci. 33, 1471–1480.

Kruger, E.L., Somasundaram, L., Kanwar, R.S., Coats, J.R., 1993. Movement and degradation of [^{14}C]atrazine in undisturbed soil columns. Environ. Toxicol. Chem. 12, 1969–1975.

Lindstrom, F.T., Boersma, L., 1971. A theory on the mass transport of previously distributed chemicals in a water saturated porous medium. Soil Science 111, 192–199.

Oostrom, M., Dane, J.H., Güven, O., 1992. Dispersivity values determined from effluent and nonintrusive resident concentration measurements. Soil Sci. Soc. Am. J. 56, 1754–1758.

Parlange, J.-Y., Starr, J.L., Van Genuchten, M.Th., Barry, D.A., Parker, J.C., 1992. Exit condition for miscible displacement experiments. Soil Sci. 153, 165–171.

Pignatello, J.J., Ferrandino, F.J., Huang, L.Q., 1993. Elution of aged and freshly added herbicides from a soil. Environ. Sci. Technol. 27, 1563–1571.

Toride, N., Leij, F.J., Van Genuchten, M.Th., 1993. Flux-averaged concentrations for transport in soils having nonuniform initial solute distributions. Soil Sci. Soc. Am. J. 57, 1406–1409.

Toride, N., Leij, F.J., Van Genuchten, M.Th., 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Version 2.0. Research Report no. 137. US Salinity Laboratory, Riverside CA.

Van Genuchten, M.Th., Alves, W.J., 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation. USDA Technical Bulletin 1661. US Government Printing Office, Washington, DC.

Van Genuchten, M.Th., Parker, J.C., 1984. Boundary conditions for displacement experiments through short laboratory soil columns. Soil Sci. Soc. Am. J. 48, 703–708.

Van Genuchten, M. Th., Wierenga, P.J., 1986. Solute dispersion coefficients and retardation factors. In: Klute, A. (Ed.), Methods of soil analysis. Part 1 — Physical and mineralogical methods, 2nd edn. ASA and SSSA, Madison, WI. pp. 1025–1054.

Van Heerden, C., Tiktak, A., 1994. Het grafische programma XY. Een programma voor visualisatie van de resultaten van rekenprogramma's (in Dutch). Report no. 715501 002, National Institute of Public Health and the Environment, Bilthoven, the Netherlands.

Veling, E.J.M., 1993. ZEROCD and PROFCD. Description of two programs to supply quick information with respect to the penetration of tracers into the soil. Report no. 725206009. National Institute of Public Health and the Environment, Bilthoven, the Netherlands.

Walter, J., 1973. Regular eigenvalue problems with eigenvalue parameter in the boundary condition. Mathematisch Zeitschrift 133, 301–312.