

Spatial moment analysis of transport of nonlinearly adsorbing pesticides using analytical approximations

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[1] Analytical approximations were derived for solute transport of pesticides subject to Freundlich sorption, and first-order degradation restricted to the liquid phase. Solute transport was based on the convection-dispersion equation (CDE) assuming steady flow. The center of mass (first spatial moment) was approximated both for a non-degraded solute pulse and for a pulse degraded in the liquid phase. The remaining mass (zeroth spatial moment) of a linearly sorbing solute degraded in the liquid phase was found to be a function of only the center of mass (first spatial moment) and the Damköhler number (i.e., the product of degradation rate coefficient and dispersivity divided by flow velocity). This relationship between the zeroth and first spatial moments was shown to apply to nonlinearly sorbing pulses as well. The mass fraction leached of a pesticide subject to Freundlich sorption and first-order degradation in the solution phase only was found to be a function of the Damköhler number and of the dispersivity, so independent of sorption. Hence perceptions of the effects of sorption on pesticide leaching should be reconsidered. These conclusions equally hold for other micropollutants that degrade in the solution phase only.

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1. Introduction

[2] Pesticide use in agriculture is one of the main sources of groundwater contamination. As early as the 1980s, tens of pesticides had been detected in groundwater, in concentrations up to 100 $\mu\text{g/L}$ [e.g., *Leistra and Boesten*, 1989]. The maximum admissible concentration for pesticides in drinking water is 0.1 $\mu\text{g/L}$ in the European Community [*Council of the European Communities*, 1980]. When groundwater pumped up for the drinking water supply contains pesticide concentrations above this standard, the water has to be purified with expensive technologies.

[3] Pesticide leaching to groundwater is determined basically by the sorption and degradation properties of the pesticide [*Jury and Gruber*, 1989; *Tiktak et al.*, 2004]. Sorption isotherms have experimentally been shown to be nonlinear for many contaminants and pesticides [e.g., *Brusseau and Rao*, 1989; *Calvet et al.*, 1980; *Turin and Bowman*, 1997]. Pesticide sorption isotherms can usually be described with the nonlinear Freundlich isotherm. Decreasing the Freundlich exponent of non-degrading solutes results in later breakthrough and increased tailing of effluent curves [*van Genuchten and Cleary*, 1979]. Decreasing the Freundlich exponent may strongly decrease the percentage leached below 1 m depth for pesticides that are degraded in both the liquid and solid phase [*Boesten*, 1991]. However,

assuming degradation in both the liquid and solid phase is debatable as *Ogram et al.* [1985] have shown that the degradation rate of 2, 4-Dichlorophenoxyacetic acid (2, 4-D) in soil is proportional to the concentration in liquid phase. At present, pesticide degradation is commonly attributed to the liquid phase [*Haws et al.*, 2006; *Alexander*, 2000; *Scow and Alexander*, 1992]. It is therefore relevant to assess whether the sensitivity of pesticide leaching to sorption parameters is similarly high if it is assumed that the transformation rate is proportional to the concentration in liquid phase only.

[4] To assess the risks of groundwater contamination, pesticide leaching to groundwater is often simulated with mathematical models [e.g.; *Hutson and Wagenet*, 1992; *Beltman et al.*, 1995; *Tiktak et al.*, 2004; *Boesten*, 2007; *Stenemo et al.*, 2007]. To check and evaluate mathematical models, analytical solutions are needed. Analytical solutions for the spatial moments of linearly adsorbing solutes that are not degraded were derived by *Jury and Roth* [1990] and *Roth and Jury* [1993]. Their solutions for the first spatial moment (average location of the concentration distribution) and the second spatial moment (variance of the concentration distribution) also apply to solutes that are degraded in both solid and liquid phase, because for linearly sorbing solutes the distribution of a solute over the liquid and solid phase is independent of its (local) concentration [*Jury and Roth*, 1990]. In contrast, the distribution of a nonlinearly sorbing solute over the phases depends on its concentration. Modeling of nonlinear sorption indicated that a model based on linear sorption cannot provide accurate simulations of transport and degradation when the Freundlich-exponent N is less than about 0.9 [*Brusseau*, 1995]. Analytical approximations for the first and second

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spatial moment of nonlinearly sorbing solutes in two-dimensional systems were derived by *Bosma et al.* [1996] using analytical solutions from *Grundy et al.* [1994] and from *Dawson et al.* [1996]. Degradation of the solute was not considered by *Bosma et al.* [1996] and by *Dawson et al.* [1996]. An analytical solution for a continuous solute injection subject to nonlinear sorption and first-order degradation in the liquid phase was derived by *Bosma and van der Zee* [1993]. They showed that for the continuous injection the long term concentration distribution is independent of sorption nonlinearity. Surprisingly, the interaction between sorption nonlinearity and degradation rate was only addressed occasionally. Analytical solutions describing concentration as a function of depth and time are not available for a nonlinearly sorbing solute pulse, except approximations for a pulse that is not transformed [*Serrano*, 2003] and solutions for a continuous input of transforming solute [*Bosma and van der Zee*, 1993]. Analytical solutions are needed to determine the pesticide mass and to determine when this mass arrives at a certain depth.

[5] The large time behavior of decaying compounds (degraded in either both liquid and adsorbed or degraded only in liquid phase) in the infinite domain was studied with solutions for the interfaces of the spreading compound (the boundary between the contaminated and the uncontaminated soil solution) by *Escobedo and Grundy* [1996]. These solutions could not then be linked to the mass of the compound that remains from the initial mass. Using the interface approach, spatial moments were computed by *van Duijn et al.* [1997] for the case without degradation. Because the moments would then depend on the initial mass distribution, calculating the moments for solutes that are degraded was not possible.

[6] Thus our aim is to quantify the major effects of nonlinear sorption on transport of pesticides in soil, with emphasis on the combined effects of nonlinear sorption and first-order degradation. We developed analytical approximations for the spatial moments of solute pulses moving through soil that are subject to nonlinear sorption and first-order degradation in solution. We are particularly interested in the zeroth moment (the total mass of the solute in the system), and the first moment (the mass weighted average of the travel distance of the solute pulse in the system). In this paper, we use mass to denote the zeroth moment of the total mass and center of mass for the first spatial moment.

2. Mathematical Model

2.1. Solute Transport and Degradation

[7] We describe pesticide transport by the one-dimensional convection-dispersion equation (CDE), assuming first-order degradation kinetics in the liquid phase only:

$$\rho \frac{\partial q}{\partial t} + \theta \frac{\partial c}{\partial t} = \theta D \frac{\partial^2 c}{\partial x^2} - \theta v \frac{\partial c}{\partial x} - \theta kc \quad (1)$$

where ρ is the dry bulk density (M L^{-3}), q is the mass sorbed per mass of dry soil (M M^{-1}), t is time (T), θ is the volumetric water content of the soil ($\text{L}^3 \text{L}^{-3}$), c is the concentration in solution (M L^{-3}), D is the hydrodynamic dispersion coefficient ($\text{L}^2 \text{T}^{-1}$), x is the distance (L), v is the

filtration velocity (L T^{-1}) and k is the degradation rate coefficient (T^{-1}). Note that only degradation in the liquid phase is considered. See the Notation section for a full description of the symbols. We consider equilibrium nonlinear sorption, which is described by the Freundlich equation,

$$q = K_F c_r \left(\frac{c}{c_r} \right)^N \quad (2)$$

where K_F is the Freundlich sorption coefficient ($\text{L}^3 \text{M}^{-1}$), c_r is a reference concentration at which the Freundlich sorption coefficient has been estimated (M L^{-3}) and N (–) is the Freundlich power which is assumed to satisfy $0 < N \leq 1$. We consider a semi-infinite system, where initially the concentration is zero in the entire system. A flux pulse is introduced at $t = 0$ and $x = 0$, which contains an initial mass M_0 per unit surface (M L^{-2}). The mass in the system M (M L^{-2}) is defined as

$$M = \int_R \left[\theta c + \rho K_F c_r \left(\frac{c}{c_r} \right)^N \right] dx \quad (3)$$

Combining equations (1) and (2) results in

$$\frac{\partial}{\partial t} \left[c + \frac{\rho}{\theta} K_F c_r \left(\frac{c}{c_r} \right)^N \right] = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - kc \quad (4)$$

Equation (4) may be written in a non-dimensional form

$$\frac{\partial C}{\partial T} + S \frac{\partial C^N}{\partial T} = \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} - wC \quad (5)$$

by introducing the following dimensionless parameters

$$C = \frac{c}{c_r} \quad T = \frac{vt}{L_d} \quad X = \frac{x}{L_d} \quad S = \frac{\rho}{\theta} K_F \quad w = \frac{kL_d}{v} \quad (6)$$

where $L_d = D/v$ is the dispersivity (L). The parameter w is the Damköhler number [*Boucher and Alves*, 1959]. The dimensionless mass per surface area M_c in this system is defined as

$$M_c = \int_R [C + S C^N] dX \quad (7)$$

which results in the following relationship between M_c and M

$$M_c = \frac{M}{\theta c_r L_d} \quad (8)$$

We eliminated the dimensionless sorption coefficient S from the system by substitution of

$$u = C \left(S^{\frac{1}{N-1}} \right) \quad (9)$$

Substitution of equation (9) into equation (5) gives

$$\frac{\partial[u + u^N]}{\partial T} = \frac{\partial^2 u}{\partial X^2} - \frac{\partial u}{\partial X} - wu \quad (10)$$

The dimensionless mass per surface area, M_u , is defined by:

$$M_u = \int_R [u + u^N] dX \quad (11)$$

Solutions of equation (10) are valid for every dimensionless sorption parameter S , differing only by a constant factor from each solution for C , as given by equation (9). Combining equations (7), (9) and (11) shows that M_u is the following function of the dimensionless mass per surface area.

$$M_u = S^{\frac{1}{N-1}} M_c \quad (12)$$

We consider solutions for applications of pesticides deposited at the soil surface, giving the initial condition

$$u = \delta(X) M_{u,0} \quad X > 0 \quad T = 0 \quad (13)$$

where $\delta(X)$ is the Dirac- δ function in space, and $M_{u,0}$ is defined as the dimensionless dose introduced into the system.

2.2. Leached Mass Fraction

[8] With respect to pesticide leaching, the main interest is in the fraction of the applied mass that arrives in groundwater, i.e., the leached fraction. For linear sorption ($N = 1$) and ignoring dispersion, the leached fraction F that passes a defined reference distance L (L) over infinite time, is determined by

$$F = \frac{M_{L,\infty}}{M_0} = \exp\left[-\frac{kL}{v}\right] \quad (14)$$

as shown by *Jury and Roth* [1990] and applied by *van der Zee and Boesten* [1991].

[9] *Jury and Gruber* [1989] derived the analytical solution for the leached fraction of a linearly sorbing and degrading pesticide subject to dispersion. They assumed degradation both in liquid and sorbed phases. Using their solution we derived the following solution for the leached fraction for a system with degradation in only the liquid phase:

$$F_d = \frac{M_{L,\infty}}{M_0} = \exp\left[-0.5 \frac{L}{L_d} (\sqrt{1 + 4w} - 1)\right] \quad (15)$$

van Genuchten and Cleary [1979] presented an equation for the steady state value of the resident concentration during breakthrough of a continuous feed solution of a linearly sorbing solute that is degraded in the liquid phase. On the basis of results from numerical calculations of nonlinearly sorbing solutes, they observed that their steady state solution holds regardless of adsorption of the solute, and hence is independent of the particular form of the sorption

isotherm. This follows also from equation (4) assuming a continuous input, i.e., $\partial c/\partial t = 0$. We rewrote their equation in terms of flux concentrations and found again equation (15). In view of this, equation (15) is likely to be valid as well for pulses of nonlinearly sorbing solutes that are degraded in the liquid phase.

2.3. Approximations for the Remaining Mass and the Center of Mass

[10] We focus our study on the spatial moments [*Valocchi*, 1989] of the total mass of the pulse in the liquid and the solid phase. The zeroth spatial moment has already been defined in equation (7). The first spatial moment (the position of the center of mass) or the mean traveled distance μ^* is defined as

$$\mu^* = \frac{1}{M_c} \int_R X(C + S C^N) dX \quad (16)$$

We use the spatial moments to assess the impacts of the three dimensionless parameters that determine the transport of nonlinearly sorbing solutes according to equations (10), (11) and (13): (1) mass in the system M_u , (2) Freundlich exponent N and (3) Damköhler number w .

[11] Our goal is to find analytical approximations of M_u and μ^* . The procedure is to base these approximations on simplifications and to demonstrate later that these simplifications are defensible by comparing them with numerical solutions. We start with the approximation for M_u . The simplification is that an approximation for a system with a Freundlich isotherm can be based on a system with a linear sorption isotherm. The inspiration for this simplification comes from the claim in section 2.2 (based on *van Genuchten and Cleary* [1979]) that the solution for the fraction leached (i.e., equation (15)) derived for a linear isotherm is valid also for non-linear sorption. Similarly, we base an analytical expression for the total remaining amount of pesticide residing in the soil profile also on a system for a linear isotherm.

[12] To derive this analytical expression for M_u , we use solutions given by *Jury and Roth* [1990]. They derived analytical solutions for the spatial moments using a Laplace transform of the travel distance PDF representing the solute resident concentrations as a function of distance x at a fixed time t from a pulse input (Dirac- δ) of an inert substance to the CDE [pp. 55 and 181]. We included linear sorption and transformation in the liquid phase in the CDE and applied *Jury and Roth's* Laplace transforms, obtaining the following expression for remaining mass

$$M_u = M_{u,0} \exp\left(-\frac{wT}{R}\right) \quad (17)$$

(where $R = 1 + S$) and for the center of mass:

$$\begin{aligned} \mu^* = & \sqrt{\frac{T}{\pi}} \exp\left(-\frac{T}{4R}\right) \\ & + \frac{1}{2} \left[\left(1 + \frac{T}{R}\right) \operatorname{erfc}\left(-\frac{1}{2} \sqrt{\frac{T}{R}}\right) - \operatorname{erfc}\left(\frac{1}{2} \sqrt{\frac{T}{R}}\right) \right] \end{aligned} \quad (18)$$

Equation (18) is the same as the solution derived by Jury and Roth, but with T replaced by T/R . Hence for large times T the center of mass is approximated by:

$$\mu^* = 1 + \frac{T}{R} \quad (T/R \gg 4) \quad (19)$$

We combine equations (17) and (19) and thus obtain a relation between the mass and the center of mass for linear sorbing pulses,

$$M_u = M_{u,0} \exp[-w(\mu^* - 1)] \quad (20)$$

Equation (20) is valid for $T/R \gg 4$, hence for $\mu^* \gg 5$ (see equation (19)), which means the traveled distance is larger than 5 times the dispersivity L_d . Equation (20) includes neither sorption parameters nor time T , which implies that the mass remaining in the system centered at $X = \mu^*$ depends neither on sorption nor time. As described before, we expect that equation (20) is also valid for nonlinear sorbing solutes. We use this as a working hypothesis that will be checked numerically later.

[13] To proceed, we make the following simplifications: (1) at large times, the mass in the liquid phase can be ignored due to nonlinear sorption, because at low total concentration most of the mass is sorbed, the concentration in the solute phase becomes small, and $u + u^n$ in the left side of equation (10) can be approximated by u^n [van Duijn *et al.*, 1997], (2) the dispersion term in equation (10) can be ignored because nonlinear sorption dominates pulse spreading at large times and pore scale dispersion is of lesser importance [Fesch *et al.*, 1998; Bosma *et al.*, 1996], and (3) that no transformation is assumed to occur. The last assumption is shown later in this paper to be appropriate, when we substitute equation (20) into the analytical expression found for μ^* and compare the approximation with numerical solutions of equation (10). After the mentioned simplifications, the reduced equation describing transport of a nonlinearly sorbing pulse becomes

$$\frac{\partial u^N}{\partial T} + \frac{\partial u}{\partial X} = 0 \quad (21)$$

Using a similarity variable [see Grundy *et al.*, 1994], we derived the following expression for the center of mass based on equation (21):

$$\mu^* = \alpha_N M_{u,0}^{1-N} T^N \quad (22)$$

where α_N denotes

$$\alpha_N = \frac{N^{-N}(1-N)^{N-1}}{2-N} \quad (23)$$

See Appendix A for the derivation of equations (22) and (23). Equation (23) results in $\alpha_N = 1.33$ for $N = 0.5$, in $\alpha_N = 1.42$ for $N = 0.7$ and in $\alpha_N = 1.0$ for $N = 1$, hence α_N goes through a maximum between $N = 0.5$ and $N = 1$.

[14] We can now obtain an approximation for the center of mass for a system with first-order transformation in

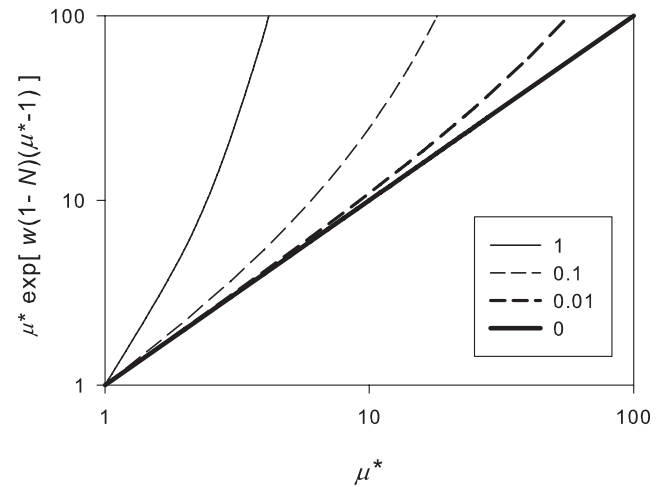


Figure 1. The function $\mu^* \exp[w(1-N)(\mu^*-1)]$ of equation (25) as a function of μ^* for different values of $w(1-N)$ as indicated.

the liquid phase, by substituting the expression for M_u of equation (20) into equation (22), resulting in

$$\mu^* = \alpha_N \{M_{u,0} \exp[-w(\mu^* - 1)]\}^{1-N} T^N \quad (24)$$

Equation (24) can be rewritten to

$$\mu^* \exp[w(1-N)(\mu^* - 1)] = \alpha_N M_{u,0}^{1-N} T^N \quad (25)$$

Equation (25) is an implicit function of μ^* that cannot be further simplified. Its right hand side is identical to that of equation (22), which concerns a non-degrading pulse. Hence the term $\exp[w(1-N)(\mu^* - 1)]$ is responsible for the impact of transformation on the movement.

[15] To grasp the behavior of equation (25), the left side of equation (25) is plotted in Figure 1 as a function of μ^* for different values of $w(1-N)$. If $w(1-N) = 0$, the function reduces to the 1:1 line and equation (25) reduces to the solution for no degradation. For the other values of $w(1-N)$, the figure gives a measure of the impact of the term $\exp[w(1-N)(\mu^* - 1)]$ on the resulting μ^* value. The faster the degradation proceeds, the stronger the reduction in movement. With increasing time, the value of the right side of equation (25) increases. Hence increasing time implies shifting to higher values of the vertical axis in Figure 1, which shows increasing divergence of the four lines for higher values of the vertical axis. Consequently Figure 1 implies that the deviation from the “ T^N type of behavior” of equation (25) increases with increasing time.

[16] Now, with equations (20) and (25), we have obtained analytical approximations for the mass and for the center of mass of nonlinearly sorbing solutes transformed in the liquid phase, which are tested and explored in the results section.

2.4. Procedures for Numerical Solutions

[17] A numerical procedure was developed to check the analytical approximations. Equation (10) was solved nu-

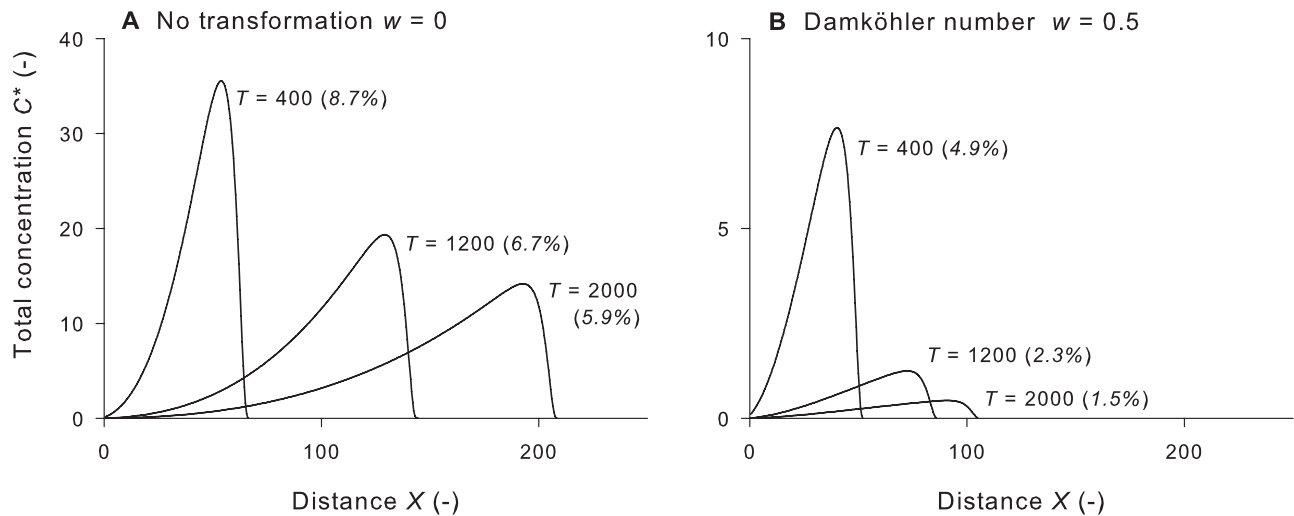


Figure 2. The dimensionless total concentration C^* ($= C + SC^N$), for $T = 400, 1200$ and 2000 as calculated numerically using equations (5) and (6) for $\nu = 0.02 \text{ m d}^{-1}$, $\theta = 0.5$, $\rho = 1000 \text{ kg m}^{-3}$, $L_d = 0.1 \text{ m}$, $c_r = 1 \text{ g m}^{-3}$, $\Delta x = 0.2 \text{ m}$, $\Delta t = 0.1 \text{ d}$, $K_F = 1 \text{ L kg}^{-1}$, $N = 0.7$, $k = 0.01 \text{ d}^{-1}$ and $M_0 = 0.1 \text{ g m}^{-2}$. Part A shows results for no degradation and part B for $w = 0.5$. Between brackets the percentage of total mass in the system that is dissolved is indicated. Note that the scales of the vertical axes in A and B differ.

merically using an explicit finite difference scheme. The concentration between the grid points was estimated with a central difference approximation which suppresses numerical dispersion [van Genuchten and Wierenga, 1974]. Time integration was carried out with Euler's method. The procedure was checked against analytical solutions for a system with linear sorption.

[18] For most of the numerical simulations, we defined 100 to 2000 layers with thickness $\Delta X = 0.5$ and used a time step of $\Delta T = 0.2$. At the start of the simulations, the applied pesticide was assumed to be present in the top layer. All system properties are assumed to be constant in space and time. We calculated the concentration distributions in the system to determine the spatial moments for a number of combinations of M_u , N and w . The moments as defined by equations (7) and (16) were calculated via numerical integration.

3. Results and Approximations

3.1. Illustrative Concentration Profiles

[19] To illustrate the impact of nonlinear sorption on solute transport, Figure 2 shows some concentration profiles calculated with equation (10) and a numerical solution procedure. First, the concentration profiles without degradation are discussed (Figure 2a). The skewness of the front of the solute profile increases in time, leaving a concentration tail behind, which is characteristic for the nonlinearly sorbing pulse [see van Genuchten and Cleary, 1979]. The velocity of a nonlinearly sorbing solute pulse decreases with depth [Bosma et al., 1996]. Because of the sorption nonlinearity, the ratio dissolved:adsorbed shifts to less solute in the liquid phase, illustrated by the 8.7% decrease of the total mass in solution at $T = 400$ to 5.9% at $T = 2000$. Then, as time increases and the penetration of the pulse into the soil increases, the pulse velocity decreases.

[20] Figure 2b shows results that include degradation of the solute. The progress of the pulse through the system slows down. A decreasing part of the total mass in the system is dissolved, illustrated in Figure 2b by the number of 4.9% of the total mass present in solution at $T = 400$ decreasing to 1.5% at $T = 2000$, and therefore less available for transport, as well as less available for degradation.

[21] Hence solute transport, assuming degradation in the liquid phase, is affected by sorption in a complex way if sorption is a nonlinear process. Both movement and degradation are affected. In this paper, we assess the interaction between these two processes.

3.2. Mass Fraction Leached

[22] We tested our hypothesis that the leached fraction of a pulse for a system described by equation (10) with a nonlinear sorption isotherm is equal to the leached fraction of the corresponding system with a linear isotherm. We did so for a range of parameters as shown in Figure 3. The leached fraction calculated numerically corresponds very well with the analytical prediction from equation (15). Appendix B shows that the leached fractions calculated for a two-site sorption model using N values ranging from 0.8 to 1 were also predicted well with equation (15). We conclude that the hypothesis (the leached fraction of a pulse does not depend on the sorption model) is strongly supported by our calculations. Hence despite the impact of sorption nonlinearity on the traveltime of the pulse through the soil, the fraction of the dose that leaches to groundwater does not depend on the slope or the shape of the sorption isotherm. The only loss process in the model is degradation. Thus pulses of strongly sorbing substances move slower through soil than pulses of weakly sorbing substances, but strongly sorbing substances are also degraded slower than weakly sorbing substances. The confirmation of our hypothesis shows that these opposing effects cancel out

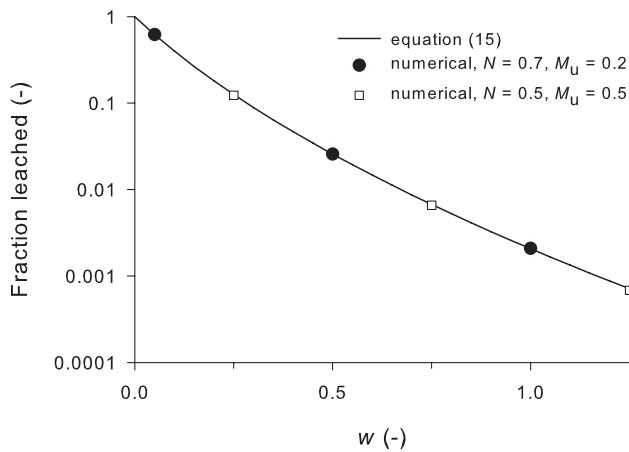


Figure 3. Comparison of analytically and numerically calculated leached fraction as a function of the Damköhler number w . The line is the analytical solution calculated with equation (15) for $L_d = 0.1$ m and a depth, L , of 1 m. The dots are numerical solutions for parameter values as indicated in the figure.

exactly with respect to the fraction that passes a certain depth.

3.3. Remaining Mass in System

[23] We tested the extent to which equation (20) can be used to predict the remaining mass for a system with nonlinear sorption as a function of the center of mass. A few examples of these checks (Figure 4) show that our analytical approximation corresponds very well with the numerical results. A restriction on the use of equation (20) is $\mu^* \gg 5$. Nevertheless, even for values of μ^* below 5, the correspondence between numerical result and approximation is very good. The curves cross at $\mu^* = 1$ (not shown). Below $\mu^* = 1$ the equation gives unrealistic results of mass higher than the initial mass. The relationship described by equation (20) was also tested for other M_u and for N values between 0.5 and 1, and similar results were obtained.

[24] The theoretical backing for the successful prediction of equation (20) for systems with nonlinear sorption is similar to that of the indifference of the mass fraction leached to sorption: pulses of strongly sorbing substances move slower through soil. Hence strongly sorbing substances need more time to reach a certain average depth than weakly sorbing substances. At first glance, one would expect that the remaining mass of a strongly sorbing substance when it has reached a certain depth is smaller than that of a weakly sorbing substance. However, strongly sorbing substances are also degraded more slowly than weakly sorbing substances. The success of equation (20) shows that these opposing effects also cancel out each other so that the remaining mass in the soil profile has the same center of mass for all combinations of sorption parameters.

3.4. Center of Mass

[25] To verify the validity of equation (25), centers of mass calculated with equations (22) and (25) are compared with centers of mass from numerical simulations for some representative combinations of N and w for realistic values of M_u (Figure 5). Figure 5 shows that equation (22) (i.e.,

the approximations for no degradation) describes the strong effect of N on the time course of the center of mass well. Equation (22) overestimates the centers of mass for all three N -values with a difference of about 10–20%, except for the first time points of $N = 0.5$. However, there is no systematic discrepancy in the approximation related to the value of the Freundlich exponent N . We therefore reject the possibility that this discrepancy is related to the Freundlich exponent. The overestimation of the centers of mass must be due to ignoring the mass in solution and ignoring dispersion as described before.

[26] Comparing the approximation including degradation with numerical results in Figures 5b to 5d shows that equation (25) describes the strong effect of N on the time course of the center of mass well also if the pesticide is degraded. With increasing Damköhler number the approximation shifts from slight overestimation of numerical centers of mass to slight underestimation of numerical centers of mass. Nevertheless, the approximations in Figures 5b to 5d describe the centers of mass, better than the approximation for Damköhler number zero in Figure 5a. Obviously the different simplifications have opposing effects on the differences between numerical and analytical results in Figure 5, thus compensating each other to some extent.

[27] The results of the simulations presented in Figure 5 indicate that the approximations given by equations (22) and (25) describe the first spatial moment of pulses well, considering that they were derived for a system without dispersion and ignoring the mass in the liquid phase. These approximations demonstrate the impact of the transport parameters on the mass and movement of nonlinearly sorbing and degrading solutes like pesticides. The mass and the movement of a solute pulse are affected by two opposing effects of sorption nonlinearity. First, when the Freundlich exponent N decreases, displacement of the pulses slows down because the mass in solution (available for movement) decreases. Secondly, when N decreases, the degradation rate decreases, because the mass in solution

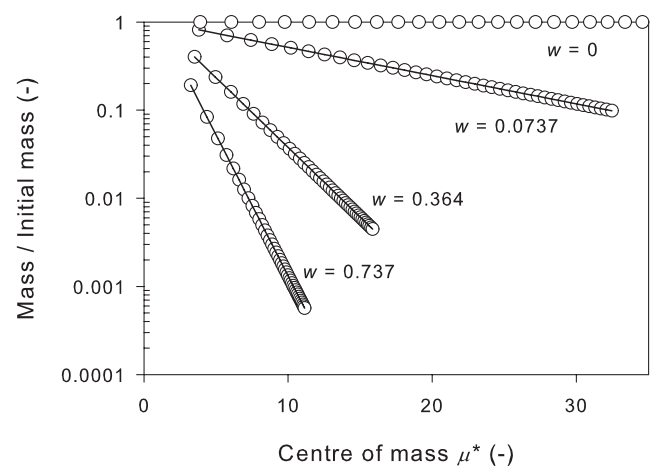


Figure 4. The dimensionless mass, M_u , as a function of the dimensionless center of mass, μ^* , for Damköhler numbers w as indicated in graph. The Freundlich exponent N is 0.7 and the initial mass $M_{u,0}$ is 0.1. The points are numerically calculated based on equation (10), and the lines are calculated with equation (20).

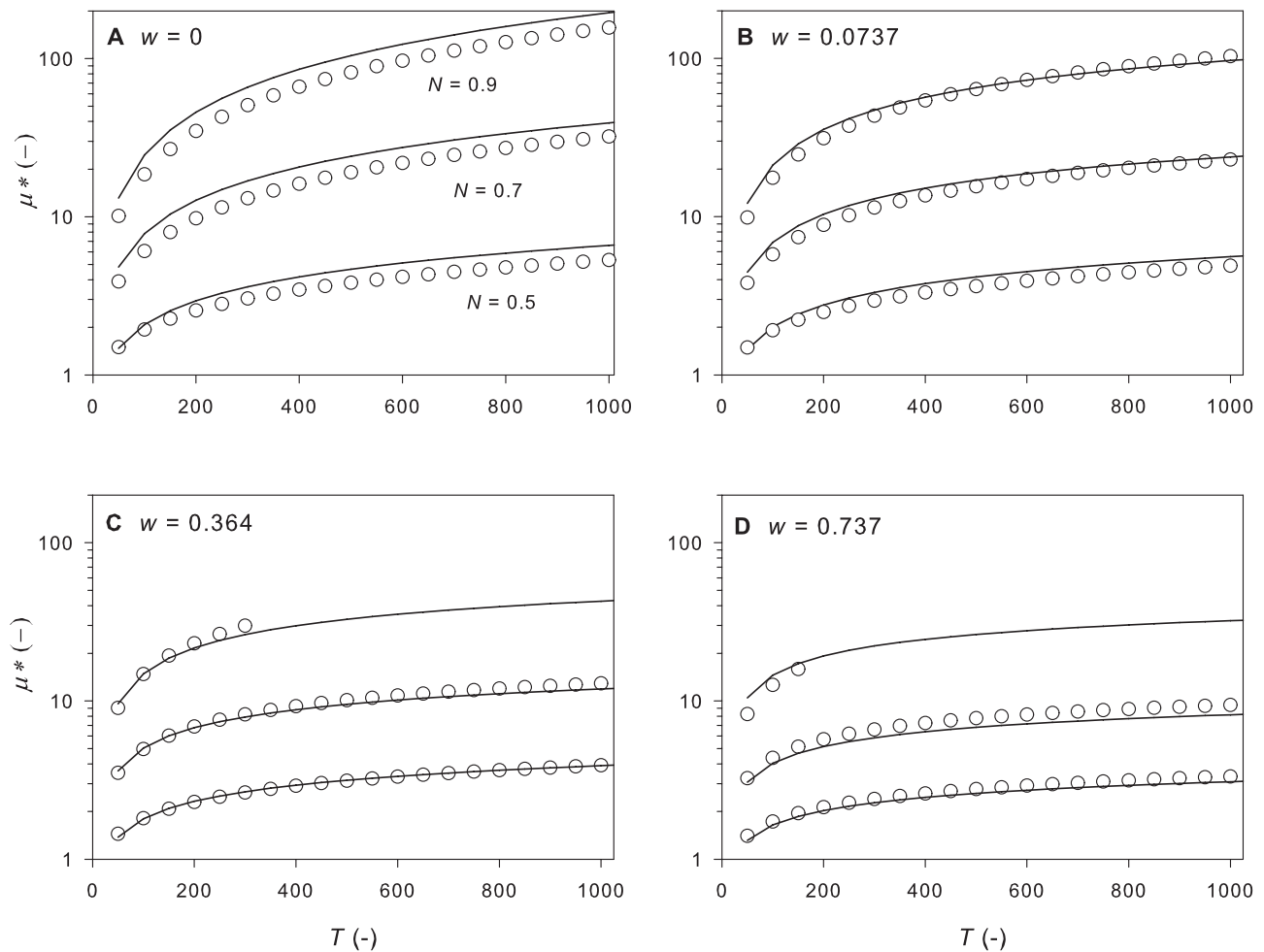


Figure 5. Comparison of the centers of mass, μ^* , calculated numerically and analytically. The numerical calculations are based on equation (5). The analytical calculations are done with equation (22) in part A, and with equation (25) in parts B – D (note that equation (25) reduces to equation (22) if $w = 0$). Calculations are carried out for N values 0.5 (lower curves), 0.7 (middle curves) and 0.9 (upper curves) as indicated in part A. The initial mass for the numerical calculations is $M_0 = 0.1 \text{ g m}^{-2}$, hence dimensionless initial mass $M_{u,0} = 0.018$ for $N = 0.5$, $M_{u,0} = 0.0031$ for $N = 0.7$ and $M_{u,0} = 0.45 \cdot 10^{-6}$ for $N = 0.9$. (a) is for Damköhler number 0, (b) for Damköhler number 0.0737, (c) for Damköhler number 0.364, (d) for Damköhler number 0.737.

(available for degradation) decreases. Consequently, each of the two processes (transport and degradation) slows down the progress of the other process; slower displacement velocities imply longer degradation periods for decreasing mass, whereas slower degradation rates imply a larger mass and therefore larger displacement velocities.

[28] To test equation (25) for masses other than presented, we performed additional calculations with injected masses that were 100 times larger and masses that were 100 times smaller, for $N = 0.7$ with $w = 0.0737$ and with $w = 0.364$. The discrepancies between analytical and numerical μ^* were comparable to those found in Figures 5b–5d for $N = 0.7$.

[29] It was expected that equation (25) would not work well in the initial period, because the assumptions made for the analytical approximation (ignoring dispersion and ignoring the mass in solution) are unlikely to be valid in the initial period. Furthermore, if μ^* is smaller than 5, then the restriction of equation (2) $\gg 4$ leads to a discrepancy.

However, also in the initial period the approximation predicts the centers of mass well.

4. General Discussion and Conclusions

[30] The spatial moments, mass (zeroth moment) and center of mass (first moment) of a solute pulse moving through the soil system were approximated analytically. First, by ignoring mass present in the liquid phase and dispersion, an approximation was derived for the center of mass of a nondegraded nonlinear sorbing solute. Secondly, for a linear sorbing solute that is degraded in the liquid phase a relation was derived between the mass and center of mass. Combining the two results gave an implicit solution for the center of mass of a nonlinear sorbing solute degraded in the liquid phase as a function of time.

[31] Analytical and numerical solutions showed that the fraction of a pesticide application that leaches to groundwater depends neither on the Freundlich sorption coefficient

nor on the curvature of the Freundlich isotherm. The mass leached appeared to be a function of the Damköhler number, i.e., the product of degradation rate coefficient (k) and dispersivity (L_d) divided by flow velocity (v). Furthermore, mass as a function of center of mass is also a function of the Damköhler number. Our analytical solution approximated the progress of the center of mass of a nonlinear sorbing pulse as calculated by a numerical model very well. Comparing these spatial moments of nonlinearly sorbing solutes with spatial moments of linearly sorbing solutes revealed that the nonlinearity of sorption increases the traveltime of a solute pulse through the system. However, it also decreases the degradation rate of the solute pulse. These two effects were shown to compensate each other exactly, if we consider the mass fraction leached beyond a certain depth.

[32] Our results describe the fate of pesticides that leach to groundwater. Nonlinear sorption has no impact on the total amount of pesticide that in due course leaches to groundwater. The traveltime of the center of mass to the groundwater table increases strongly with increasing nonlinearity of sorption. For nonlinearly sorbing pulses the shape of the concentration distribution becomes more skewed with increasing nonlinearity of sorption, with a steep upstream gradient. Therefore the first traces of nonlinearly sorbing pesticides enter groundwater later than first traces of linearly sorbing pesticides. At the time the center of mass passes the groundwater table, the front of linearly sorbing pesticide pulses has penetrated deeper into the groundwater than the front of the skewed distributed nonlinearly sorbing pesticides. On the other hand, it also means that linearly sorbing pulses will pass the groundwater table relatively quickly, whereas the tail of nonlinearly sorbing pesticide may be very slow. Thus traces of pesticides may still cross the groundwater table long after the center of mass passed.

[33] We made assumptions regarding (1) a uniform soil profile (so sorption and degradation rate uniform with depth), (2) steady state water flow, (3) application of individual pulses, and (4) zero and first spatial moments of concentration profiles. Assessments of pesticide leaching to groundwater are usually based on (1) heterogeneous soil profiles (sorption and degradation rate function of depth), (2) non-steady water flow, (3) multiple applications, and (4) leaching concentrations at 1 m depth averaged over periods of typically one to three years (see e.g., the FOCUS groundwater scenarios used in EU pesticide registration [FOCUS, 2000]). Hence it is still open for debate whether the message of this paper should have implications for pesticide registration. To address this issue, we did calculations for one of these FOCUS groundwater scenarios with (A) the conventional degradation rate concept (rate proportional to total concentration) and (B) a degradation rate proportional to θc (i.e., the approach followed in this paper). This was done with the PEARL model which is based on a Darcian water flow model combined with a CDE-type leaching model [Boesten, 2007], and is an accepted instrument in EU pesticide registration. Appendix C shows that for such a heterogeneous soil with non-steady flow both the leached mass and the leaching concentration as used in EU pesticide registration become much less sensitive to the sorption coefficient and becomes completely insensitive to the Freundlich exponent when concept A is

replaced by concept B. This indicates that switching to the concept of a degradation rate that is proportional to θc may turn out to be a major improvement of the regulatory risk assessment of pesticide leaching.

[34] The results in this paper can be applied to the transport of pesticides in groundwater to drinking water wells, by considering transport to take place along a one-dimensional stream tube to the well. Protection zones around drinking water wells, where no pesticides may be applied, can be smaller, taking into account the effect of degradation in the saturated zone [Neupauer and Wilson, 2003; Beltman *et al.*, 1995]. This study shows that sorption does not affect the pesticide mass that will arrive at a reference point, i.e., in the well, under the condition that pesticides degrade in the liquid phase only. Hence by combining degradation rates in the saturated zone with traveltime distributions of capture zones of a drinking water well the protected zone can be estimated, without the need to consider sorption processes.

[35] In the risk assessment pesticide sorption is held to be of great influence on pesticide leaching to groundwater. Our analysis suggests that the sorption is often attributed the wrong role: it does affect the moment of leaching, but not the amount leached. Therefore our work suggests a redirection of sorption research. More attention should be given to how sorption affects the degradation of pesticides in soil. We note, that the focus toward pesticides in this work concerns only the parameter values that were considered. Regarding the conclusion of independency of the leached quantities on sorption, it is clear that it holds for all first order degradable contaminants for which degradation occurs in the liquid phase only (excluding radioactive decaying solutes).

Appendix A: First Spatial Moment (Center of Mass) of $u(X, T)$

[69] Grundy *et al.* [1994] introduced a similarity variable for $u(X, T)$ for $N < 1$,

$$\eta = \frac{X}{T^N} \quad (\text{A1})$$

with

$$u(X, T) = \frac{\lambda(\eta, T)}{T} \quad (\text{A2})$$

Substitution of equations (A1) and (A2) into equation (21) to get the time independent partial differential equation for λ gives

$$N \eta \frac{\partial \lambda^N}{\partial \eta} + N \lambda^N - \frac{\partial \lambda}{\partial \eta} = 0 \quad (\text{A3})$$

[Grundy *et al.*, 1994]. The solution for λ is then

$$\lambda = (N\eta)^{\frac{1}{1-N}} \quad (\text{A4})$$

[Grundy *et al.*, 1994]. Then the solution for u is

$$u = T^{-1} \left(\frac{NX}{T^N} \right)^{\frac{1}{1-N}} \quad (\text{A5})$$

Equation (A5) implies that u increases continuously with depth. Because of the mass conservation condition (equation (11)), ignoring dissolved mass and under the condition that the solution is confined to the interval $0 < \eta < \eta_2$, M_u can be calculated as [see *Grundy et al.*, 1994]:

$$M_u = \int_0^{\eta_2} \left[(N\eta)^{1/(1-N)} \right]^N d\eta \quad (\text{A6})$$

We substitute η of equation (A1), apply that the mass is conserved between 0 and η_2 and then bring η_2 to the left side of the equation giving the upper boundary for which the solution equation (A4) is valid

$$\eta_2 = N^{-N} (1 - N)^{N-1} M_u^{1-N} \quad (\text{A7})$$

[*Grundy et al.*, 1994]. Above this upper boundary, i.e., $\eta > \eta_2$, the value of λ is zero.

[70] Using the above results from *Grundy et al.* [1994], we derive the first spatial moment (equation (16)) of the concentration distribution. Ignoring the dissolved mass we get

$$\mu^* = \frac{\int_0^{X_2} X u^N dX}{\int_0^{X_2} u^N dX} \quad (\text{A8})$$

where $X_2 = \eta_2 T^N$. Substituting the solution for u (equation (A5)) and using equation (A7) for the upper boundary of X results in:

$$\mu^* = M_u^{1-N} T^N \frac{N^{-N} (1 - N)^{N-1}}{2 - N} \quad (\text{A9})$$

Appendix B: Comparison of Predicted and Calculated Total Leached Fractions, Using Different Sorption Models

[71] We tested the hypothesis that the leached fraction is predicted correctly with equation (15). The test was based on calculations with sorption models that comprise nonlinear sorption and non-equilibrium sorption.

[72] In the calculations, transport of solute was described with the CDE and first order degradation kinetics (equation (1)). Two sorption models were considered: (1) Freundlich equilibrium sorption (consisting of equation (2)), (2) a two-site Freundlich sorption model that consists of equilibrium sites and non-equilibrium sites defined by equations (B1), (B2) and (B3):

$$q_{tot} = q_{eq} + q_{ne} \quad (\text{B1})$$

$$q_{eq} = K_{F,eq} c_r \left(\frac{c}{c_r} \right)^N \quad (\text{B2})$$

$$\frac{\partial q_{ne}}{\partial t} = k_d \left[K_{F,ne} c_r \left(\frac{c}{c_r} \right)^N - q_{ne} \right] \quad (\text{B3})$$

Table B1. Parameters Used in the Calculations Shown in Figure B1

Parameter and Units	Symbol	Value
Volume flux of water, $\text{m}^3 \text{m}^2 \text{a}^{-1}$	Q	0.5
Dispersivity, m	L_d	0.05
Volumetric moisture content (-)	θ	0.25
Bulk density, kg m^{-3}	ρ	1500
Pesticide dose, g m^{-2}	M_0	0.1
Degradation rate coefficient, d^{-1}	k	0.0347
Freundlich equilibrium sorption model		
Sorption coefficient equilibrium sites, L kg^{-1}	K_F	1
Freundlich non-equilibrium sorption model		
Sorption coefficient equilibrium sites, L kg^{-1}	$K_{F,eq}$	0.5
Sorption coefficient non-equilibrium sites (L kg^{-1})	$K_{F,ne}$	0.5
Desorption rate coefficient, d^{-1}	k_d	0.002

with:

q_{tot} = total content sorbed to equilibrium sites, M M^{-1} ;
 q_{eq} = content sorbed to equilibrium sites, M M^{-1} ;
 q_{ne} = content sorbed to non-equilibrium sites, M M^{-1} ;
 k_d = desorption rate coefficient, T^{-1} ;
 $K_{F,eq}$ = Freundlich sorption coefficient for the equilibrium sites, $\text{L}^3 \text{M}^{-1}$.
 $K_{F,ne}$ = Freundlich sorption coefficient for the non-equilibrium sites, $\text{L}^3 \text{M}^{-1}$.

[73] We selected parameter values (see Table B1) in such a way that the cumulative leached fraction was about 0.5% of the dosage, to obtain a powerful test of the theory. The total sorption coefficient (i.e., the sum of $K_{F,eq}$ and $K_{F,ne}$) is 1 L kg^{-1} in all calculations. For the two-site model, half of this total sorption coefficient is assigned to equilibrium sorption, and the other half to non-equilibrium sorption. The Freundlich exponents N used were 1.0, 0.9 and 0.8 ($N=1$ is linear sorption).

[74] The numerical model described in equations (1) and (2) was extended with equations (B1), (B2) and (B3) for numerical simulation with the two sorption models. Numerical calculations were done with 100 layers of 0.01 m and a time step of 0.1 d. To verify the numerical calculations of the Freundlich non-equilibrium model, we used the analytical solution for the flux concentration as a function of time for a specified depth derived by *Toride et al.* [1993], which is their equation (14). This analytical solution assumes a linear sorption isotherm ($N=1$). Figure B1 shows that the numerical results of the two-site model correspond very well with their analytical solution. So the numerical solution was sufficiently accurate.

[75] Figure B1 shows that the arrival time of the solute pulse below 1 m depth increases with decreasing Freundlich exponent N , as could be expected. The shapes of the curves show that the solute dispersal increases with decreasing N . This solute dispersal becomes larger when non-equilibrium sorption is included. Most important is that the cumulative leached fraction after ‘‘infinite’’ time (in practice about 10 000 d) was accurately predicted by equation (15) in all cases, whereas equation (15) does not contain any sorption parameter.

[76] Equation (14) of *Toride et al.* [1993] shows that the flux concentration for the two-site model ($N=1$) is a very complicated function of time: e.g., it already contains an

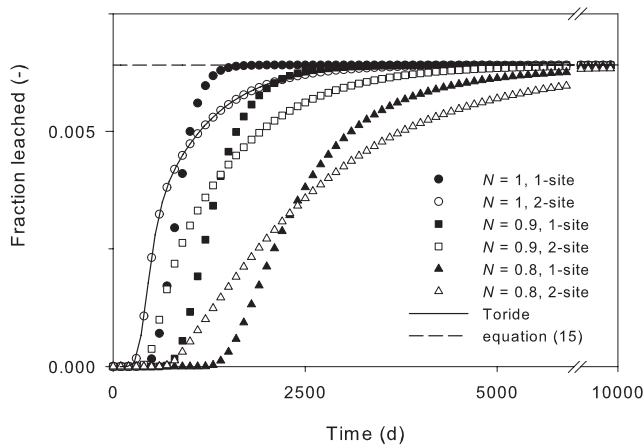


Figure B1. Cumulative leached fraction at 1 m depth as a function of time calculated with a Freundlich 1-site equilibrium sorption model and with a Freundlich two-site equilibrium/non-equilibrium sorption model. The markers denote numerical calculations for Freundlich exponents $N = 1, 0.9$ and 0.8 . The solid line shows the result of the analytical solution of *Toride et al.* [1993] for the two-site model with $N = 1$. The dashed horizontal line shows the total leached fraction calculated with equation (15). Note the interruption of the horizontal axis (necessary to demonstrate the convergence of all calculated lines to the dashed line).

integral over time of the modified Bessel function of order one. It seems practically impossible to solve the infinite time integral of the flux concentration via analytical methods, so the theory that results in equation (15) seems also to be very powerful in mathematical terms, as it provides an analytical solution of the infinite time integral of the extremely complicated analytical function of *Toride et al.* [1993]. Even more surprisingly, our equation (15) provides an analytical solution for the infinite time integral of the flux concentration for equilibrium and non-equilibrium Freundlich systems for which no analytical expression of the flux concentration itself is available.

[77] Hence the calculations shown in this appendix support the hypothesis that the comparatively simple equation (15) for the infinite integral of the flux concentration in linear sorption systems is valid in general for all sorption systems in which degradation occurs in the liquid phase only.

Appendix C: Sensitivity of Pesticide Leaching to Sorption Parameters Assuming Degradation Only in the Liquid Phase for a FOCUS Groundwater Scenario

C1. Procedure

[78] Calculations were carried out for one of the nine FOCUS groundwater scenarios which are used for the assessment of leaching in the pesticide registration procedure in the EU [FOCUS, 2000]. Calculations were done with the PEARL model for which *Boesten* [2007] gives a description of both the model and the calculation procedure used in the FOCUS scenarios. Two types of models were used: (A) the standard n of the model used for

regulatory risk assessment (version FOCUS_PEARL v3.3.3, available at <http://viso.ei.jrc.it/focus>) which assumes a degradation rate proportional to the total concentration in soil, and (B) a modified version of PEARL that assumes transformation in the liquid phase only. Hence model (A) was based on the following rate equation:

$$R = k_{tot} \left[\theta c + \rho K_F c_r \left(\frac{c}{c_r} \right)^N \right] \quad (C1)$$

where R is the rate of degradation of the pesticide ($M L^{-3} T^{-1}$) and k_{tot} is the rate coefficient for degradation of the pesticide in the combined liquid and solid phases (T^{-1}). This coefficient k_{tot} is the product of a rate coefficient at reference conditions, $k_{tot,ref}$ and three factors accounting for effects of soil temperature, soil moisture content and soil depth. From this $k_{tot,ref}$ the half-life at reference conditions, $DegT50$, can be calculated as $\ln [2]/k_{tot,ref}$. The reference conditions are defined as $20^\circ C$, field capacity, and topsoil.

[79] Model (B) was based on the equation:

$$R = k \theta c \quad (C2)$$

where k is the product of a rate coefficient at reference conditions, k_{ref} , and the same three factors as above. From this k_{ref} the half-life at reference conditions in the liquid phase, $DegT50_{liq}$, can be calculated as $\ln [2]/k_{ref}$.

[80] Calculations were made for the FOCUS Hamburg scenario (see *Boesten* [2007] for a detailed description of the scenario parameters). The top 60 cm of the soil is sandy loam and it is sand below 60 cm. The organic matter content decreases from 2.6% in the top 30 cm to 0 below 75 cm depth. The crop was summer wheat and pesticide was applied every three year at a rate of 1 kg/ha on 30 March just before crop emergence. The weather consisted of a 60-year time series of daily values.

[81] Calculations were made for a range of hypothetical pesticides with varying values of $DegT50$, $DegT50_{liq}$, N and the organic-matter/water distribution coefficient K_{OM} (defined as K_F divided by the mass fraction of organic matter). Thus K_F varies with depth using the organic matter profile. All other properties (molar mass, water solubility, vapor pressure etc.) of the hypothetical pesticides were equal to those described in Table 2 of *Boesten* [2007]. Only equilibrium sorption based on a Freundlich isotherm was taken into consideration. Simulations were made for application every 3 year using a 66-year simulation period. Results of the first 6 year (the so-called warming-up period) were not evaluated, resulting in a 60-year evaluation period. Leaching was characterized by (i) cumulative mass of pesticide leached at 1 m depth over the 60-year evaluation period and (ii) flux concentrations at 1 m depth averaged over 3-year periods. The 3-year averages were characterized by the 80th percentile concentration from a series of 20 triennial periods [FOCUS, 2000]. This 80th percentile was calculated by taking the 17th value of the 20 ranked values and is called “the FOCUS leaching concentration”. The cumulative mass of the dose leached was considered because it is closely related to the leached fraction. The FOCUS leaching concentration was considered because it is used in EU pesticide registration.

[82] When assessing the effect of the model choice on the sensitivity of the Freundlich exponent, the starting point has to be a single pesticide that has the same leaching concentration for both models. The model substance D as defined by FOCUS [2000] was considered suitable for that purpose because its FOCUS leaching concentration is $0.053 \mu\text{g/L}$, so close to the $0.1 \mu\text{g/L}$ which is the groundwater criterion within the EU. The $DegT50$ of substance D is 20 d, its K_{OM} is 35 L/kg and its N is 0.9. The corresponding $DegT50_{liq}$ value was estimated by inverse modeling using the model based on equation (C2) and by requiring that this model produces the same leaching concentration ($0.053 \mu\text{g/L}$). This resulted in a $DegT50_{liq}$ value of 2.7 d.

[83] The effect of the Freundlich exponent N was assessed by calculations with the model based on equation (C1) using a $DegT50$ of 20 d and a variable N . These were compared to calculations with the model based on equation (C2) using a $DegT50_{liq}$ of 2.7 d and a variable N . The effect of the K_{OM} was assessed by calculations with both models using (1) $DegT50 = DegT50_{liq} = 2.7$ d and (2) $DegT50 = DegT50_{liq} = 20$ d.

C2. Results

[84] Figure C1 shows that the calculated FOCUS leaching concentration is very sensitive to the Freundlich exponent N for the model based on equation (C1) but that this sensitivity disappears completely for the model based on equation (C2). This is important because N is currently an important parameter in the leaching risk assessment whereas it seems to become almost irrelevant when the degradation process is restricted to the liquid phase. Figure C2 shows that also the sensitivity to the K_{OM} is much less for the model based on equation (C2) than for the model based on equation (C1). The line for $DegT50 = 20$ d coincides with the line for $DegT50_{liq} = 20$ d when the K_{OM} is zero. This could be expected because then equation (C1) reduces to equation (C2), so the models become identical. Similarly the line for $DegT50 = 2.7$ d coincides with the line for

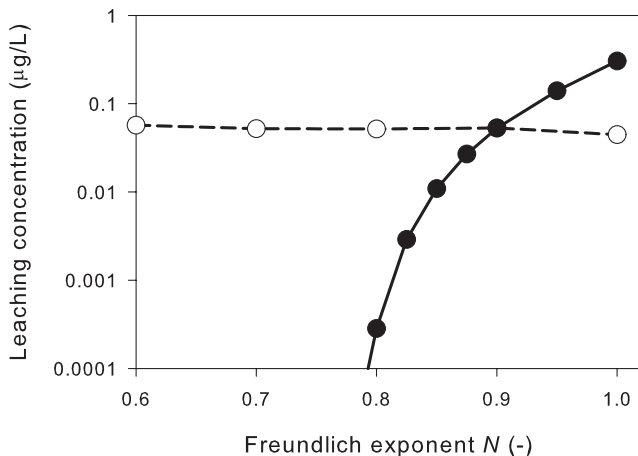


Figure C1. The FOCUS leaching concentration as a function of the Freundlich exponent for the FOCUS Hamburg scenario. The solid line was calculated with the model that simulates degradation in the combined liquid and solid phases using equation (C1) and a $DegT50$ of 20 d. The dashed line was calculated with the model that simulates degradation in only the liquid phase using equation (C2) and a $DegT50_{liq}$ of 2.7

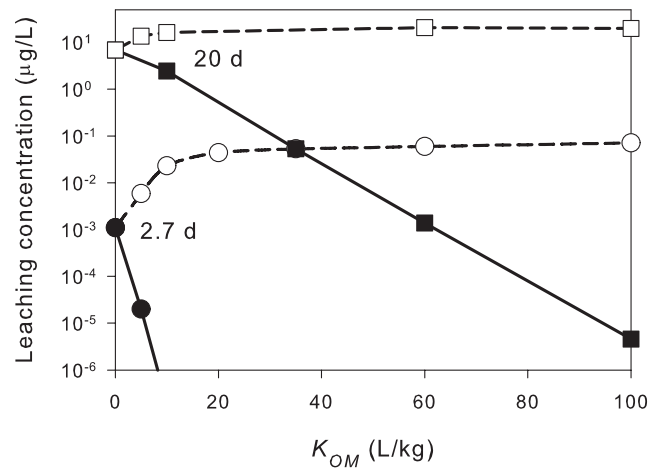


Figure C2. FOCUS leaching concentration as a function of the organic-matter/water distribution coefficient K_{OM} for the FOCUS Hamburg scenario. Solid lines were calculated with the model that simulates degradation in liquid and solid phase using equation (C1). Dashed lines were calculated with the model that simulates degradation in the liquid phase only using equation (C2). Lines with squares were calculated with $DegT50 = DegT50_{liq} = 20$ d and lines with circles were calculated with $DegT50 = DegT50_{liq} = 2.7$ d.

$DegT50_{liq} = 2.7$ d when the K_{OM} is zero. The line for $DegT50_{liq} = 20$ d (upper dashed line) shows almost no sensitivity to the K_{OM} whereas the line for $DegT50_{liq} = 2.7$ d (lower dashed line) shows sensitivity between $K_{OM} = 0$ and $K_{OM} = 10$ L/kg but again hardly any sensitivity above $K_{OM} = 10$ L/kg. Only few pesticides will have K_{OM} values below 10 L/kg, so in practice also the sensitivity to the K_{OM} has disappeared almost completely. Analysis of the calculated cumulative masses of pesticide leached over the 60-year evaluation period showed that these masses could be described well as a function of the FOCUS leaching concentrations by assuming that the masses were directly proportional to the concentrations. Hence graphs with the cumulative masses on the vertical axes showed the same shapes as those in Figures C1 and C2. The results in Figures C1 and C2 are of course of exploratory nature. However, they indicate that using equation (C2) may be a very promising scientific innovation in the risk assessment of leaching to groundwater.

Notation

- c concentration in the liquid phase, M L^{-3}
- c_r reference concentration in the liquid phase, M L^{-3}
- C dimensionless concentration, 1
- D hydrodynamic dispersion coefficient, $\text{L}^2 \text{T}^{-1}$
- F leached fraction, system without dispersion, 1
- F_d leached fraction, system with dispersion, 1
- k degradation rate coefficient, T^{-1}
- K_F Freundlich sorption coefficient, $\text{L}^3 \text{M}^{-1}$
- L reference distance, e.g., distance to groundwater table, L
- L_d dispersivity, L
- M areic mass, M L^{-2} (“areic” means divided by area)
- M_0 initial areic mass, M L^{-2}

M_c	dimensionless areic mass, 1
$M_{L,\infty}$	dimensionless areic mass passing reference distance L after infinite time, 1
M_u	dimensionless areic mass scaled to retardation, 1
$M_{u,0}$	initial mass, scaled to retardation, 1
N	Freundlich power, 1
q	pesticide content sorbed to the solid phase, $M M^{-1}$
t	time, T
T	dimensionless time, 1
S	dimensionless sorption coefficient, 1
u	dimensionless concentration, 1
v	flow velocity of pore water, $L T^{-1}$
w	Damköhler number (dimensionless degradation rate coefficient), 1
x	distance, L
X	dimensionless distance, 1
η	similarity variable
θ	volume fraction of liquid in the soil, $L^3 L^{-3}$
λ	similarity variable
μ^*	first spatial moment of the dimensionless system: center of mass, 1
ρ	dry bulk density of the soil, $M L^{-3}$

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