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Analytical Model for Removal of a Uniformly Distributed Single-Component NAPL Under Nonequilibrium Conditions

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Abstract

In this paper a simple analytical model is presented for the one-dimensional transport equation describing the removal of a uniformly distributed, single-component NAPL under nonequilibrium conditions. Both advective and dispersive transport are included in the model. The model describes two distinct stages: a solution for the time the amount of NAPL declines but the length of the NAPL-containing region remains constant, and a solution from the moment the front, behind which all NAPL is depleted, starts to move. The model is valid for both dissolution (i.e., by water) or volatilization (i.e., by air). Dissolution (or volatilization) is considered a first-order rate process with a constant mass-transfer rate coefficient. As expected, the model approaches the solution for equilibrium conditions if the mass-transfer coefficient tends to infinity. Even though the model is based on some rigorous assumptions, the simplicity of the model makes it useful for obtaining an initial mass-transfer rate coefficient from experimental data, which can be used to estimate the time required to dissolve all NAPL, as shown for two data sets taken from the literature.

Introduction

Soils contaminated with nonaqueous phase liquids (NAPLs) are a serious environmental problem. The presence of a NAPL creates a major source of contaminants that can escape into the atmosphere by volatilization or contaminate water resources by dissolution in ground water. When a soil is found to be contaminated with a NAPL, remediation is often necessary. To optimize real-scale remediation processes, much research is being done on the distribution and behavior of NAPLs in the subsurface.

An important aspect of NAPL-contaminated soil is the dissolution or volatilization of the NAPL into the water and air phase, respectively. Most of the time these processes are subject to nonequilibrium conditions. Several models have been developed to describe nonequilibrium mass transfer between NAPL and mobile phase. Baldwin and Gladden (1996) divide these models into three types: linear mass-transfer models, pore-diffusion models, and shrinking core models. The linear mass-transfer model, which states that the change in concentration is proportional to the difference between the maximum and actual concentration in water or air, is the most commonly used. The mass-transfer rate coefficient in this model is a function of the contact area and contact time between NAPL and transporting phase (Hunt et al. 1988; Miller et al. 1990; Powers et al., 1992, 1994a, 1994b).

Column experiments with NAPL contaminated soils generally show elution profiles with an initial plateau fol-

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lowed by a decrease in concentration, often ending in a prolonging tail (Geller and Hunt 1993; Imhoff et al. 1994; Powers et al. 1994a; van der Ham and Brouwers 1998; Fortin et al. 1998; Powers et al. 1998). The initial plateau represents the time during which the length of the mass-transfer zone is constant and the mass-transfer rate coefficient is not affected by a declining NAPL volume. The mass-transfer zone is defined here as the zone in which there is a net mass transfer from the residual NAPL to the transporting phase. When the dissolution process continues, the NAPL mass reduces, eventually resulting in a decreasing mass-transfer zone; mass-transfer constraints increase due to a diminishing interfacial area between NAPL and contacting fluid. Both phenomena cause the solute concentration at the end of the NAPL-containing region to decrease. This represents the second stage of the elution profile. The tailing end of the elution profile is a result of slow release of contaminants from small NAPL droplets with limited access to the mobile phase and/or desorption from the solid phase.

Several investigators have developed analytical solutions for the initial stage of the dissolution process for which steady-state conditions can be assumed, with or without dispersion (Fedkiw and Newman 1978; van Genuchten and Alves 1982; Hunt et al. 1988; Miller et al. 1990; Fortin et al. 1998; Soerens et al. 1998). The purpose of this paper is to develop a simple analytical model that describes the complete removal of a uniformly distributed, single-component NAPL under nonequilibrium conditions. The presented model includes the initial stage in which a steady-state condition can be assumed, followed by a decrease in concentration as a result of a diminishing mass-transfer zone. To keep the model simple, a number of assumptions are made, so the complex process of changing mass-transfer rates and desorption are not incorporated in the model. Consequently, the tailing end of the elution profile is not described by the model. Although these assumptions introduce errors, based on a reasonable estimation of the mass-transfer coefficient and the initial mass present, the model can still provide a rough indication of the time required to remove a major part of a residual NAPL.

Model Development

Assumptions

To solve the problem of the removal of a residual, single-component NAPL from a contaminated soil, the following assumptions are made:

1. Transport is considered in only one dimension.
2. Dissolution of the NAPL is described by a linear mass-transfer model with a constant mass-transfer rate coefficient.
3. The system is assumed homogeneous and the NAPL is assumed to be uniformly distributed.
4. The NAPL saturation is assumed to be small such that the volume of the transporting fluid in the contaminated region can be considered constant.
5. Since desorption becomes relevant only when all free NAPL is removed and the sorbed mass will generally be negligible compared to the mass of the NAPL, sorption is ignored.
6. The actual contaminated region will be considered part of a semi-infinite system, as is expressed in the exit boundary condition.

These assumptions may be far from reality, especially compared to field situations. In particular, the second and fifth assumptions ignore the tailing end of the elution profile. Nevertheless, these assumptions lead to simple analytical expressions that provide an easy tool to get a first estimate of the mass-transfer coefficient or time required to remove most of the NAPL.

Basic Equations

Based on the assumptions mentioned, the aqueous phase concentration of a solute in a NAPL-contaminated soil can be described by the following one-dimensional transport equation (Powers et al. 1991; Geller and Hunt 1993; Imhoff et al. 1994; Soerens et al. 1998):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - k(C - C_s) \qquad (1)$$

where C is the concentration in the aqueous solution, t is time, D is the hydrodynamic dispersion coefficient, x is the main direction of flow, v is the interstitial ground water velocity, k is a modified first-order mass-transfer rate coefficient ($k = K_l/n$, where K_l is the conventional first-order mass-transfer coefficient that is a function of the specific interfacial area between NAPL and water, and n is the porosity), and C_s is the solubility of the NAPL in water, i.e., the equilibrium concentration for water in contact with a single-component NAPL. Equation 1 states that the change in concentration depends on dispersive transport, advective transport, and the transfer of mass between the NAPL and water (source term). In case of remediation by air, C represents the concentration in the air phase and C_s is replaced by HC_s, in which H is Henry's law constant.

The following boundary conditions apply:

$$vC - D\frac{\partial C}{\partial x} = 0 \quad \text{at} \quad x = 0 \qquad (2)$$

and

$$\frac{\partial C}{\partial x} = 0 \quad \text{at} \quad x \to \infty \qquad (3)$$

Besides the transport equation, a mass-balance equation for the NAPL is required. The change in mass of NAPL is described by

$$\rho_N\frac{\partial S_N}{\partial t} = k(C - C_s) \qquad (4)$$

where ρ_N is the density of the NAPL, S_N is the NAPL saturation defined as the fraction of pores occupied by the NAPL, and all other parameters are as defined before.

To scale the problem, it is common to rewrite the equations in nondimensional parameters. This yields for Equation 1:

$$\frac{\partial C^*}{\partial T} = \frac{1}{Pe}\frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} + \omega(C^* - 1) \qquad (5)$$

with boundary conditions

$$C^* - \frac{1}{Pe}\frac{\partial C^*}{\partial X} = 0 \quad \text{at} \quad X = 0 \qquad (6)$$

and

$$\frac{\partial C^*}{\partial X} = 0 \quad \text{at} \quad X \to \infty \qquad (7)$$

and for Equation 4

$$\frac{\partial S^*}{\partial T} = \frac{\omega}{P}(C^* - 1) \qquad (8)$$

where

$$C^* = \frac{C}{C_s} \qquad (9)$$

$$T = \frac{vt}{L} \qquad (10)$$

$$X = \frac{x}{L} \qquad (11)$$

$$Pe = \frac{vL}{D} \qquad (12)$$

$$\omega = \frac{kL}{v} \qquad (13)$$

$$S^* = \frac{S_N}{S_{N0}} \qquad (14)$$

$$P = \frac{S_{N0}\rho_N}{C_s} \qquad (15)$$

C* is a relative concentration; T is a dimensionless time referred to as pore volume; X is a relative distance; Pe is the Peclet number, indicating the ratio between advective and dispersive mass transport; ω is a dimensionless parameter, often referred to as the Damkohler number (Powers et al. 1991) or Merkel number (Brouwers and Li 1995), indicating the ratio between the residence time of water in the contaminated zone and the characteristic time for mass-transfer; S* is the relative NAPL saturation remaining in the soil, over time decreasing from one to zero; S_{N0} is the initial NAPL saturation; and P is a dimensionless parameter indicating the number of pore volumes required to remove all NAPL under equilibrium conditions without dispersion, i.e., the absolute minimum number of pore volumes to be flushed for complete removal.

In the following sections Equations 5 and 8 are solved analytically for two distinguished stages: the initial steady state and the moving boundary.

Analytical Solution for Initial Stage: Steady State

At T = 0 a clean solution ($C^* = 0$) enters the contaminated zone. While the water passes through the contaminated zone, the NAPL dissolves into the water phase. After the flushing of a few pore volumes, a constant concentration profile is developed such that steady state ($\partial C^*/\partial T = 0$) can be assumed and Equation 5 reduces to

$$-\frac{1}{Pe}\frac{\partial^2 C^*}{\partial X^2} + \frac{\partial C^*}{\partial X} + \omega C^* = \omega \qquad (16)$$

Equation 16 is a nonhomogeneous second-order linear differential equation for which the general solving procedure is given in standard calculus textbooks. The solution of Equation 16 is

$$C^* = ae^{\lambda_+ X} + be^{\lambda_- X} + 1 \qquad (17)$$

where

$$\lambda_{\pm} = \frac{1}{2}\left(Pe + \sqrt{Pe^2 + 4Pe\omega}\right) \qquad (18)$$

and a and b are integration constants. Note that λ_+ is a positive number, λ_- is a negative number. Applying the boundary conditions, Equations 6 and 7, it follows that a = 0 and b = $-1/(1-\lambda_-/Pe) = \lambda_-/\omega$, yielding the solution

$$C^* = 1 - \frac{\omega^*}{\omega}\exp(-\omega^* X) \qquad (19)$$

where

$$\omega^* = -\lambda_- = -\frac{1}{2}\left(Pe - \sqrt{Pe^2 + 4Pe\omega}\right) \qquad (20)$$

ω* is a pseudo Damkohler number in which both the effect of dispersion and mass transfer are incorporated. As a result of dispersion, ω* is smaller than ω. When Pe tends to infinity, i.e., the dispersion coefficient D tends to zero corresponding to piston displacement or plug flow, ω* approaches its maximum value ω. Equation 19 describes the increase in concentration as a function of distance in the contaminated zone.

Substitution of Equation 19 for C* in Equation 8 yields

$$\frac{\partial S^*}{\partial T} = -\frac{\omega^*}{P}\exp(-\omega^* X) \qquad (21)$$

Integration of Equation 21 and applying the initial condition

$$S^*(T = 0) = 1 \qquad (22)$$

yields

$$S^* = 1 - \frac{\omega^* T}{P}\exp(-\omega^* X) \tag{23}$$

Equation 23 describes for a given system the residual NAPL saturation as a function of X and T. Equations 19 and 23 are the solutions for the initial stage of the dissolution process during which the length of the NAPL-containing region remains unchanged.

Analytical Solution for Second Stage: Moving Boundary

When the NAPL-containing region is flushed with clean water, the NAPL volume declines and eventually disappears. This will happen first at the edge where clean water enters the contaminated zone (X = 0) and will gradually move in the direction of flow. The dimensionless time at which this moving boundary develops is indicated by the critical pore volume, T_c, and can be calculated from Equation 23 by inserting $S^* = 0$ at $T = T_c$ and $X = 0$:

$$T_c = \frac{P}{\omega^*} \tag{24}$$

Behind the moving boundary C^* and S^* are equal to zero. Ahead of the moving boundary it is assumed that the concentration profile remains the same, only shifted in the direction of flow beginning at the moving boundary $X_m(T)$. This can be explained by the fact that the length of the mass-transfer zone remains the same given a constant mass-transfer rate coefficient. Hence, the concentration profile at $T > T_c$ can be described by

$$C^* = 1 - \frac{\omega^*}{\omega}\exp\Big(-\omega^*(X - X_m(T))\Big) \tag{25}$$

Equation 25 would also follow from solving Equation 16, yielding Equation 17, and application of the boundary conditions Equation 6 (now at $X = X_m(T)$) and 7.

Substitution of Equation 25 into Equation 8 and integration from T_c to any $T > T_c$ yields

$$S^* = S^*(T_c) - \frac{\omega^*}{P}\int_{T_c}^{T}\exp\Big(-\omega^*(X - X_m(T))\Big)dT \tag{26}$$

where $S^*(T_c)$, according to Equations 23 and 24, equals

$$S^*(T_c) = 1 - \exp(-\omega^* X) \tag{27}$$

Equations 25 and 26 describe C^* and S^* as a function of X and T; however, $X_m(T)$, the location of the moving boundary at any $T > T_c$, is unknown in these equations. An expression for $X_m(T)$ can be derived from an overall mass balance which states that the amount of NAPL removed during a certain period should be equal to the difference between the amount of NAPL present at the beginning and end of that period. The total amount of NAPL present in the contaminated region at $T = T_c$ can be found by integration of Equation 27:

$$\int_0^1 S^*(T_c)dX = 1 - \frac{1}{\omega^*}\Big(1 - \exp(-\omega^*)\Big) \tag{28}$$

In Equation 28 the amount of NAPL at T_c is expressed as a fraction of the initial amount of NAPL. For the actual mass one has to multiply Equation 28 by $V\rho_N n S_{N0}$ where V is the total volume of the contaminated region.

The amount of NAPL present at any $T > T_c$ can be found by integrating Equation 26 from $X_m(T)$ to 1, giving

$$\int_{X_m(T)}^1 S^* dX = \int_{X_m(T)}^1 \left(1 - \exp(-\omega^* X) - \frac{\omega^*}{P}\exp(-\omega^* X)\int_{T_c}^{T}\exp\Big(\omega^* X_m(T)\Big)dT\right)dX$$

$$= 1 - X_m(T) + \frac{1}{\omega^*}\exp(-\omega^*) - \frac{1}{\omega^*}\exp(-\omega^* X_m(T))$$

$$+ \frac{1}{P}\exp(-\omega^*)\int_{T_c}^{T}\exp(\omega^* X_m(T))dT$$

$$- \frac{1}{P}\exp\Big(-\omega^* X_m(T)\Big)\int_{T_c}^{T}\exp\Big(\omega^* X_m(T)\Big)dT \tag{29}$$

The amount of NAPL leaving the contaminated zone between t_c and t, $\dot{m}$, is equal to

$$\dot{m} = A\int_{t_c}^{t}\left(UC - nD\frac{\partial C}{\partial x}\right)\Bigg|_{x=L} dt \tag{30}$$

where A is the cross-sectional area of the contaminated zone and U is the Darcy flux or superficial ground water velocity. Dividing by $V\rho_N n S_{N0}$ to express this amount as the fraction of the initial amount of NAPL similar to Equations 28 and 29, and rewriting the equation in nondimensional parameters gives

$$\dot{m}^* = \frac{1}{P}\int_{T_c}^{T}\left(C^* - \frac{1}{Pe}\frac{\partial C^*}{\partial X}\right)\Bigg|_{X=1} dT \tag{31}$$

where $C^*(X = 1)$ and $\left.\frac{\partial C^*}{\partial X}\right|_{X=1}$ follow from Equation 25:

$$C^*(X = 1) = 1 - \frac{\omega^*}{\omega}\exp\Big(-\omega^*(1 - X_m(T))\Big) \tag{32}$$

$$\left.\frac{\partial C^*}{\partial X}\right|_{X=1} = \frac{\omega^{*2}}{\omega}\exp\left(-\omega^*(1 - X_m(T))\right) \quad (33)$$

yielding

$$\dot{m}^* = \frac{1}{P}\int_{T_c}^{T}\left(1 - \exp(-\omega^*(1 - X_m(T))\right)dT \quad (34)$$

In deriving Equation 34, the equality $\omega^*/\omega + \omega^{*2}/Pe\omega = 1$, which follows from Equation 20, has been inserted. According to the overall mass balance, the amount of NAPL leaving the contaminated zone between T_c and T (Equation 34) should equal the amount of NAPL present at T_c (Equation 28) minus the amount of NAPL present at any T (Equation 29). The derivative of this mass balance to T should also obey this equality. Since the amount of NAPL present at T_c is independent of T, the derivative of Equation 28 equals zero. The overall mass balance by combining and differentiating Equations 29 and 34 therefore yields

$$\frac{1}{P} - \frac{1}{P}\exp\left(-\ \omega^*(1 - X_m(T))\right) - \frac{\partial X_m(T)}{\partial T}$$

$$+\exp\left(-\omega^*X_m(T)\right)\frac{\partial X_m(T)}{\partial T} + \frac{1}{P}\exp\left(-\omega^*(1 - X_m(T))\right)$$

$$+\frac{\omega^*}{P}\exp(-\omega^*X_m(T))\frac{\partial X_m(T)}{\partial T}\int_{T_c}^{T}\exp(\omega^*X_m(T))dT - \frac{1}{P} = 0 \quad (35)$$

or

$$-\frac{\partial X_m(T)}{\partial T} + \exp\left(-\omega^*X_m(T)\right)\frac{\partial X_m(T)}{\partial T}$$

$$+\frac{\omega^*}{P}\exp\left(-\omega^*X_m(T)\right)\frac{\partial X_m(T)}{\partial T}\int_{T_c}^{T}\exp\left(\omega^*X_m(T)\right)dT = 0 \quad (36)$$

Dividing by $\exp\left(-\omega^*X_m(T)\right)\frac{\partial X_m(T)}{\partial T}$ and differentiating again with respect to T yields

$$\frac{\partial X_m(T)}{\partial T} = \frac{1}{P} \quad (37)$$

Integration of Equation 37 from T_c to T and applying $X_m(T = T_c) = 0$ yields

$$X_m(T) = \frac{T - T_c}{P} \quad (38)$$

Or after substitution of Equation 24, the position of the moving front as function of dimensionless time for T > Tc reads

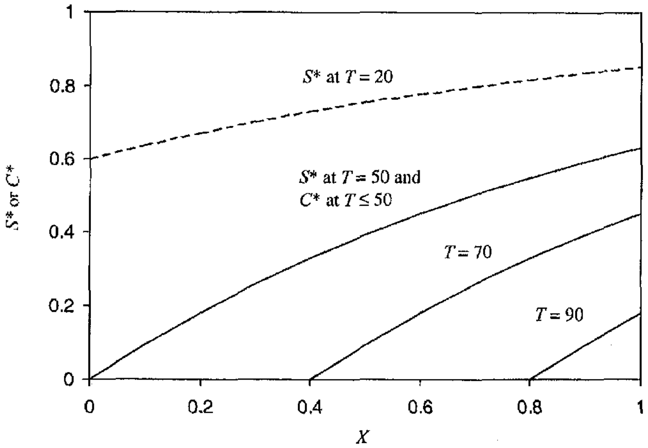

Figure 1. Saturation (dashed line) and concentration profiles (solid lines) for P = 50 and $\omega^* = \omega = 1$ (i.e., $T_c = 50$ and $T_r = 100$) at T = 20, 50, 70, and 90. For $T \geq T_c$: $S^* = C^*$.

$$X_m(T) = \frac{T}{P} - \frac{1}{\omega^*} = \frac{1}{\omega^*}\left(\frac{T}{T_c} - 1\right) \quad (39)$$

Substitution of Equation 38 into Equation 25 now reveals the relative concentration as a function of T and X for $T \geq T_c$:

$$C^* = 1 - \frac{\omega^*}{\omega}\exp\left(\frac{T}{T_c} - 1 - \omega^*X\right) \quad (40)$$

To find the NAPL saturation as a function of T and X, Equation 38 can be substituted into Equation 26. After integration this yields

$$S^* = 1 - \exp\left(\frac{T}{T_c} - 1 - \omega^*X\right) \quad (41)$$

The total cleanup or remediation time, T_r, is the time elapsed until $X_m(T) = 1$. From Equation 39 it follows that

$$T_r = P + T_c = P\left(1 + \frac{1}{\omega^*}\right) \quad (42)$$

For equilibrium conditions, when ω^* tends to infinity, it follows that T_r approaches P, the number of pore volumes required to remove all NAPL under equilibrium conditions, as expected. Note that, according to Equation 42, the time required for the NAPL front, $X_m(T)$, to move from zero to one, $(T_r - T_c)$, equals the time required to remove all NAPL under equilibrium conditions, P. A summary of the analytical solutions is given in Table 1.

Model Results and Analysis

Simulation Results

Figure 1 shows an example of the NAPL saturation and concentration profile at different pore volumes, calculated with the model developed in previous section for the following conditions: P = 50 and $\omega^* = \omega = 1$ (imply-

Table 1
Summary of the Analytical Solutions

Analytical Solution	Range Valid	Equation
$C^* = 1 - \frac{\omega^*}{\omega}\exp(-\omega^* X)$	$0 \le T < T_c$	19
$S^* = 1 - \frac{T}{T_c}\exp(-\omega^* X)$	$0 \le T < T_c$	23
$C^* = 1 - \frac{\omega^*}{\omega}\exp\left(\frac{T}{T_c} - 1 - \omega^* X\right)$	$T_c \le T \le T_r$	40
$S^* = 1 - \exp\left(\frac{T}{T_c} - 1 - \omega^* X\right)$	$T_c \le T \le T_r$	41
$T_c = \frac{P}{\omega^*}$		24
$T_c = P + T_c$		42
$\omega^* = -\frac{1}{2}\left(Pe - \sqrt{Pe^2 + 4Pe\omega}\right)$		20

ing that dispersion can be neglected and $T_c = 50$ and $T_r = 100$). Initially the NAPL is uniformly distributed ($S^* = 1$) between $X = 0$ and $X = 1$. Starting from $T = 0$ clean water enters the contaminated region at $X = 0$. The NAPL dissolves and hence the concentration increases while the fluid passes through the NAPL-containing region. The figure shows that for given ω the contact time between NAPL and water is too short to reach equilibrium, i.e., $C^* < 1$, at $X = 1$.

While the water passes through, the NAPL saturation decreases. The NAPL saturation decreases more at the beginning of the contaminated region because there the difference between the actual and equilibrium concentration, the driving force for mass transfer, is largest. At $T = 50$ the NAPL saturation has become zero at $X = 0$. From this moment the relative saturation and relative concentration profiles are equal when $\omega^* = \omega$ (See Equations 40 and 41) and start to move in the direction of flow. This is illustrated by the subsequent pore volumes $T = 70$ and 90. It can be seen from these curves that the NAPL- containing region, and hence the mass-transfer zone, diminishes and as a result the concentration at the outlet decreases.

In Figure 2 the breakthrough curves at the end of the NAPL-containing region ($X = 1$) are shown for $P = 50$ and $\omega = \omega^* = 0.5, 1, 5$ and ∞. A Damkohler number of infinity corresponds to equilibrium conditions (plug flow). If the Damkohler number becomes smaller, the mass transfer is slower and therefore the length of the mass-transfer zone to reach equilibrium will be longer. When the mass-transfer zone is limited by the size of the NAPL- containing region, the exit concentration, C^*, drops below unity. For smaller Damkohler numbers it takes longer before the NAPL at the beginning of the contaminated zone is depleted and the NAPL front starts to move, hence the initial steady-state concentration lasts longer. Note that the time required for the NAPL front, $X_m(T)$, to move from zero to one and the concentration to drop from the initial value to zero is the same under all conditions and equal to P, as was previously observed from Equation 42.

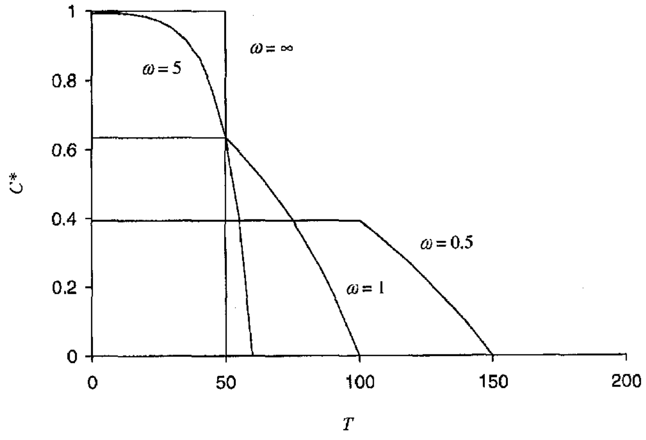

Figure 2. Breakthrough curves at X = 1 for P = 50 and ω* = ω = 0.5, 1, 5, and ∞.

As was mentioned before, the analytical model is based on several simplifying assumptions that make the model less accurate. With the current model the effects of the exit boundary condition and dispersion can easily be analyzed and are discussed in the following section.

Effect of Exit Boundary Condition

In Equations 3 and 7 an infinite system was assumed. In reality the contaminated zone is finite and therefore an exit boundary defined at $X = 1$ would be more appropriate. To keep the analytical solution simple the boundary condition was defined for $X \rightarrow \infty$, which will give an over-prediction of the concentration at $X = 1$. For the boundary condition

$$\frac{\partial C^*}{\partial X} = 0 \quad \text{at} \quad X = 1 \tag{43}$$

the analytical solution for the relative concentration at $X = 1$ for the initial stage of the dissolution process in which steady state is assumed ($T < T_c$) is

$$C^* = ae^{\omega^* + Pe} + be^{-\omega^*} + 1 \tag{44}$$

with

$$a = \frac{Pe\omega^* e^{-2\omega^* - Pe}}{Pe(\omega^* + \omega)e^{-2\omega^* - Pe} - (\omega^* + Pe)^2} \tag{45}$$

and

$$b = \frac{1}{\left(\frac{\omega^* + \omega}{\omega^* + Pe}\right)e^{-2\omega^* - Pe} - \frac{\omega^*}{Pe} - 1} \tag{46}$$

This solution is obviously more complex than the solution for an infinite system, Equation 19. Figure 3 shows the

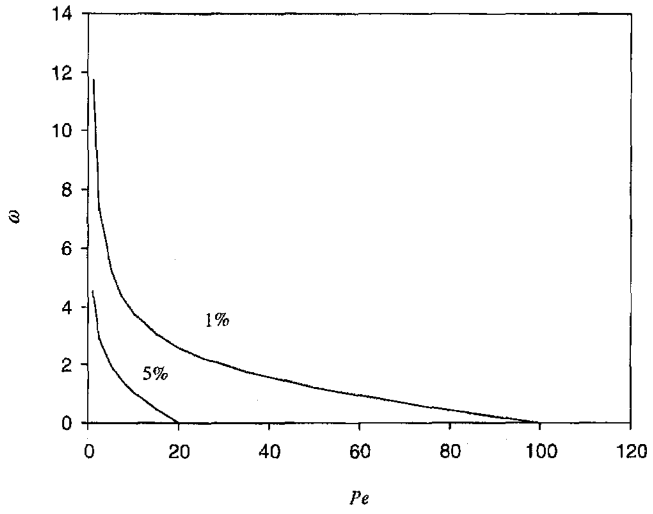

Figure 3. Combinations of values for ω and Pe that result in a 1% and 5% difference between the steady-state concentration at X = 1 for an infinite and finite boundary condition. The concentration for the infinite system is always larger than for the finite system.

combinations of ω and Pe, which result in a 1% and 5% difference between the steady-state concentration at X = 1 for an infinite and finite boundary condition, in which the solution for the infinite system is always larger than for the finite system. As can be seen from this graph, the deviation between the finite and infinite system becomes larger when ω and/or Pe become smaller.

Another problem with assuming an infinite system instead of a finite system is back dispersion. In a presumed infinite system, dispersion causes mass to flow back into the NAPL-containing region. This increases the concentration and slows down the dissolution process. As a result T_c and T_r increase, and the total recovered mass at $T = T_r$ will be more than P. In addition, at T_c and T_r the NAPL saturation will become zero at X = 0 and 1, respectively, however the corresponding concentrations are not zero due to back dispersion. This effect is more pronounced when Pe becomes smaller.

Importance of Dispersion

The presented model includes dispersion, however, the importance of dispersion is uncertain. The model was used to evaluate the importance of dispersion in the NAPL-contaminated region. In Figure 4, ω* is plotted against ω for different Peclet numbers. When ω* deviates more from ω, dispersion has a larger impact. From the figure it is clear that dispersion is only important when ω is large, i.e., when equilibrium conditions are approached. Since equilibrium conditions are not commonly found for NAPL dissolution and given the uncertainties in these problems, it may be concluded that dispersion is of little significance.

Application of the Model to Experimental Data

In this section, the analytical model will be applied to two sets of experimental data. The first data set is taken from Imhoff et al. (1994) who performed column experiments with trichloroethylene (TCE) at residual saturation. In this study, both the elution profile and the changing TCE saturation were monitored. Figure 5 shows the elution profile of their Experiment 6. The solid squares represent the concentration in the effluent samples without centrifugation, the plus signs represent the concentration in the centrifuged samples. The difference between these samples indicates that small amounts of TCE leave the column as colloidal-size particles. Based on an order of magnitude analysis, it was concluded that the dispersion term in this study could be neglected compared to the advective and source terms. Therefore, ω* is set equal to ω. Initially, the effluent concentration equals the solubility (C* = 1), which indicates that the passage through the contaminated zone is long enough to reach equilibrium. In this case the elution profile cannot be used to estimate the mass-transfer coefficient with the derived model until the concentration starts to drop. However, since the change in NAPL saturation was also monitored in this study, the mass-transfer coefficient can be derived from these data. In Experiment 6, the residual saturation at the beginning of the column was reduced to zero somewhat later than 25 pore volumes. This time corresponds to T_c in the presented model. From the data was derived that P = 204, hence, based on Equation 24, ω = 8.2. The solid line in Figure 5 is the result of the analytical model for these values.

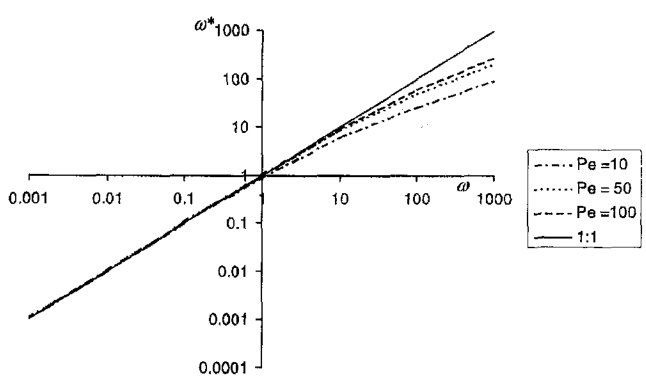

Figure 4. Deviation of ω* from ω for different Peclet numbers.

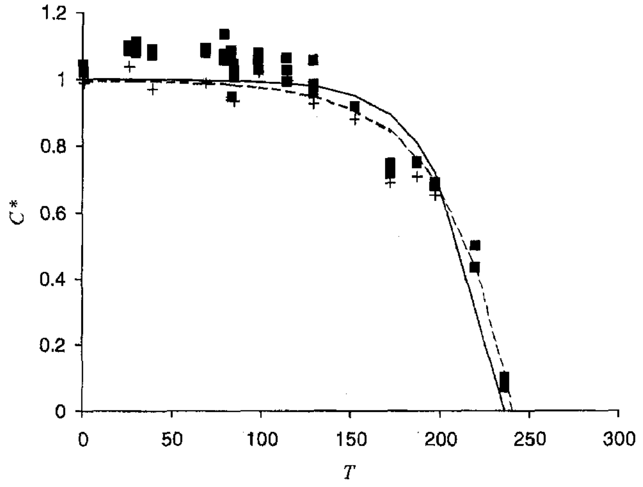

Figure 5. Data from Imhoff et al. (1994) fitted with the analytical model, Equations 19 and 40. P = 204; ω = 8.2 (solid line) and ω = 5.6 (dashed line).

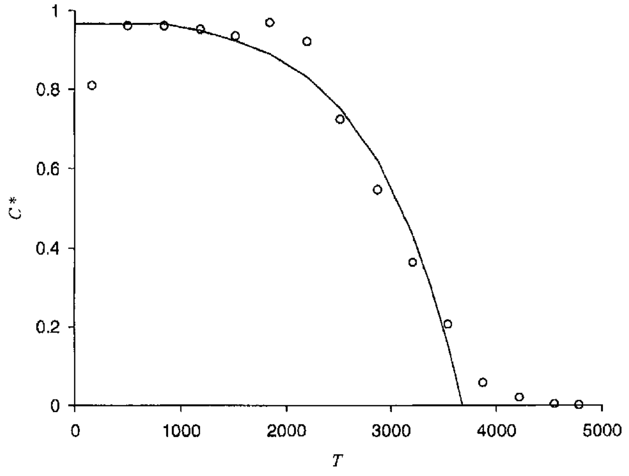

Figure 6. Data from van der Ham and Brouwers (1998) fitted with the analytical model, Equations 19 and 40. P = 2843; T_c = 517; T_r = 3360; ω = 3.4.

Given a Darcy or superficial velocity U (= vn) of 0.92 m/day and a column length of 7 cm, this corresponds to a value for K_l of 107 d^{-1}. Commonly T_c is not known, such that ω can only be derived from fitting the elution profile up to the point where the relative concentration drops below unity. To illustrate this procedure, the first eight data points (centrifuged samples) were fitted by the model. The best fit was obtained by changing the value for the Damkohler number, ω, such that the sum of the squared differences between the experimental data and model prediction was minimal. This revealed a value for ω of 5.6 ($K_l = 74\ d^{-1}$). The dashed line in Figure 5 is based on this value for the Damkohler number. This value is much lower than the value calculated above because the model provides some average of the Damkohler number representative for the data used. The first estimate for ω was based on data available after 25 pore volumes, the second estimate on data available after approximately 150 pore volumes. Since the mass-transfer coefficient decreases in time, the average Damkohler number over a longer time period will be smaller. Nevertheless, both estimates for the Damkohler number provide reasonable fits to the data. This means that the model is not very sensitive to this range of ω values.

As was mentioned previously, the model presented in this paper does not only apply to dissolution, but can also be used for gas phase partitioning. In the latter case, the mass-transfer coefficient represents a combination of the mass-transfer constraints directly from the NAPL to the vapor phase, from the NAPL to the water phase, and from the water to the vapor phase. As an example, the data from van der Ham and Brouwers (1998) were used. They performed column experiments in which *n*-tetradecane was removed by steam stripping. Figure 6 shows the breakthrough curve of Experiment C in their study (symbols). Initially the effluent concentration is approximately constant but slightly lower than the equilibrium concentration, indicating that the passage through the NAPL-containing region is not long enough to reach equilibrium. Dispersion was not considered in this study; therefore, ω^* is again assumed to be equal to ω. The initial plateau (data points 2 to 4) was fitted to Equation 19, yielding a value for ω of 3.4 (P = 2843). Given a superficial vapor velocity U of 0.07 m/s and a column length of 0.93 m, this corresponds to a mass-transfer rate coefficient K_l of 0.41 s^{-1}. Note that the mass-transfer rate coefficient for steam stripping is several orders of magnitude larger than for dissolution. The estimated value for the Damkohler number was used in the developed model to calculated the entire elution profile (solid line in Figure 6). As can be seen from Figure 6, the model fits the data reasonably well, except for the tail at the end of the breakthrough curve. This tailing is caused by increasing mass-transfer constraints due to shrinking NAPL ganglia and droplets, which were not included in the model. The exact cleanup time is often difficult to determine in laboratory experiments and even more so in field situations because the elution profile approaches zero concentration asymptotically. If we consider the total mass recovered as an indication for cleanup, the cleanup time derived from the model, T_r = 3672, corresponds to the time at which 98.5% of the initial mass is removed. It should be noted, however, that the mass recovered is not always the best criterion for reaching remediation requirements.

Even though there are several simplifying assumptions made to derive the presented model, it can be concluded that the model describes the experimental data reasonably well. This is because the initial mass-transfer coefficient determines to a great extent the shape of the breakthrough curve. An advantage of the used laboratory data is that the initial amount of NAPL in the column, which determines the area under the curve (equal to P), was known. In the field the amount of NAPL is often unknown, which may therefore be one of the largest uncertainties in predicting remediation times.

Summary and Conclusions

In this paper an analytical one-dimensional model is presented for the removal of a single-component NAPL under nonequilibrium conditions, taking account of both advection and dispersion (Table 1). The removal process of NAPL was divided in two stages. In the first stage water or air leaving the NAPL-contaminated region has a constant concentration. This concentration builds up as water or air flows through the NAPL-containing region and the NAPL dissolves into the water phase or volatilizes into the gas phase. The relative concentration leaving the NAPL-contaminated region depends on the flow velocity, the mass-transfer rate coefficient and the length of NAPL-contaminated region. The second stage begins when all NAPL is dissolved/volatilized at the position where clean water/air enters the NAPL-contaminated region. This point will gradually move in the direction of flow toward the end of the NAPL-contaminated region. During the second stage, the length of the NAPL-contaminated region decreases; therefore, the contact time decreases and the concentration at the exit boundary also decreases. The beginning of stage two is indicated by the dimensionless critical pore volume, T_c.

In reality, the concentration at the exit of the NAPL-containing region may start to decrease earlier because the mass-transfer rate coefficient decreases as the NAPL volume declines. Due to this process the mass-transfer constraints increase continuously, resulting in tailing at the end of the breakthrough curve. At this time, desorption may also start to play a role. Although these processes are important for the complete recovery of the contaminant, they were ignored here to keep the model simple. This means that the model does not describe the end of the elution profile, and therefore provides only a rough indication of the time in which a large part of the NAPL mass is removed, but not all of it. Another assumption is an exit boundary condition based on a semi-infinite system. This assumption becomes more erroneous when the mass-transfer coefficient decreases and dispersion increases. Dispersion is included in the model but the expectation is that dispersion does not play an important role compared to the effects of the assumptions made to derive the model and the uncertainties involved in NAPL dissolution problems.

Fitting the model to experimental data showed good agreement between data and model fit. This indicates that the model can be useful in estimating the cleanup time based on a mass-transfer rate coefficient obtained from data of the early part of the experiment. If no data of the elution profile is available, a mass-transfer coefficient can be estimated from the literature, but this introduces more uncertainty. When the amount of NAPL is known, the model provides a more realistic prediction of the cleanup time than based on the equilibrium assumption. In the field the exact amount of NAPL is often unknown and the conditions are more variable, so application of the model to field situations should be done with even more care. Nevertheless, the model provides a simple tool to obtain a rough but quick estimate of the approximate cleanup time based on only a few parameters. Given the simplifying assumptions, the model cannot be used to elucidate underlying processes, nor can the obtained mass-transfer coefficients be extrapolated to other conditions.

Notation

a, b	integration constants, see Equations 17 and 44
A	cross-sectional area of contaminated zone (L^2)
C	concentration (ML^{-3}).
C_s	solubility of the NAPL in water (ML^{-3})
D	hydrodynamic dispersion coefficient (L^2T^{-1})
H	Henry's law constant
k	modified mass-transfer rate coefficient, $k = K_l/n$ (T^{-1})
K_l	conventional mass-transfer rate coefficient (T^{-1})
L	length of column or contaminated zone (L)
$\dot{m}$	cumulative mass leaving the contaminated zone (M)
n	porosity
S_N	NAPL saturation
S_{N0}	initial NAPL saturation
t	time (T)
t_c	critical time at which NAPL-containing region starts to decrease (T)
U	superficial velocity of the transporting phase (LT^{-1})
v	interstitial velocity of the transporting phase, $v = U/n$ (LT^{-1})
V	total volume of the contaminated zone (L^3)
x	distance in the flow direction (L)

Greek Symbols

ρ_N	density of the NAPL (ML^{-3})
λ	coefficient resulting from integration (Equation 17)

Dimensionless Parameters

C^*	relative concentration, $C^* = C/C_s$
$\dot{m}^*$	fraction of initial mass of NAPL removed from the contaminated zone
P	dimensionless parameter indicating the number of pore volumes required to remove all NAPL under equilibrium conditions, $P = S_{N0}\rho_N/C_s$
Pe	Peclet number, $Pe = vL/D$
S^*	relative saturation, $S^* = S_N/S_{N0}$
T	pore volume, $T = vt/L$
T_c	critical pore volume where $S^*(X = 0) = 0$
T_r	cleanup time in pore volumes
X	relative distance, $X = x/L$
$X_m(T)$	position of the moving boundary at T pore volumes
ω	Damkohler number, $\omega = kL/v$
ω^*	modified Damkohler number including Pe (Equation 20)

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