

SIMULATION OF REACTIVE CONTAMINANT TRANSPORT OF CHLORINATED SOLVENTS*

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Abstract. In this paper, the simulation of distribution and remediation of chlorinated solvents in groundwater is discussed. Tetrachloroethene (perchloroethene or PCE) is a common groundwater contaminant. If spilled into the subsurface it provides a long-term source of contamination. Upon dissolution in groundwater, they are subject to mass transport processes and degradation. The distribution and the remediation of PCE are considered to be stimulated by (two following aspects,) transport under natural groundwater flow (or caused by extraction wells) and sequential decay of PCE.

The whole process can be modelled by a system of partial differential equations (PDEs) for water and each contaminant. The transport of chlorinated solvents is caused by advection (water flow), molecular diffusion and mechanical dispersion. These PDEs are advection dominated which is a source of troubles in computation. We propose a numerical scheme, which is based on suitable time discretization and linearization. At each time-step of a time partitioning we solve a decoupled system of linear PDEs. The space discretization is based on finite element method (FEM). We compute some typical scenarios in order to make some predictions about the remediation process.

Simulation results for modelled scenarios show that pure sequential decay of chlorinated solvents as remediation is a very slow process which cannot be efficient and a biodegradation should be applied.

Key words. reaction contaminant transport equation, sequential decay, advection dominated transport

AMS subject classifications. 76R99, 35K57

1. Contaminant transport in groundwater. The rate of contaminant transport in groundwater is governed by many factors including advection, dispersion, diffusion, dilution, retardation, and decay. Advection is the movement of dissolved contaminants along with the groundwater flow. During advection, molecules spread both along and perpendicular to the flow direction, a process called dispersion. Diffusion of contaminants is typically a very slow process that occurs along a concentration gradient. The combination of advection, dispersion, and diffusion results in dilution of the contaminant. Retardation is a slowing of the transport of contaminants relative to the groundwater flow rate as the result of sorption of the contaminants onto aquifer matrix material. Sorption depends on the type of contaminant, the aquifer mineralogy, and the presence of organic matter in the aquifer matrix. Sorption of contaminants is normally described with an equilibrium distribution coefficient K_d $\left[\frac{m^3}{kg}\right]$. The K_d value affects the retardation R of the contaminant by the relationship

$$R = 1 + \frac{\rho_b K_d}{\phi},$$

where

*Antónia Balážová was supported by the BOF project no. 011D03603 of Gent University.

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- ρ_b - bulk density of aquifer material $\left[\frac{kg}{m^3}\right]$
- ϕ - porosity of porous medium [1].

Retardation R is the ratio of the rate of bulk groundwater flow to the rate of contaminant transport. Values are generally less than 10.

The use of K_d values is a simplifying approach to a complex process. A limitation of the method is that, by using a linear isotherm, the model does not limit the amount of solute that can be sorbed, see [1]).

The decay (cf. Fig. 1.1) due to biodegradation of volatile organic compounds (VOCs) such as TCE (trichloroethene) can be modeled in an approximate fashion by using a half-life approach. In this manner, a first-order rate of degradation of the compound due to biochemical processes governs the amount of parent chemical mass remaining.

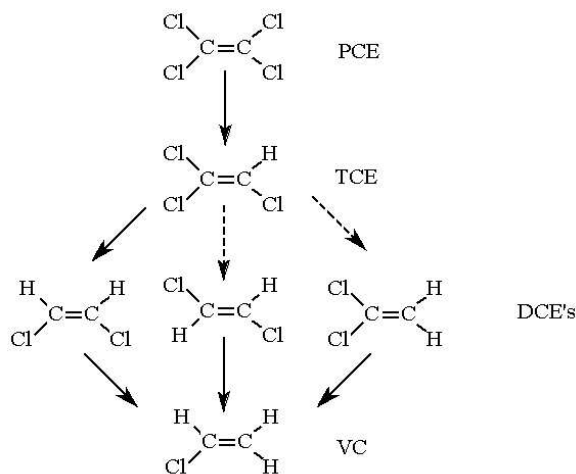


FIG. 1.1. Sequential decay of PCE

TCE biodegrades in the aquifer environment, but its rate of natural degradation depends on subsurface conditions, including the type and prevalence of microbial populations, and whether aerobic or anaerobic conditions are present. TCE degrades to cis-1,2-dichloroethylene, with lesser amounts of trans-1,2-dichloroethylene and 1,1-dichloroethylene in an anaerobic environment (cf. [2]). The isomers of dichloroethene (DCE) further degrade to vinyl chloride (VC). VC is commonly believed to degrade to ethene only under aerobic conditions; however, this process has also been known to occur under anaerobic conditions in a laboratory (cf. [3, 4, 5]). The ethene is further degraded to ethane (see [4]). For a complex model together with a computer simulation we refer the reader to [6, 7].

2. Model. We assume that the water flow is governed by Darcy's law

$$(2.1) \quad \mathbf{q} = -\frac{k\rho g}{\mu} \nabla \left(\frac{p}{\rho g} + z \right) = -K \nabla \left(\frac{p}{\rho g} + z \right) = -K \nabla h,$$

where

- z - elevation head (vertical coordinate) [m]

- h - piezometric head/potential [m] is the sum of pressure head $\left(\frac{p}{\rho g}\right)$ and the elevation head z
- $K = \frac{k\rho g}{\mu}$ - hydraulic conductivity $\left[\frac{m}{s}\right]$
- k - proportionality (permeability) factor [m^2]
- μ - dynamical viscosity of the fluid $\left[\frac{kg}{ms}\right]$
- g - gravity constant $\left[\frac{m}{s^2}\right]$.

Let Ω be a bounded domain (which has to be remediated) with the boundary $\Gamma = \Gamma_{Neu} \cup \Gamma_{Dir}$. Due to the fact that the remediation of contaminants from the subsurface is a very long process, it is reasonable to assume a steady-state flow regime. Therefore, we consider saturated flow of water in porous media described by the continuity equation

$$(2.2) \quad \nabla \cdot \mathbf{q} = f \quad \text{in } \Omega,$$

where $f \left[\frac{1}{s}\right]$ denotes possible sinks/sources. We assume the boundary conditions of the following form

$$(2.3) \quad \begin{aligned} \mathbf{q} \cdot \boldsymbol{\nu} &= g_{Neu} && \text{on } \Gamma_{Neu} \\ h &= h_{Dir} && \text{on } \Gamma_{Dir}. \end{aligned}$$

Diffusion/dispersion process of a single contaminant can be generally described by ([8, Chap. 14])

$$D = d_m \mathbf{I} + |\mathbf{q}| [d_l \mathbf{E}(\mathbf{q}) + d_t (\mathbf{I} - \mathbf{E}(\mathbf{q}))] - \text{diffusion/dispersion tensor} \left[\frac{m^2}{s}\right]$$

along with

- $\mathbf{E}_{ij}(\mathbf{q}) = \frac{q_i q_j}{|\mathbf{q}|^2}$
- d_m - molecular diffusion coefficient
- d_l - longitudinal dispersion coefficient
- d_t - transverse dispersion coefficient.

Four different chloroethenes will be considered in the reactive model. Let 1, 2, 3 and 4 be the indices corresponding to PCE, TCE, DCE and VC, respectively. Three of them, namely PCE, TCE and DCE make up the major part of a contaminant mixture, which is usually presented in a polluted subsurface. The concentration of VC is typically low.

For $i = 1, \dots, 4$ we denote by R_i the retardation factor, by D_i the diffusion/dispersion tensor, by λ_i the first-order degradation coefficient and by y_i the yield constant.

The yield constants y_1, \dots, y_4 are incorporated to account for molecular weight differences between parent and daughter compounds. The constants are necessary because kinetic expressions are valid on a molar basis only. The yield coefficients are dimensionless values, for example, y_1 represents the mg of TCE produced per unit mg of PCE destroyed.

The sequential decay $\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC}$ can be described by

$$(2.4) \quad \begin{aligned} R_1 \partial_t C_1 &= \nabla \cdot (D_1 \nabla C_1) - \mathbf{q} \nabla C_1 - \lambda_1 C_1 \\ R_2 \partial_t C_2 &= \nabla \cdot (D_2 \nabla C_2) - \mathbf{q} \nabla C_2 - \lambda_2 C_2 + y_1 \lambda_1 C_1 \\ R_3 \partial_t C_3 &= \nabla \cdot (D_3 \nabla C_3) - \mathbf{q} \nabla C_3 - \lambda_3 C_3 + y_2 \lambda_2 C_2 \\ R_4 \partial_t C_4 &= \nabla \cdot (D_4 \nabla C_4) - \mathbf{q} \nabla C_4 - \lambda_4 C_4 + y_3 \lambda_3 C_3 \end{aligned}$$

For simplicity, this system is accompanied with the following boundary conditions

$$(2.5) \quad C_1 = C_2 = C_3 = C_4 = 0 \quad \text{on } \Gamma.$$

3. Numerical scheme. For the space discretization in 1D we use Galerkin FEM with the basis functions, which are locally polynomials of third order. These are chosen in such a way that they guarantee the continuity of the first derivative (i.e. of the flow) across the boundaries of adjacent elements.

First, the approximation of the flow field is constructed. Due to the fact that we consider a steady-state problem, the flow field will be fixed in the whole remediation process.

We consider the contaminant transport within the time interval $[0, T]$. For simplicity we choose an equidistant time-partitioning of $[0, T]$ with the time steps $t_i = i\tau$ for $i = 1, \dots, n$, where $t_n = T$.

Due to the fact that the transport equation is advection dominated (which means that advection is much larger than diffusion/dispersion), we cannot directly apply the standard backward Euler method for the time discretization. Instead of this, we use the method of characteristics. Which is in fact nothing else as an operator splitting method, see e.g. [9, 10, 11]. We explain this on the following simple example

$$\partial_t u - \partial_{xx} u + v \partial_x u = w.$$

Let $u_i(x)$ be the approximation of $u(t_i, x)$ at the time step t_i . Then:

1. Shift the value u_i at the place x along the advection for a distance $v\tau$. If the new position $x + v\tau$ of u_i is outside the domain Ω , take into account the boundary condition for u_i .
2. Solve the diffusion, i.e.,

$$\frac{u_{i+1}(x) - u_i(x - v\tau)}{\tau} - \partial_{xx} u_{i+1}(x) = w_i(x)$$

taking into account the boundary conditions for u_{i+1} .

3. Increase the time step $i \mapsto i + 1$.

The reaction system (2.4) is coupled in the right-hand side. Therefore we have to decouple it at each time step. We do it in the following way (j denotes the number of contaminant, i is the number of a time step):

1. The values of $C_j(t_i)$ are given for all $j = 1, \dots, 4$.
2. Solve (2.4) for PCE by operator splitting method described above.
3. Solve (2.4) for TCE by operator splitting method described above.
4. Solve (2.4) for DCE by operator splitting method described above.
5. Solve (2.4) for VC operator splitting method described above.
6. Increase the time step $i \mapsto i + 1$.

4. Computer simulations. In this section we describe two different scenarios of sequential reduction of PCE, TCE, DCE and VC: with and without pumping.

First scenario.

We consider the 1D domain of the length 100 m . The extraction well is located in the middle of the domain and it has a diameter of 20 cm . The pumping intensity¹ is 1.728 $\frac{1}{day}$ will be fixed during the whole remediation. We assume that the aquifer under consideration is homogeneous with the hydraulic conductivity $K = 10^{-5} \frac{m}{s}$,

¹In a 3D-case, the multiplication of pumping intensity $[\frac{1}{s}]$ by the water density $[\frac{kg}{m^3}]$ and integration over the space $[m^3]$ gives the well discharge $[\frac{kg}{s}]$. To get the well discharge in $[\frac{m^3}{s}]$, it is sufficient to integrate the pumping intensity over the space $[m^3]$.

λ_1	λ_2	λ_3	λ_4
0.0025	0.006	0.00181	0.00156

TABLE 4.1
 First order degradation coefficients λ_i $\left[\frac{1}{day}\right]$ for $i = 1, \dots, 4$

y_1	y_2	y_3
0.792	0.738	0.644

TABLE 4.2
 Yield constants y_i $[-]$ for $i = 1, 2, 3$

which corresponds to a sand aquifer. The piezometric head at the boundary of the domain has a constant value of 10 m.

From this data we can compute the flow field towards the extraction well.

For all contaminants we consider the same retardation factor $R_1 = R_2 = R_3 = R_4 = 3.5 [-]$ and the same diffusion/dispersion coefficient $D_1 = D_2 = D_3 = D_4 = 10^{-5} \left[\frac{m^2}{day}\right]$. The degradation coefficients $\lambda_i, i = 1, \dots, 4$ for all chlorethenes can be found in Table 4.1. The dimensionless values of all yield constants are stated in Table 4.2. Further, we assume the homogeneous boundary condition for all contaminants, i.e., $C_1(t) = C_2(t) = C_3(t) = C_4(t) = 0$ on the boundary during the whole remediation process. The initial data are chosen as follows:

$$(4.1) \quad C_1(0) = 100 \left[\frac{mg}{l}\right], \quad C_2(0) = C_3(0) = C_4(0) = 0 \left[\frac{mg}{l}\right],$$

which is true inside the polluted sub-domain $[10m, 30m]$ and all concentrations vanish outside this polluted sub-domain. This means that the contaminated area is located in $[10m, 30m]$ at the beginning.

The time interval of the remediation process is 5 years. The time step for computations is given by $\tau = 10 \text{ days}$. The time evolution of PCE is shown in Fig. 4.1; PCE is depicted in Fig. 4.2, DCE is rendered in Fig. 4.3 and VC is displayed in Fig. 4.4. In all pictures we can see how the advection moves the contaminant plume towards the extraction well. We painted concentration profiles at the time $t = 0, 300, 600, 1000, 1400 \text{ days}$. The concentration of PCE is decreasing with increasing time due to the degradation to TCE. In fact, PCE vanishes for $t = 1400 \text{ days}$.

The amount of TCE is increasing due to the fact that only a part of existing TCE changes to DCE. TCE concentration at the beginning of remediation process was 0. The same is the truth for $t = 1400 \text{ days}$ due to the pumping.

Also DCE increases because only a part of existing DCE degrades to VC. DCE also started with 0 concentration and vanishes for $t = 1400 \text{ days}$ due to the pumping.

We also observe the increasing concentration of VC until it reaches the extraction well. Initial concentration of VC was 0 and VC vanishes for $t = 1400 \text{ days}$.

The behavior of all contaminant concentrations is determined by the sequential decay until the contaminant plume reaches the extraction well. Then the extraction of contaminated water rapidly reduces the concentration of all ethenes until they vanish.

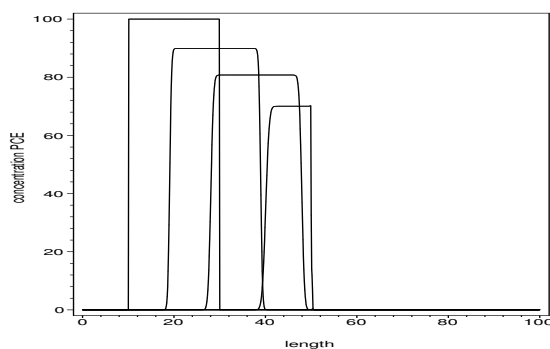


FIG. 4.1. Concentration of PCE in $[\frac{mg}{l}]$ (y -axis) versus the domain $[m]$ (x -axis). Time profiles at $t = 0, 300, 600, 1000, 1400$ days. Extraction well at 50m. Initial data for PCE is given by (4.1).

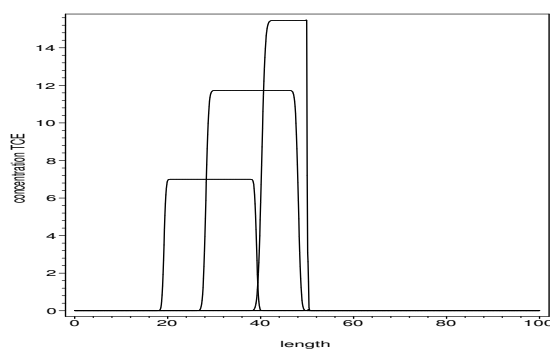


FIG. 4.2. Concentration of TCE in $[\frac{mg}{l}]$ (y -axis) versus the domain $[m]$ (x -axis). Time profiles at $t = 0, 300, 600, 1000, 1400$ days. Extraction well at 50m. Initial data for TCE is given by (4.1).

Fig. 4.5 shows the time evolution of the maximal concentration (in the whole remediation area) of each contaminant. We recall that the point, where this maximum is reached, is moving in space towards the extraction well due to the advection field.

Second scenario.

In this computer simulation we consider the same data as in the previous one, but we close the extraction well. Therefore, the contaminant will not move and the sequential degradation will run at the same place without any advection. The time evolution during 30 years of all concentration profiles is painted in Fig. 4.6. The development of all profiles corresponds to the their development by the first scenario up to the moment when the concentration plum reaches (in the first scenario) the extraction well. Due to the fact, that the well discharge is zero in the second computer simulation, the concentrations are not reduced due to pumping. Therefore, chloroethenes remain in the subsurface much longer.

Future work. We simulated sequential decay of chloroethenes. For biodegradation there are known two ways. The first possibility is anaerobic reductive dechlorination. Anaerobic reductive dechlorination is dependent on many environmental factors (e.g., anaerobic conditions, presence of fermentable substrates, and appropriate microbial populations). Second is cometabolic reductive dechlorination under aerobic condition. This process is supported by microbial activity although the bacteria do not gain energy from the degradation process.

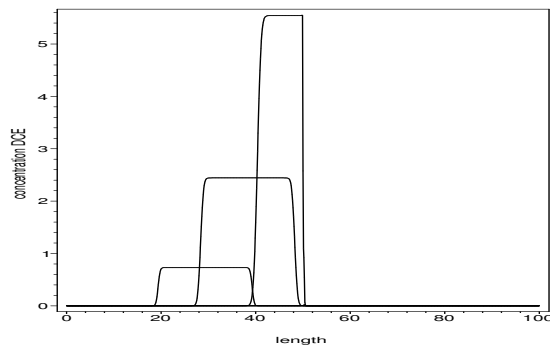


FIG. 4.3. Concentration of DCE in $[\frac{mg}{l}]$ (y-axis) versus the domain $[m]$ (x-axis). Time profiles at $t = 0, 300, 600, 1000, 1400$ days. Extraction well at 50m. Initial data for DCE is given by (4.1).

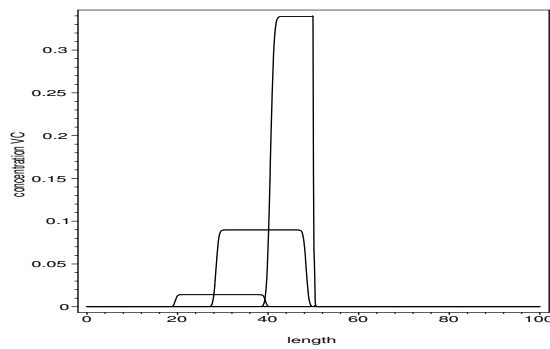


FIG. 4.4. Concentration of VC in $[\frac{mg}{l}]$ (y-axis) versus the domain $[m]$ (x-axis). Time profiles at $t = 0, 300, 600, 1000, 1400$ days. Extraction well at 50m. Initial data for VC is given by (4.1).

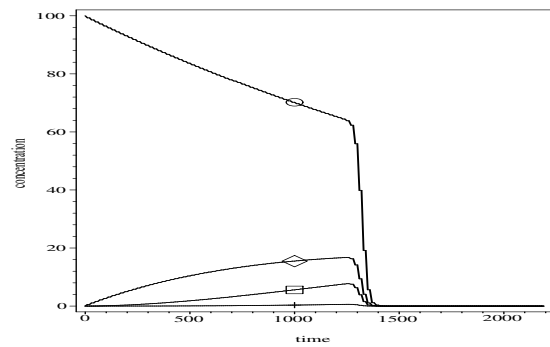


FIG. 4.5. Maximal concentration in the domain of all contaminants in $[\frac{mg}{l}]$ (y-axis) versus time $[day]$ (x-axis). Notation: PCE - circle, TCE - diamond, DCE - box, VC - cross. Extraction well at 50m.

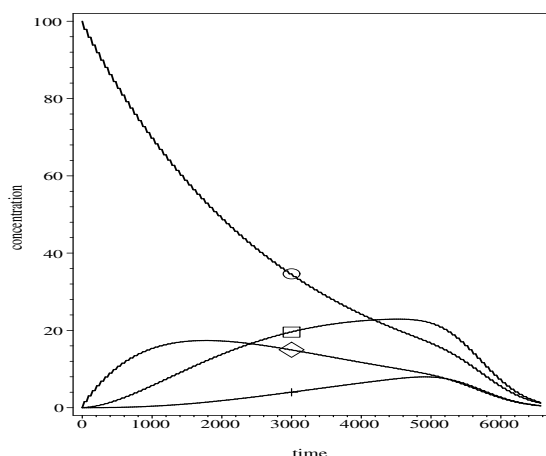


FIG. 4.6. Concentration of all contaminants in $\left[\frac{\text{mg}}{\text{l}}\right]$ (y -axis) versus time [day] (x -axis). Notation: PCE - circle, TCE - diamond, DCE - box, VC - cross. No advection. The time step for computation was 30 days.

Our next work will be to combine groundwater flow model and reactive transport model for more than one dimension which will be applied for prediction of bioremediation in situ.

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