Numerical simulation of transport and sequential biodegradation of chlorinated aliphatic hydrocarbons using CHAIN_2D

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Abstract:

Microbiological degradation of perchloroethylene (PCE) under anaerobic conditions follows a series of chain reactions, in which, sequentially, trichloroethylene (TCE), *cis*-dichloroethylene (c-DCE), vinylchloride (VC) and ethene are generated. First-order degradation rate constants, partitioning coefficients and mass exchange rates for PCE, TCE, c-DCE and VC were compiled from the literature. The parameters were used in a case study of pump-and-treat remediation of a PCE-contaminated site near Tilburg, The Netherlands. Transport, non-equilibrium sorption and biodegradation chain processes at the site were simulated using the CHAIN_2D code without further calibration. The modelled PCE compared reasonably well with observed PCE concentrations in the pumped water. We also performed a scenario analysis by applying several increased reductive dechlorination rates, reflecting different degradation conditions (e.g. addition of yeast extract and citrate). The scenario analysis predicted considerably higher concentrations of the degradation products as a result of enhanced reductive dechlorination of PCE. The predicted levels of the very toxic compound VC were now an order of magnitude above the maximum permissible concentration levels. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS   biodegradation; sorption; transport; chlorinated aliphatic hydrocarbons (CAH's); numerical modelling

INTRODUCTION

Chlorinated aliphatic hydrocarbons (CAH's) are some of the most widespread groundwater contaminants in the industrialised world (Kästner, 1991; Wilson, 1996). Perchloroethylene (PCE) and trichloroethylene (TCE) are used on a large scale as solvents, degreasing agents for metal surfaces and electronics, dry-cleaning and for a wide range of applications in chemical reactions. Because of spills and accidents, these hydrocarbons have become important contaminants in soil and groundwater. There is a growing concern about these compounds since they are known to persist in the environment over a long period of time, because of their xenobiotic origin, and because they are suspected carcinogens, even at low concentrations. Concern about contamination with PCE or TCE has become more acute, owing to the observation that certain anaerobic bacteria in groundwater are able to transform these compounds to *cis*-dichloroethylene (c-DCE) and vinylchloride (VC). The latter compound is known to be a potent mutagen and carcinogen in humans (Badaracco, 1985). Anaerobic biological transformations of some CAH's can occur within the time frame of interest in groundwater (McCarty, 1997). In certain situations, biological degradation of CAH's can be

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stimulated by providing optimal redox conditions or by adding nutrients, co-enzymes or electron donors. This can increase the rate of remediation and decrease the mass of contaminant to be treated (Madsen, 1991; Fetter, 1992).

Numerical modelling, in addition to laboratory and field-scale experimentation, provides the means to investigate the influence of different processes on the effectiveness of remediation techniques and the risk of accumulation of toxic degradation products. A thorough understanding of the basic processes of transport and fate of CAH's in the environment is necessary in order to reduce the risk to human health, and to successfully formulate and implement remediation techniques.

Most sites contaminated with chlorinated aliphatic hydrocarbons are remediated by pump-and-treat techniques (EPA, 1997). Numerical models, often embedded in optimization routines, are often used to predict the effectiveness of and the time needed for such clean-up operations.

In the present study, a numerical code, CHAIN_2D (Šimůnek and van Genuchten, 1994), was used to evaluate the clean-up of a PCE-contaminated shallow aquifer. CHAIN_2D incorporates chemical chain reactions in classical solute transport equations to make it possible, not only to predict the concentration of the contaminants themselves, but also the concentration of their reaction products. The decrease in contaminant concentration due to biodegradation becomes especially significant at low pumping rates, and needs to be incorporated in the model. The objectives of this study were to: (1) compile values for degradation rate constants, sorption coefficients and mass exchange rates from a literature review; (2) compare field observations on PCE degradation under pump-and-treat conditions with model predictions obtained without extensive model calibration; and (3) numerically illustrate the effect of stimulated biodegradation on reaction products such as the toxic VC.

THEORY

Reductive dechlorination

Abiotic chemical degradation of PCE occurs very slowly. More important is the microbiological transformation of this chemical. Oxidation of PCE in aerobic environments is unlikely because of the high oxidation grade of the molecule (Vogel *et al.*, 1987). PCE can only be degraded successfully by reductive processes (Seng, 1991). This reaction occurs preferentially under methanogenic or sulfate-reducing conditions (Wilson, 1996). Such conditions are commonly found in the saturated zone of the soil, or can be created by adding organic compounds. Microorganisms may be using CAH's in their energy metabolism. This process involves unique reactions since the microorganisms use CAH's as electron acceptors similar to the use of oxygen by aerobic organisms. This, in turn, requires suitable electron donors such as sugars or short aliphatic chains (McCarty, 1997). The anaerobic degradation process also requires, besides a sufficient concentration of electron donors, an optimal redox potential. Other chemical compounds can influence the degradation of CAH's in different ways: they can affect the solubility, and thus the bioavailability, of CAH's; have a stimulating or toxic influence on microbial growth; serve as a primary substrate for bacteria; influence redox conditions; or induce the production of enzymes necessary for CAH degradation (Praamstra, 1996). The most important pathway for anaerobic biodegradation of highly chlorinated CAH's (e.g. PCE, TCE) is reductive dechlorination (Vogel *et al.*, 1987). The chlorinated ethenes can be reductively dechlorinated in a sequential manner, ultimately yielding ethene, which is environmentally acceptable and does not cause direct health effects (Bosma, 1994; Gosset and Zinder, 1997) (see Figure 1).

In this process, the four chlorine atoms are sequentially replaced by hydrogen atoms in a hydrogenolysis reaction (Hollinger, 1992). The hydrogen atoms are provided by the substrate that is being oxidized (i.e. the electron donor). The release of chlorine atoms in water provides energy. A relatively large amount of substrate is necessary for this reaction pathway (Geritse *et al.*, 1995). The rate of degradation of these contaminants strongly depends on the concentration of the substrate. First-order kinetics is, in most cases, adequate for describing reductive dechlorination at relatively low concentrations (Fetter, 1992; Praamstra, 1996).
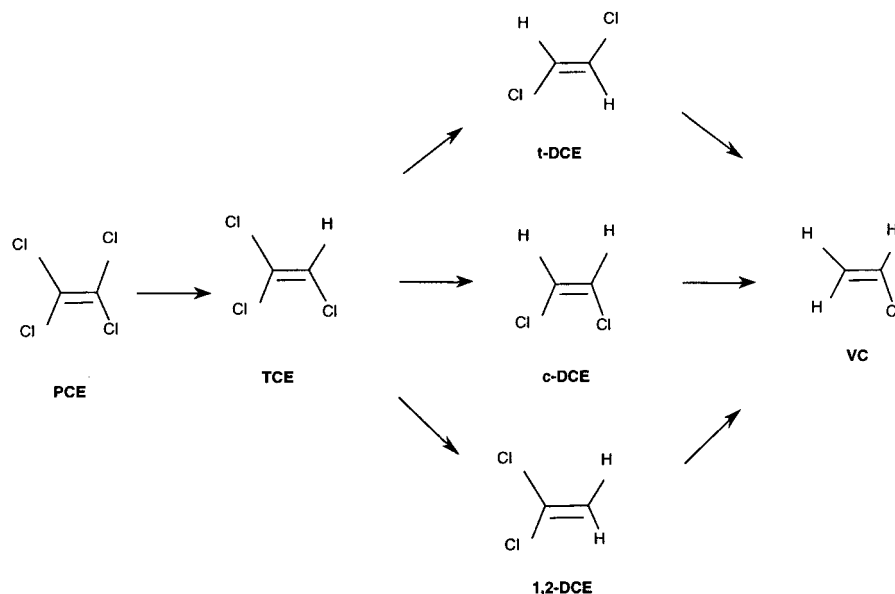
Figure 1. Reductive dechlorination of chlorinated ethenes under anaerobic conditions

Biostimulation

In some cases, natural degradation processes are sufficient to solve the problem of site contamination with CAH's (Madsen, 1991; Fetter, 1992). However, as the degradation of PCE at contaminated sites often occurs under relatively unfavourable conditions (i.e. low temperature; low concentration of electron donors, bacteria and nutrients; low bioavailability of the contaminants), it is often recommended to enhance the rate of biodegradation. This can be achieved in several ways: essential nutrients like phosphate and nitrate can be provided, co-enzymes can be supplied or electron donors like methanol, methane, glucose, acetate, citrate (e.g. Bagley and Gosset, 1990; Hollinger, 1992; Travis and Rosenberg, 1997) can be added. Buchanan *et al.* (1994) used yeast extract (co-enzymes) and citrate (electron donor) to enhance reductive dechlorination of PCE.

Sorption

Sorption on soil organic matter is an important factor affecting the transport of organic contaminants during pump-and-treat remediation. Pump-and-treat, however, often creates artificially large groundwater flow velocities, a situation that may lead to the presence of different types of sorption- and diffusion-related non-equilibria (Brusseau and Rao, 1991). Sorption of chlorinated ethenes on soil organic matter is, in essence, a partitioning process between the organic matrix and water. By losing the organic molecule, the water phase wins free energy (Scow and Johnson, 1997). At high groundwater velocities, desorption from the organic matrix may become rate limited, leading to kinetic or chemical non-equilibrium (van Genuchten and Cleary, 1979; Pignatello and Xing, 1996). Since the (de)sorption of contaminants on (from) soil organic matter determines their bioavailability (Brusseau, 1995; Scow and Johnson, 1997), their transport characteristics, sorption characteristics and desorption rates are important parameters for solute modelling during pump-and-treat remediation.

Description of the numerical model

The numerical model CHAIN_2D (Šimůnek and Genuchten, 1994) may be used to numerically simulate two-dimensional water flow, heat movement and solute transport in saturated and unsaturated soils. Variably saturated water flow in porous media is based on the Richards equation. Sequential first-order

transformation reactions such as those that occur during sequential dechlorination have been incorporated in CHAIN_2D. Transport of the different components of the degradation chain is described by advection–dispersion type equations. The equations for the reagent and the reaction products are, respectively:

$$\frac{\partial \theta c_1}{\partial t} + \frac{\partial \rho s_1}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_1^{ij}\frac{\partial c_1}{\partial x_j}\right) - \frac{\partial q_i c_1}{\partial x_i} - (\mu_1 + \mu_1')\theta c_1 \tag{1}$$

$$\frac{\partial \theta c_k}{\partial t} + \frac{\partial \rho s_k}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_k^{ij}\frac{\partial c_k}{\partial x_j}\right) - \frac{\partial q_i c_k}{\partial x_i} - (\mu_k + \mu_k')\theta c_k + \mu_{k-1}'\theta c_{k-1} \tag{2}$$

with $k \in (2, \ldots, n_s)$, and where c is the solute concentration in soil–water [M L^{-3}], s the sorbed solute concentration [M M^{-1} soil], ρ is the bulk density [M L^{-3}], t is time [T], x_i are the spatial co-ordinates [L], θ is the water content [L^3 L^{-3}], D^{ij} the dispersion coefficient tensor [L^2 T^{-1}], q_i the ith component of the Darcian velocity [L T^{-1}], μ a first-order degradation rate constant [T^{-1}], μ' the first-order rate constant providing connection between individual species in the chain reaction [T^{-1}], k represents the kth chain number, and n_s is the number of chemical substances in the chain reaction. Although CHAIN_2D includes provisions for transport in the gas phase assuming linear equilibrium between liquid and gaseous phase, these options were not considered in the simulations. Degradation assumes that Equations (1) and (2) only occur in the liquid phase. Scow and Johnson (1997) showed that this hypothesis is, in many circumstances, acceptable. Degradation is often mimicked by a first-order process:

$$-\frac{\partial c_k}{\partial t} = \mu_k c_k \tag{3}$$

Sorption on the solid phase s_k is described in CHAIN_2D by a generalized equation, of the following form:

$$s_k = \frac{K_{d,k}c_k^{\beta_k}}{1 + n_k c_k^{\beta_k}} \tag{4}$$

where $K_{d,k}$ [L^3 M^{-1}] and n_k [L M^{-1}] are empirical coefficients. The Freundlich, Langmuir and linear adsorption equations are special cases of Equation (4). In this study we assume $n_k = 0$ such that $\beta_k = 1$ [Equations (1) and (2) are linear, and Equation (4) reduces to the linearized Freundlich equation]. Chemical non-equilibrium is described by a two-site approach, to permit consideration of rate-limited desorption. The two-site sorption concept proposes that sorption sites can be divided into two fractions, s_k^e and s_k^n, following:

$$s_k = s_k^e + s_k^n \tag{5}$$

Sorption on type-1 sites (s_k^e) [M M^{-1} soil] is assumed to be instantaneous, while sorption on the remaining type-2 sites (s_k^n) [M M^{-1} soil] is considered to be time dependent. At equilibrium, the sorbed concentrations on type-1 (equilibrium) and type-2 (kinetic) sites are, respectively:

$$s_k^e = F_k s_k \tag{6}$$

$$s_k^n = (1 - F_k)s_k \tag{7}$$

where F_k is the fraction of exchange sites in equilibrium with the solution phase [-] and s_k is the total amount of sorption sites. Because type-1 sorption sites are always at equilibrium, differentiation of Equation (6) yields the sorption rate for the type-1 equilibrium sites:

$$\frac{\partial s_k^e}{\partial t} = F_k s_k \frac{\partial s_k}{\partial t} \tag{8}$$

Sorption on type-2 sites is assumed to be a first-order kinetic process. Differentiation of Equation (7) gives:

$$\frac{\partial s_k^n}{\partial t} = \alpha_k \left[(1 - F_k) \frac{K_{d,k} c_k^{\beta_k}}{1 + n_k c_k^{\beta_k}} - s_k^n \right] \tag{9}$$

where α_k is the rate constant for adsorption of the kth solute on type-2 sites.

LITERATURE REVIEW ON TRANSPORT AND BIODEGRADATION PARAMETERS

To model transport and degradation of chlorinated ethenes, sorption, mass exchange and degradation parameters for each chemical in the degradation chain of Figure 1 are required. The parameters characterizing sorption and biodegradation of CAHs were collected from recent literature and are listed in Tables I–III. The literature review of parameter values helps to determine a reasonable parameter range.

Table I. Literature values of K_{OW} and estimated values of K_{OC} using the equation $\log K_{OC} = 0.95 \log K_{OW} - 0.2$ (Ball and Roberts, 1991)

Solute	$\log K_{OW}$ (-)	K_{OC} (m³/kg)	Reference
PCE	2·82	0·303	Fetter, 1988
PCE	2·88	0·343	EPA, 1979
PCE	2·60	0·186	Ball and Roberts, 1991
PCE	2·60	0·186	Fetter, 1992
PCE	2·60	0·186	Curtis et al., 1986
PCE	2·53	0·160	Banerjee et al., 1980
PCE	2·88	0·343	Schwarzenbach and Westall, 1981
PCE	2·76	0·269	Brusseau et al.,1991
PCE	2·61	0·190	Brusseau et al., 1990
PCE	2·60	0·186	Keizer, 1992
PCE	2·95	0·400	Minister of Supply and Services, 1993a
TCE	2·50	0·152	Fetter, 1988
TCE	2·29	0·138	EPA, 1979
TCE	2·50	0·152	Banerjee et al., 1980
TCE	2·42	0·125	Schwarzenbach and Westall, 1981
TCE	2·34	0·132	Hutzler et al., 1986
TCE	2·39	0·118	Hutzler et al., 1986
TCE	2·20	0·078	Keizer, 1992
TCE	2·15	0·071	Brusseau, 1992
TCE	2·10	0·062	Brusseau et al., 1991
TCE	2·15	0·070	Brusseau et al., 1991
TCE	2·45	0·137	Brusseau et al., 1991
TCE	2·35	0·107	Minister of Supply and Services, 1993b
c-DCE	1·48	0·016	EPA, 1979
c-DCE	2·07	0·059	Rippen, 1984
t-DCE	2·07	0·059	Rippen, 1984
t-DCE	1·88	0·039	Fetter, 1988
t-DCE	1·87	0·038	Brusseau et al., 1991
t-DCE	1·48	0·016	EPA, 1979
1,1-DCE	1·48	0·016	EPA, 1979
1,1-DCE	2·12	0·065	Rippen, 1984
1,1-DCE	2·67	0·217	Fetter, 1988
VC	0·6	0·0023	EPA, 1979
VC	1·17	0·0082	Rippen, 1984
VC	0·60	0·0023	Schwarzenbach and Westall, 1981

Table II. Regression values for the mass transfer rate ($\log \alpha = D \log K_{\mathrm{d}} + E$) for a groundwater velocity of 4 cm/h and a soil temperature of 10 °C

Solute	D	E	r^2	Reference
HOC's	−0·668	0·301	0·95	Brusseau *et al.*, 1989
TCE	−0·83	0·92	—	Brusseau *et al.*, 1991
PCE, TCE, t-DCE	−0·47	0·56	0·85	Brusseau and Rao, 1991
PCE, TCE, TCM, DCB, BP, naphthalene, xylene	−0·70	−1·67	0·80	Brusseau *et al.*, 1991

Table III. Published first-order biodegradation rates (μ) and half-time values ($t^{1/2}$) for reductive dechlorination of CAH's

Solute	$k(\mathrm{d}^{-1})$	$t^{1/2}$ (d)	System characteristics	Organic carbon content (%)	T (°C)	Reference
PCE	0·002	347	Aquifer, sand, anaerobic conditions	2·8		Roberts *et al.*, 1982
PCE	0·0075–0·071	9·8 92	Anaerobic conditions, sulfate-reducing conditions	0·25	35	Bagley and Gosset, 1990
PCE	0·0079	88	Anaerobic conditions		35	Bouwer *et al.*, 1981
PCE	0·0021	330				Praamstra, 1996
TCE	0·003	231	Aquifer, sand, anaerobic conditions	2·8		Roberts *et al.*, 1982
TCE	0·001–0·003	231 693	*In situ* aquifer, anaerobe		10	Wilson *et al.*, 1994
TCE	0·008	87	Microcosm, silt/clay/sand, anaerobic conditions	0·34	17	Wilson *et al.*, 1996
TCE	0·0062	112	Microcosm loamy sand, sulfate reducing	2	25	Barrio-Lage *et al.*, 1987
TCE	0·004	173	*In situ*, no addition	1		Poulsen *et al.*, 1996
TCE	0·0001–0·003	231 6930	Microcosm aquifer, anaerobic conditions			Martin and Imbrigiotta, 1994
TCE	0·0033	210	Microcosm aquifer, anaerobic conditions			Kleopfer *et al.*, 1985
TCE	0·006	116	Anaerobic conditions		35	Bouwer *et al.*, 1981
c-DCE	0·0014–0·002	347 495	*In situ*, aquifer, anaerobic conditions		10	Wilson *et al.*, 1994
c-DCE	0·004	173	Microcosm sediment, anaerobic conditions		25	Barrio-Lage *et al.*, 1986
t-DCE	0·0017	408	*In situ*, aquifer, anaerobic conditions			Wilson *et al.*, 1994
t-DCE	0·007	99	Microcosm sediment, anaerobic conditions			
1,1-DCE	0·001–0·0026	267 693	*In situ*, aquifer, anaerobic conditions			Wilson *et al.*, 1994
1,1-DCE	0·0084	83	Alluvial silt/clay/sand, Anaerobic conditions			Wilson, 1996
1,1-DCE	0·0052	133	Microcosm sediment, anaerobic conditions			Barrio-Lage *et al.*, 1986
1,1-DCE	0·006	116	Microcosm sediment, anaerobic conditions			Barrio-Lage *et al.*, 1986
VC	0·0005–0·002	347 1386	*In situ*, aquifer, anaerobic conditions			Wilson *et al.*, 1994

Soil water partitioning coefficients

Organic chemicals generally are subject to partitioning between the liquid phase and the solid phase (mostly on soil organic matter). Partitioning between the liquid and solid phases in soils with organic carbon content $>0.1\%$ can be assessed from the organic carbon–water partitioning coefficient, K_{OC} [$L^3 M^{-1}$] (Harmon and Roberts, 1994):

$$K_d = K_{OC}*f_{OC} \tag{10}$$

where K_d [$L^3 M^{-1}$] is the soil–water partitioning coefficient, and f_{OC} [-] is the fraction of organic carbon of the soil. The value of K_{OC}, in turn, can be assessed from K_{OW} [-], the octanol–water partitioning coefficient. The value of K_{OW} reflects the hydrophobic characteristics of the molecule and can be assessed either from the chemical structure or can be measured. An empirical correlation between K_{OC} and K_{OW} is (Scow and Johnson, 1997):

$$\log K_{OC} = A \log K_{OW} + B \tag{11}$$

where A and B are regression coefficients. Ball and Roberts (1991) and Schwarzenbach and Westall (1981) give a review of regression values for A and B. The value of A was mostly in a range of 0·9–1·0, whereas B ranged between -0.3 and 0·4. Previously published K_{OC} values are listed in Table I.

Fraction of type 1 sites

The fraction of type-1 sites (equilibrium) was similarly estimated by means of a regression equation. Brusseau *et al.* (1991) determined the regression equation for CAH's as:

$$F_k = 0.102 \log K_{OW} + C \tag{12}$$

with $r^2 = 0.80$. The value of F_k was found to change slightly with groundwater velocity (Brusseau *et al.*, 1991); for chlorinated ethenes the value of F varied between 0·4 and 0·6 (Brusseau *et al.*, 1991; Brusseau, 1992). We found that CHAIN_2D predictions were not very sensitive to this parameter for given adsorption rates (Schaerlaekens, 1997).

First-order mass transfer rate

Several empirical relationships exist for the correlation between the soil–water partitioning coefficient and the mass transfer coefficients for given values of the pore–water velocity (Brusseau and Rao, 1991; Brusseau *et al.*, 1991; Brusseau, 1992):

$$\log \alpha = D \log K_d + E \tag{13}$$

where D and E are regression coefficients. A summary of regression values from the literature is given in Table III for a flow velocity of 4 cm h^{-1} and a soil temperature of 10 °C.

Biodegradation rate

A wide range of values was found for biodegradation rates of CAH's. The values are very site specific and differ as a function of oxidation potential, nutrients present, concentration of contaminants, and presence of microorganisms, among other factors. Whereas different degradation rate equations exist, we assumed that first-order degradation is a reasonable assumption for biological degradation involving electron acceptors at low concentrations (Praamstra, 1996). Very few field data were available for biodegradation rates, and we obtained most data from literature microcosm experiments. If no values were given, the rate was calculated from the published half-life times. A review for parameters obtained in this manner is given in Table III.

Table IV. Measured initial soil–water concentrations as
a function of radial distance to extraction well

s (m)	c_{PCE} (mg/l)
4·3	26·00
8·6	16·25
17·2	9·75
23·5	6·50
30·1	5·20
33·0	1·95
38·1	0·65
44·0	0·19
53·9	—

CASE STUDY

Field site

The CHAIN_2D code was applied to a heavily polluted site near the town of Tilburg, The Netherlands. The site contained many chlorinated hydrocarbons, of which 65% consisted of PCE and 30% of 1,1,1-tricloroethane (TCA). Degradation products of these contaminants were below the detection limits. The site was previously characterized and described by Praamstra (1996) and served the purpose of evaluating CHAIN_2D calculations. The 13-m thick top layer of the aquifer consisted of a sandy, Pleistocene material, with 0·44% organic matter and several loam and peat lenses. The groundwater level was 1 m below the surface. The regional flow was negligible. CAH contamination was found throughout the whole saturated zone of the aquifer and reached the extremely low permeability bottom clay layer. A three-dimensional characterization of the contaminant plume was based on Praamstra (1996). PCE concentrations of the contaminants were measured as a function of the radial distance to the extraction well. Results are shown in Table IV. Decay products of PCE, that were probably present at low concentrations owing to degradation were not detected at the site.

A single-well pump-and-treat scheme was installed over the full depth of the saturated zone and pumping was started on 14 July 1994, with an average extraction rate of 144 m^3 d^{-1}. The pump was disconnected twice, from 12–18 December 1994 and from 13–28 March 1995. Chemical analyses of PCE concentrations in the pumped water were carried out monthly.

MODEL IMPLEMENTATION

A 110-m diameter, circular computational domain, with the pumping well at its centre, was generated using the unstructured mesh generator provided in HYDRUS_2D (Šimůnek *et al.*, 1996). At each node a set of flow and transport parameters, based on the properties of the present soil type and the measured initial PCE concentrations, were assigned. No decay products were detected at the site. Modelling the site's history in order to estimate these initial concentrations would require an extended knowledge of the history of the contamination and of the (bio)chemical properties of the soil, which were not available. Site-specific values for chemical transport parameters, based on laboratory measurements, were not available. Therefore, all parameters were estimated from the values and relationships discussed in the literature review. Table V lists chemical transport and degradation parameters for PCE and its daughter products as used for the simulation.

The soil–water partitioning coefficients were calculated from the organic carbon–water partitioning coefficients by applying Equation (10) using the site-specific fraction of soil organic matter, with $f_{OC} = 0·004$. The latter was calculated from the octanol–water partitioning coefficients of the different chemicals. The degradation rates for PCE and TCE were taken from Roberts *et al.* (1982) whereas those for

Table V. Chemical transport and biodegradation input parameters for the CHAIN_2D model. K_s denotes the saturated conductivity, ρ the bulk density, F_k the fraction of type 1 sites, K_d the partition coefficient soil–water, μ the first-order degradation rate and α the mass transfer rate

Parameter	Soil	PCE	TCE	c-DCE	VC
K_s (m/s)	8.10×10^{-5}				
ρ (kg/m³)	1550				
F_k (−)	0·45				
K_d (m³/kg)		784	277	153	10·6
α (d⁻¹)		0·002	0·003	0·0014	0·0005
μ (d⁻¹) without biostimulation		0·005	0·005	0·005	0·005
μ (s⁻¹) in case of biostimulation		3.82×10^{-7}	2.43×10^{-7}	2.20×10^{-7}	5.78×10^{-8}

c-DCE and VC were taken from Wilson *et al.* (1994). The first-order rate constants for desorption from type-2 sorption sites, presumably mainly organic matter (Pignatello and Xing, 1996), were obtained from Brusseau (1992). The fraction of type-1 sites was taken from Praamstra (1996).

MODELLING RESULTS

Figure 2 shows numerical calculations of the concentration of PCE and its degradation products in the extraction water, from the start of the pumping ($t = 0$) until 1000 days later. Measured PCE concentrations are also indicated. The measured reaction products never reached concentrations above the detection limit of 1 mg l⁻¹. Concentrations of simulated decay products were never higher than this detection limit. Since no
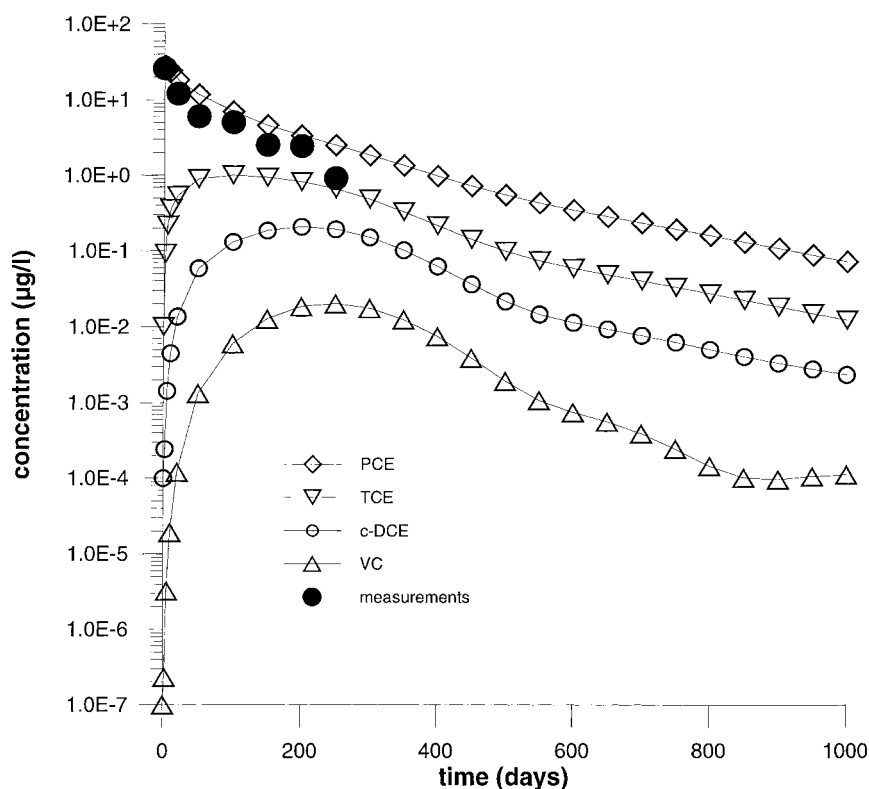

Figure 2. Simulated concentrations of PCE and its reaction products in pumping water

decay products were detected at the start of the pump-and-treat remediation, a zero concentration initial condition was applied for all decay products, although it is reasonable to suppose non-zero concentrations of TCE, c-DCE and VC owing to degradation. Lack of information on the history of the contamination (including details on the source term) did not allow them to be estimated by numerical simulation. These limitations to the numerical study, however, do not affect the predicted PCE concentrations.

In spite of the fact that all physicochemical parameters were estimated from the literature, the numerical simulation follows the measured values quite well, except for the last measured value of PCE, which was almost three times lower than the calculated value. The somewhat lower measured PCE values, certainly of the last data point, could possibly be the result of volatilization of PCE from the sampled well water, since PCE is known to have a relatively high Henry's constant. The remediation was terminated after about 250 days because remediation objectives were judged to be met (Praamstra, 1996). The calculated concentrations of the reaction products in soil and groundwater were very low and of no harm to public health. TCE and DCE have almost the same soil–water partitioning coefficient as PCE, and are extracted at relatively the same rate as PCE. VC on the other hand has a substantially lower partitioning coefficient and is removed much faster. Since no initial concentrations were known for these degradation substances, it is difficult to make a good estimate of their concentrations in the initial phase of the pumping.

For the biostimulation scenario, the degradation rates of Buchanan *et al.* (1994) were used (Table V). Their data were based on *in situ* tests in which yeast extract and citrate were added to an aquifer in order to stimulate growth of methanotrophic bacteria, and thus enhance PCE degradation. The degradation rates for the different chlorinated ethenes in the case of biostimulation were considerably higher than without biostimulation. Figure 3 shows the results of the scenario analysis with the higher degradation rates. The
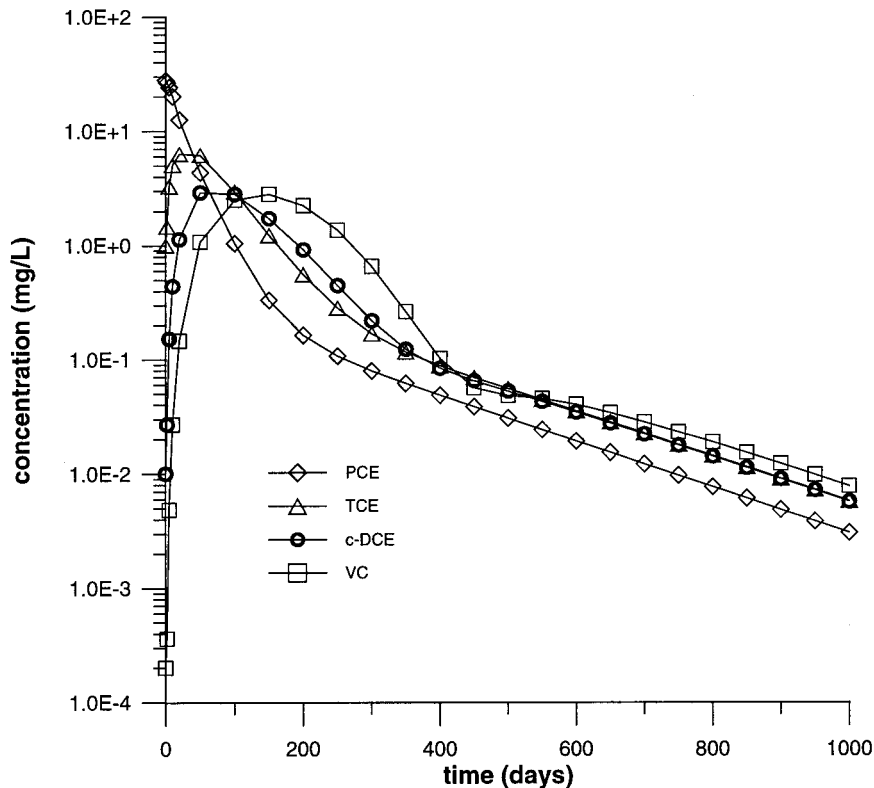

Figure 3. Simulated concentrations of PCE and its reaction products in a biostimulation scenario

total concentration of chlorinated ethenes in the extraction water declined much faster than for the scenario without stimulation.

However, the reaction products now reached higher concentrations than in the standard scenario, and exceeded the groundwater standards. Since the concentrations obtained for these chemicals are higher than the detection limit, the zero concentration initial condition has no major influence on the conclusions for this scenario; only the absolute values could have been higher. Since VC is much more hazardous than PCE, the pumping had to continue until the concentration of the reaction products reached acceptable values. The total remediation time, however, decreased, compared with the standard scenario.

CONCLUSIONS

Pump-and-treat remediation technologies have often been applied without considering a detailed design, based on numerical modelling, in which the physical, biological and chemical processes are represented as best as possible. Lack of detailed process models and parameters certainly contributed to this practice. In this paper a potentially useful model for the optimal design of pump-and-treat remediation is presented and applied to a PCE-contaminated site in the Netherlands. The most important parameters controlling sorption and rate-limited mass transfer between the liquid and organic matter, and the degradation rate for the chain reaction PCE $\rightarrow$ TCE $\rightarrow$ c-DCE $\rightarrow$ VC were obtained from a compilation of literature values. Given the scarcity of site-specific model parameters, simulations with CHAIN_2D of PCE removal from the aquifer were in relatively good agreement with PCE measurements. Observations and simulations showed that, in the absence of biostimulation, the concentration of PCE degradation products remained below the detection limit. Because the soil–water partitioning coefficients for TCE and c-DCE were of the same order as that for PCE, removal of TCE and c-DCE occurred at relatively the same rate as PCE removal. The toxic component, VC, had a much lower soil–water partitioning coefficient compared with that of PCE, and its removal occurred at a much faster rate (assuming the same mass transfer parameter).

When the biodegradation rates of *in situ* biostimulation conditions were simulated, PCE degradation products reached their maximum permissible level much faster than without biodegradation enhancement. The concentrations of the degradation products TCE, c-DCE and VC were now close to, respectively one, two and three orders of magnitude higher compared with the concentrations obtained in the absence of biostimulation. VC temporarily reached critical concentrations above the maximum permissible contaminant level. In the case of biostimulation it is important to closely monitor any toxic degradation products, in addition to the main contaminant; unforeseen high levels of toxic degradation products may otherwise go undetected.

LIST OF SYMBOLS

c solute concentration in soil water [M L^{-3}]

D^{ij} dispersion tensor [L^2 T^{-1}]

f_{OC} fraction of organic carbon [-]

F_k fraction of type 1 sites [-]

k subscript of the nth step in the chain reaction

K_{OC} organic carbon–water partitioning coefficient [L^3 M^{-1}]

K_{OW} octanol–water partitioning coefficient [-]

K_d soil–water partitioning constant [L^3 M^{-1}]

K_s saturated conductivity [L T^{-1}]

n_s number of compounds

q   Darcy velocity [L T^{-1}]

s   solute concentration sorbed on to the soils [M M^{-1} soil]

s^e solute concentration sorbed on type 1 sites [M M^{-1} soil]

s^n solute concentration sorbed on type 2 sites [M M^{-1} soil]

s   total solute concentration sorbed on the soil [M M^{-1} soil]

t   time [T]

x   distance [L]

α   first-order mass transfer coefficient (T^{-1})

$β^k$ Freundlich experiment (-)

μ   first-order degradation rate (T^{-1})

μ′   first-order production rate (T^{-1})

ρ   bulk density (M L^{-3})

θ   porosity or water constant at saturation (L^3/L^3)

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