MULTI-COMPONENT REACTIVE TRANSPORT MODELING OF PCE DEGRADATION AT A PILOT SCALE CONSTRUCTED WETLAND BITTERFELD, GERMANY

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Summary. Used as solvent and dry cleaner, PCE (perchloroethylene) is a widespread groundwater contaminant in industrialized countries. Recently, horizontal subsurface flow constructed wetlands (CWs) were proved to be an attractive alternative for treating PCE bearing groundwater [2].

In this context, numerical modeling is a necessary tool in evaluating the performance of CWs, and in studying and predicting the evolution of PCE plumes in CWs. In this work, a multi-component reactive transport model is used to analyze the removal processes of chlorinated ethenes in CWs. The numerical code OpenGeoSys has been used to simulate the transport and kinetically controlled PCE degradation reactions with the operator splitting sequential noniterative approach (SNIA). Parameters controlling the PCE degradation process is calibrated against field measured concentrations using the parallel-PEST software on a linux cluster.

The developed model is applied to analyze transport and biodegradation processes occurring at an unplanted pilot-scale CW scenario. The model captures the fate and transport of PCE, TCE, DCE, VC and ethene.

The numerical model used in this study is a useful engineering tool for integrating treatment performance data within a rational modeling framework, thus, would be used for designing CWs treating waters contaminated by chlorinated ethenes.

1 Introduction

Chlorinated ethenes are ubiquitous groundwater contaminants in aquifers in industrialized countries worldwide. Accidental release of perchloroethylene (PCE) can contaminate groundwater and pose risk to human health. However, PCE can be degraded to less chlorinated compounds i.e trichloroethene (TCE), dichloroethenes (DCEs) and vinyl chloride (VC) by microbial activities in subsurface environments. The maximum contaminant level (MCL) for PCE and TCE is 5 $\mu g L^{-1}$ [3] and for VC is 2 $\mu g L^{-1}$ in drinking water[1]. Natural attenuation of low concentration of chlorinated ethenes under aerobic and anaerobic conditions are proven possible [13][14] [4] [5] [6] [7] [8] [12] [11] [9] [10].

Horizontal subsurface flow constructed wetlands (CWs) are an attractive cost-effective alternative for treating PCE contaminated groundwater [15][2]. Two pilot-scale planted and unplanted constructed wetlands (CWs) with 6x1x0.5 m in dimension are constructed in Bitterfeld, Germany since 2003 [16]. The PCE contaminated water is pumped from a well installed at a depth of 22 m over a period of 5 years and the measured data is recorded along the flow path (0.5, 1, 2, 3, 4 m) at three different depths of 0, 0.1 and 0.2 m from the base of the CW. The water level is kept constant at 0.1 m below the surface of the wetland by a float valve in the open water compartment. The retention time of the CW is approximately 6 days [16].

The unplanted CW system as the reference base for the planted CW system is simulated in this work. OpenGeoSys (OGS) code applying the operator-splitting sequential non-iterative approach (SNIA) is used at this work to model PCE degradation which is mainly dechlorination processes [2] at the unplanted CW. A Monod type kinetics is considered for the PCE and its daughter products degradation chain reactions.

1.1 Governing equations

1.1.1 Flow

Based on mass conservation law, the groundwater flow equation in porous media is [17]:

$$\frac{\partial(\phi\rho)}{\partial t} + \nabla \cdot (\rho\bar{\boldsymbol{q}}) = q_s \tag{1}$$

where ϕ is the total porosity, t [T] is time, ρ [ML^{-3}] is the fluid density, q_s [T^{-1}] is the volumetric flow rate per unit volume of aquifer representing sources and sinks and $\bar{\mathbf{q}}$ [LT^{-1}] is given by Darcy's law:

$$\bar{\boldsymbol{q}} = -\frac{\boldsymbol{k}\rho g}{\mu}\nabla h \tag{2}$$

where $\boldsymbol{k}$ [L^2] in the intrinsic permeability, μ [ML^{-1}T^{-1}] is the fluid dynamic viscosity, h is the hydraulic head [L].

1.1.2 Transport

The aqueous components are transported in subsurface environments by advection, molecular diffusion and mechanical dispersion. The multi-component governing equation with source/sink and reaction is [18]:

$$\frac{\partial C}{\partial t} = \nabla(D\nabla C_i) - \nabla(\bar{v}C_i) - \frac{q_s}{\phi}C_{si} + \sum_{k=1}^{N} R_{k,i} \tag{3}$$

where D $[\mathrm{L^2T^{-1}}]$ is the hydrodynamic dispersion coefficient, $\bar{v}$ $[\mathrm{LT^{-1}}]$ is the seepage velocity, C_s $[\mathrm{ML^{-3}}]$ is the total aqueous component concentration in sources/sinks and $R_{k,i}$ (k=1,...,N)$[\mathrm{ML^{-3}T^{-1}}]$ is the rate of production or decay for component i (PCE,...,ETH) in the kth reaction.

1.1.3 Reaction

In the presence of electron donor and degrader, PCE can be degraded sequentially to ethene. These sequential reactions are modeled using Monod kinetics for the case where electron donor (H_2) is not a rate-limiting factor [19]. Accordingly, reaction rates R for PCE and its daughter products are:

$$\frac{d[PCE]}{dt} = -K_{PCE}^{ana}X\frac{[PCE]}{K_{PCE}^{mono} + [PCE]} \tag{4}$$

$$\frac{d[TCE]}{dt} = Y_{TCE/PCE}K_{PCE}^{ana}X\frac{[PCE]}{K_{PCE}^{mono} + [PCE]} - K_{TCE}^{ana}X\frac{[TCE]}{K_{TCE}^{mono} + [TCE]} \tag{5}$$

$$\frac{d[DCE]}{dt} = Y_{DCE/TCE}K_{TCE}^{ana}X\frac{[TCE]}{K_{TCE}^{mono} + [TCE]} - K_{DCE}^{ana}X\frac{[DCE]}{K_{DCE}^{mono} + [DCE]} \tag{6}$$

$$\frac{d[VC]}{dt} = Y_{VC/DCE}K_{DCE}^{ana}X\frac{[DCE]}{K_{DCE}^{mono} + [DCE]} - K_{VC}^{ana}X\frac{[VC]}{K_{VC}^{mono} + [VC]} \tag{7}$$

$$\frac{d[ETH]}{dt} = Y_{ETH/VC}K_{VC}^{ana}X\frac{[VC]}{K_{VC}^{mono} + [VC]} \tag{8}$$

where K_i^{ana} is the maximum growth rates on component i $[\mathrm{T^{-1}}]$, X is the biomass concentration $[\mathrm{ML^{-3}}]$, Y is the stoichiometric yield coefficient [-] and K_i^{mono} is the half-saturation constant of component i $[\mathrm{ML^{-3}}]$. Based on analysis of the measured data, anaerobic degradation is the dominant degradation pathway for chlorinated ethenes in the CW. Furthermore, A single type bacteria with constant concentration of 1e-6 g/L is considered throughout the simulation.

2   Model description

In order to simplify the simulation a two-dimensional homogeneous domain of 6 m long and 0.4 m deep is considered in this work. Confined condition is assumed. The data set measured during summer 2008 at the depth of 0.1 m from the base of the CW is considered for simulation. Figure 1 shows the geometry of the simulated CW with the considered boundary conditions. A fixed flux boundary condition for flow is used in bottom left side of the domain where the water is pumped in to the CW at a constant rate of 4.7 l/h. The hydraulic head is fixed on the right hand side with free exit boundary condition. The concentration is fixed to measured values at the inflow of the CW.

The domain is discretized to fine meshes (0.012 m) with 6953 nodes and 13274 elements and small time step size of 100 seconds is used to reduce numerical dispersion and oscillation. The Courant (Cr) and Peclet (Pe) numbers are 0.1 [-] and 7.6e-6 [-], respectively.

Table 1 shows the physical parameters used for the simulation. Anaerobic biodegradation as the dominant removal process of chlorinated ethenes in the system is considered [2]. A single Monod kinetic is applied for the degradation of PCE and its daughter products. The Table 2 shows the stoichiometric yield coefficient Y [-], calibrated maximum growth rates K^{ana} [T^{-1}] and the estimated half-saturation constant K_i^{mono} [ML^{-3}] of component i.

Parameter	Value	Unit
Q_{in}	1.3e-6	m^3/s
K	2.1e-3	m/s
n	0.28	-
ρ_f	1000	kg/m^3
ρ_s	2000	kg/m^3
μ	0.001	Pa.S
α_L	0.01	m
α_t	0.00025	m

Table 1: Table of input parameters.

2.1   Model calibration

Flow is calibrated based on retention time of the system of 6 days. Hydraulic conductivity and porosity are the parameters used for flow calibration of the system. Breakthrough curves of the chlorinated ethenes are used to measure the residence time of the contaminants in the system. The model calculated the residence time of 5.79 days.

Reaction calibration is carried out by the Parameter ESTimation (PEST) software. Parallel mode of PEST program is run on 100 cores of a Linux cluster with 1024 cores

Species	K^{ana} [d^{-1}]	K^{mono} [molL^{-3}]	Y [-]
PCE	1.17e-2	1e-3	1
TCE	8.12e-5	3.13e-5	1
DCE	1.0e-8	3.13e-5	1
VC	1.0e-8	1e-3	1

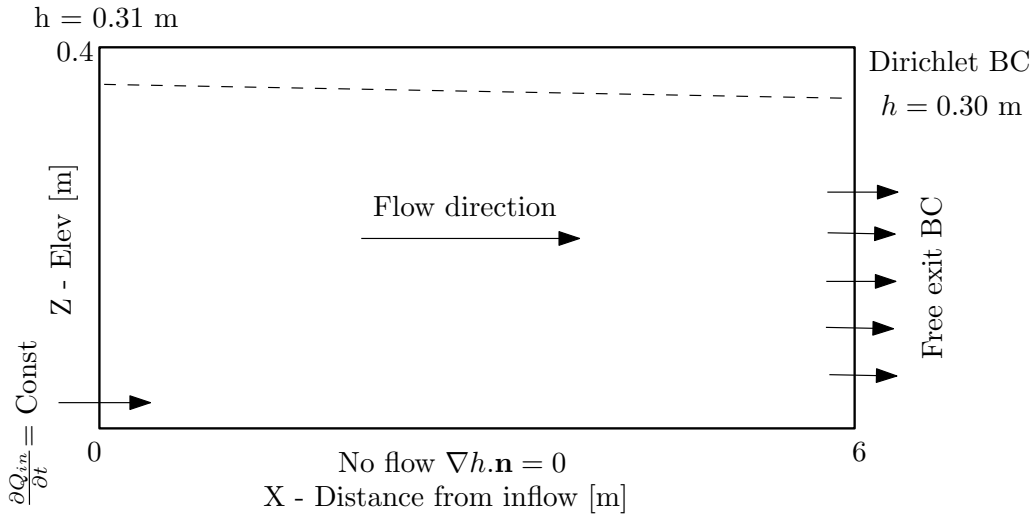Table 2: Reaction rates and stoichiometric coefficients used for simulation.

Figure 1: Schematic 2-D illustration of the simulated model with the applied boundary conditions.

to calibrate the model. Parallel PEST uses a shared file system to communicate between parallel PEST and the slaves. Four parameters, which are the anaerobic degradation rate $K^a na_i$ of PCE, TCE, DCE and VC, are calibrated with 25 mearsuement values. A weighting factor of 1 is given to each parameter meaning all 4 parameters are equally important. Each run took ca. 4 h and a total of 940 runs in 7 iterations are performed to obtain the best estimated parameters.

3 Results

Figure 2 shows the flow field and head gradient in the system. The hydraulic head gradient is 1.5 %. Breakthrough curves (BTCs) of different compounds are used to calibrate the flow field. Figure 3 shows the BTCs of chlorinated ethenes at the outlet point after 5.79 days of simulation time.

Figure 4 and 5 show the concentration profiles of PCE and its daughter products along the x axis at 0.1 m above the base of the CW. The concentration of PCE decreases exponentially and level off to zero at 5.2 m downgradient of the inflow. TCE concentration reaches its peak value at 2 m downgradient and decreases to 6 mol/L at the outlet point.

DCE and VC have a cumulative behavior and their concentrations increase throughout the simulation.
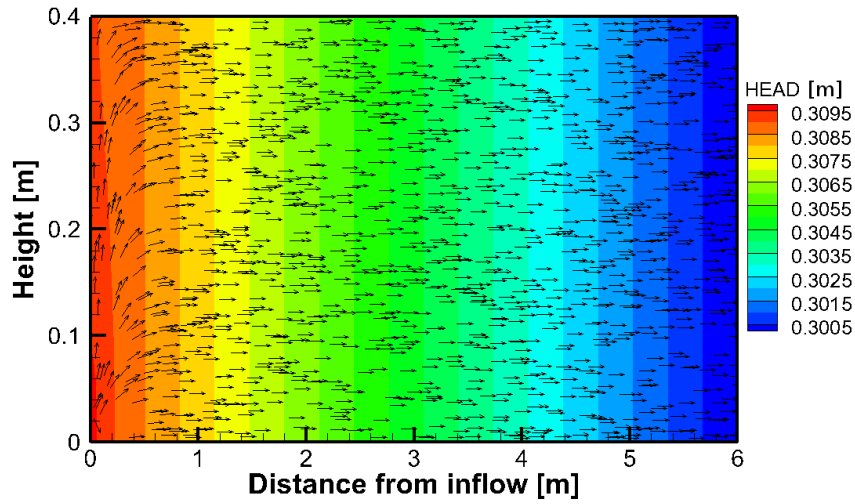

Figure 2: Simulated flow field in the CW. Arrows show the flow direction in the system. Heads difference is 1 cm.
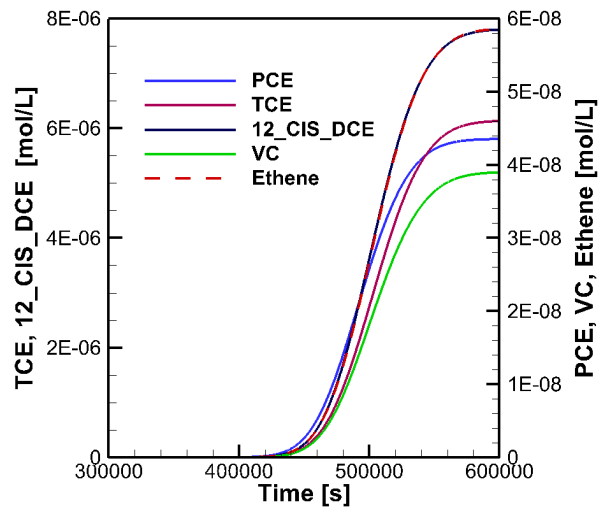

Figure 3: Breakthrough curves of chlorinated ethenes at the outlet point (x=6 m, z=0.1 m) after 6 days of simulation time.
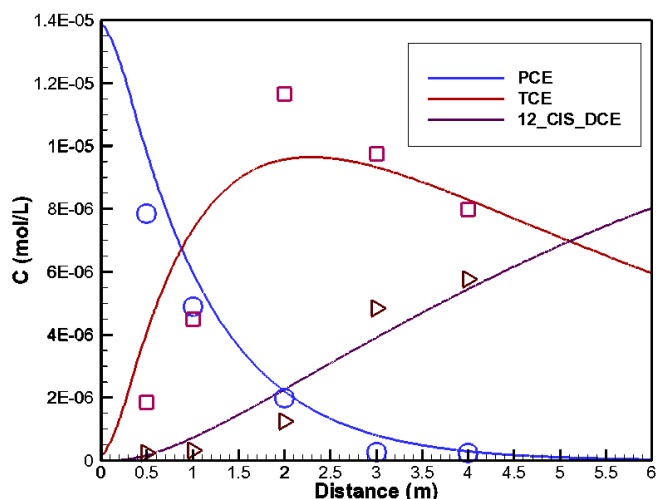
Figure 4: Simulated (solid line) and observed (symbols) concentrations profile of PCE ,TCE and 1,2-cis-DCE in the CW. Lines and symbols with the same color belong to one compound.
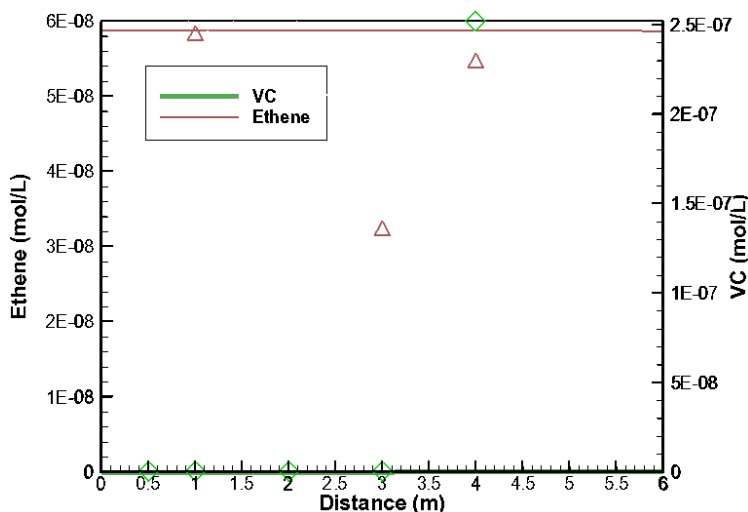

Figure 5: Simulated (solid line) and observed (symbols) concentrations profile of VC and ethene in the CW. The solid line and the symbols with the same color indicate one compound.

4   Summary and outlook

OpenGeoSys code is used to simulate multi-component reactive transport of chlorinated ethenes in a constructed wetland in Bitterfeld, Germany. Based on the pilot setup, a homogeneous aquifer is considered for the simulation. Steady-state groundwater flow is modeled based on Darcy's law (Eq. 2). Advection and diffusion/dispersion are accounted for the mass transport. A Monod Kinetics is used to account for sequential degradation reaction of chlorinated ethenes. Sequential Non-Iterative Approach is used to solve for

7

the reactions. Parallel PEST is used to calibrate reaction rates in the model.

The model was able to simulate the behavior of all chlorinated ethenes degradations fairly good. Some differences are seen between the simulated and the measured concentration of ethene in the system. Since no mechanism was considered for further mineralization of ethene or its partitioning into gas phase, the simulated concentration was deviated at measurement points (3 and 4 m) downgradient of the inflow. A small Peclet and Courant numbers were considered to avoid numerical oscillation and dispersion.

The model showed that the CW with the current geometry and physical parameters is able to successfully degrade PCE to zero concentration. The outflow concentrations of TCE (788 $\mu g L^{-1}$) and DCE (775 $\mu g L^{-1}$) are by far above the MCL of 5 $\mu g L^{-1}$. Although the outlet concentration of VC (0.62 $\mu g L^{-1}$) is below the MCL of 2 $\mu g L^{-1}$, it is expected to increase at the later time in the outflow water. The CW could not capture the major concentration profiles of TCE, and DCE in particular, which has an increasing trend. The increasing concentration of DCE increases the degradation rate of DCE which results in higher VC concentration in the system.

The residence time of the chlorinated ethenes in the CW system has to increase to solve the problem with the high outflow concentrations of chlorinated ethenes. Depending on the objective remediation rate, this can be achieved either by changing the dimension of the CW or decreasing the influx (Q_{in}) into the system.

The effect of roots and depth, which in turn determines the redox condition, on biodegradation of chlorinated ethenes in planted CW, inhibitive effect of sulphide on biodegradation and competitive inhibition between the electron acceptors will be addressed in future work.

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