# Modelling reactive transport of chlorinated hydrocarbons in groundwater under spatially varying redox conditions

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**Abstract** Chlorinated ethene degradation in groundwater has proven to be highly dependent on environmental conditions. Nevertheless, literature dealing with the interaction between chlorinated ethene degradation and inorganic electron acceptors such as nitrate is scarce. A study area located in Braunschweig (Germany), where redox conditions vary from nitrate-reducing to iron(III)-reducing conditions, is utilised for validation of a reactive transport model. A groundwater model using conventional 1st-order degradation kinetics, which was additionally optimised via sequential Monte-Carlo simulations, could not satisfactorily describe the pollutant distribution of the site. Thus, laboratory experiments considering the influence of inorganic electron acceptors were used to formulate enhanced inhibition kinetics that were implemented into the field scale model. The results yield a better accordance of simulated and measured concentration data than applying the previous 1st-order kinetics.

**Key words** DNAPL pollution; modelling; reactive transport

## INTRODUCTION

Chlorinated ethenes, like tetrachloroethene (PCE), are common organic contaminants at many polluted sites. Enquiries estimate that over 60% of all brownfield sites are contaminated with this kind of pollutant (Stupp *et al.*, 2007). Chlorinated ethenes are generally subject to degradation processes in aquifer ecosystems leading to a spectrum of conversion products found at contaminated areas. Daughter products besides PCE are trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC). Additionally, it has been demonstrated that environmental conditions like redox potential play a crucial role in contaminant degradation processes (Azadpour-Keeley *et al.*, 2001; Olaniran *et al.*, 2004). For evaluation of contaminant fate during reactive transport, groundwater models have proven to be a feasible tool. Monitored Natural Attenuation (MNA) approaches frequently use modelling techniques for assessment of contaminant fate during groundwater transport (Schaerlaekens *et al.*, 1999; Clement *et al.*, 2000).

However, information from literature dealing with varying redox conditions in groundwater models is scarce. The underlying thermodynamic processes (Dolfing *et al.*, 2006), as well as laboratory experiments for chlorinated ethene degradation (Doong *et al.*, 1996), are comprehensively reported. Further, it has been demonstrated by several laboratory studies that the presence of inorganic electron acceptors such as nitrate and sulphate inhibit reductive dechlorination (Nelson *et al.*, 2002; Shen & Sewell, 2005). However, only few publications about the application to a field scale study are available. Some publications apply different degradation rates for respective redox zones (Ling & Rifai, 2007), while Widdowson (2004) and Rolle *et al.* (2008) take into account different inorganic electron acceptors and their impact onto chlorinated ethene degradation.

This work aims to intertwine both laboratory experiments for parameter estimation and application of the determined parameters to a field scale study area in order to prove the feasibility. Enhanced degradation kinetics with inhibition terms for nitrate and sulphate enable a more precise prediction of pollutant fate and lowers the required computational effort in comparison to the complex degradation models, as discussed in literature.

## RESULTS

### Field site introduction and groundwater model establishment

Field experiments and data acquisition refer to an area of nearly 0.4 km² (Fig. 1). The sedimentary and unconfined aquifer in the study area comprises a thickness of 20–40 m and is divided into two zones by a low permeability layer. The catchment is characterised by a mainly impervious surface due to buildings and roads (mainly in the eastern part of the domain) and some natural areas (located in the western area). The whole municipal area consists of Cretaceous sediments under Holocene and Pleistocene accumulations. Fluviatile sediments mainly occur in the western part near the lake and river (Stegmann, 1969). Hydraulic conductivity of the primary aquifer was determined by Slug tests and ranges from about $1.2 \times 10^{-4}$ to $3 \times 10^{-3}$ m/s. Analyses of the grain size distribution from several bore drillings and subsequent comparison with literature confirm these values. Groundwater flow in the area is directed from the southeast to the northwest and was calculated to be approximately 36 m/year.
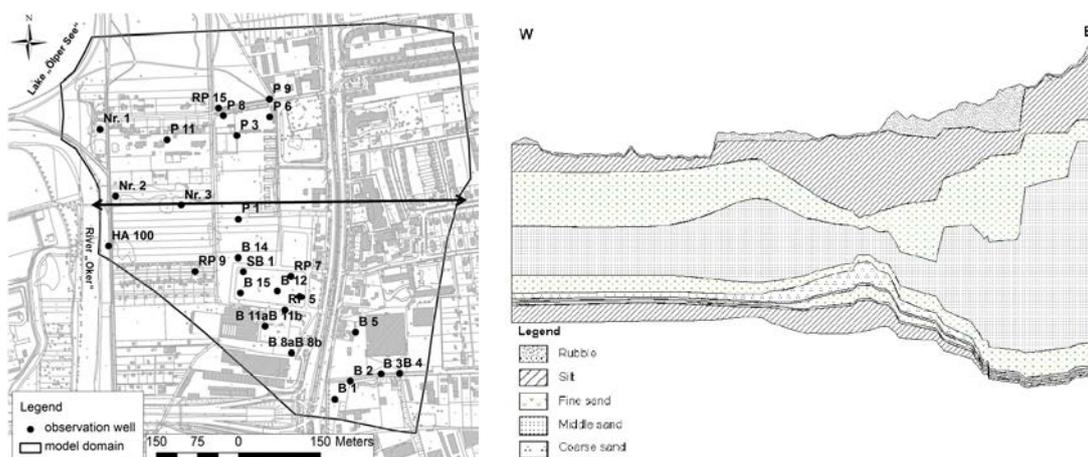


**Fig. 1** Model domain with observation wells (left) and complex stratigraphy along the horizontal line (right; vertical scale exaggerated); location: public area, City of Braunschweig.

In the southeastern part of the domain, a former chemical laundry disposed of their sewage water into the soil, leading to contamination predominantly consisting of PCE and its degradation products (TCE, cis-DCE and VC). For several decades the pollutants have been subject to transport and degradation processes, resulting in a contamination plume of approximately 500 m length and 100 m width in 2012. The major contaminant hotspots can be found in depths of down to 10 m, where a silt layer forms a barrier with low permeability.

At the study site several groundwater observation wells are available (Fig. 1). In order to validate the numerical model developed in this work, samples from 20 observation wells were taken and analysed for chlorinated ethenes. Additionally, several environmental parameters (pH, redox potential, temperature, etc.) were measured and concentrations of different ions like nitrate, sulphate and chloride were analysed. Analysed contaminant concentrations exceeded 40 000 µg/L of total DNAPLs in the core area.

Groundwater analyses further revealed that nitrate is only present in the upstream region (eastern part) in concentrations up to ~35 mg/L and drops to zero in a sharp decline, while the concentrations of iron increases further downstream (western part) up to ~20 mg/L. This observation is confirmed by redox potential measurements, which show a decline from ~+200 mV in the eastern part to ~–100 mV in the western part near River Oker and Lake Ölper.

Based on the measured concentrations and the hydrogeological data sets, a 3D Finite Element (FE) model was developed using the software Feflow (Diersch, 2009). Steady state flow boundary

conditions were chosen to characterize the hydraulic model. The DNAPL source release is estimated by reverse modelling: an infiltration period of 15 years with a concentration of 160 mg/L PCE followed by 35 years without PCE infiltration is implemented. In total, a simulation time of 50 years is assumed in the model, referring to the time period from 1960 until 2010. Flow, transport and reaction parameters are adopted from literature data and used for this reference model (Wiedemeier *et al.*, 1998; Schaerlaekens *et al.*, 1999; Wilson *et al.*, 2001; Clement *et al.*, 2002; Noell, 2009). Detailed information on the model construction and parameter evaluation is published in Greis (2012). Validation has been performed with concern to the accordance of simulation results and measurement data. The parameters chosen for this model are given in Tables 1 and 2.

**Table 1** Parameter values used in the reference reactive transport model and respective parameter variation for the optimisation approach using MC simulation.

| Layer | Textural class | Hydraulic conductivity ($10^{-4}$ m/s) | Porosity (-) | Longitudinal dispersion (m) | Transversal dispersion (m) |
|---|---|---|---|---|---|
| 1 | rubble | $5 \pm 1.25$ | $0.25 \pm 0.063$ | $13.2 \pm 3.3$ | $1.98 \pm 0.5$ |
| 2 | silt | $1.16 \pm 0.29$ | $0.05 \pm 0.013$ | $9 \pm 2.25$ | $1.35 \pm 0.34$ |
| 3 | fine sand | $4.63 \pm 1.16$ | $0.1 \pm 0.025$ | $12 \pm 3$ | $1.8 \pm 0.45$ |
| 4 | medium sand | $23.15 \pm 5.79$ | $0.12 \pm 0.03$ | $11.4 \pm 2.85$ | $1.71 \pm 0.43$ |
| 5 | fine sand | $4.63 \pm 1.16$ | $0.1 \pm 0.025$ | $12 \pm 3$ | $1.8 \pm 0.45$ |
| 6 | coarse sand | $30 \pm 7.5$ | $0.17 \pm 0.043$ | $15 \pm 3.75$ | $2.25 \pm 0.56$ |
| 7 | medium sand | $23.15 \pm 5.79$ | $0.12 \pm 0.03$ | $11.4 \pm 2.85$ | $1.71 \pm 0.43$ |
| 8 | fine sand | $4.63 \pm 1.16$ | $0.1 \pm 0.025$ | $12 \pm 3$ | $1.8 \pm 0.45$ |
| 9 | coarse sand | $30 \pm 7.5$ | $0.17 \pm 0.043$ | $15 \pm 3.75$ | $2.25 \pm 0.56$ |
| 10 | silt | $1.16 \pm 0.29$ | $0.05 \pm 0.013$ | $9 \pm 2.25$ | $1.35 \pm 0.34$ |

**Table 2** Parameter values used in the reference reactive transport model and respective parameter variation for the optimisation approach using MC simulation.

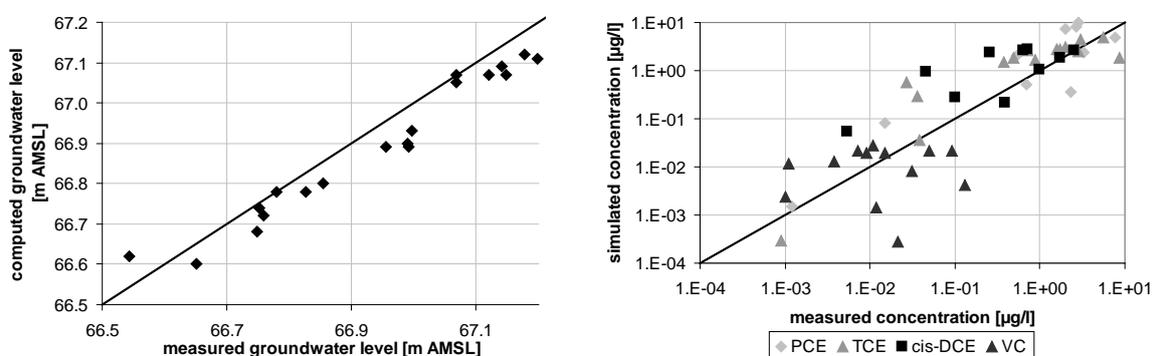| compound | KD-value ($10^{-3}$) | reaction rate ($10^{-5}$ /h) | diffusion coefficient ($10^{-8}$ m$^2$/s) |
|---|---|---|---|
| PCE | $4.44 \pm 1.11$ | $3.6 \pm 1.35$ | $5 \pm 2.5$ |
| TCE | $4.44 \pm 1.11$ | $3.6 \pm 1.35$ | $5 \pm 2.5$ |
| cis-DCE | $3.89 \pm 0.97$ | $0.36 \pm 0.067$ | $5 \pm 2.5$ |
| VC | $3.33 \pm 0.83$ | $3.6 \pm 1.35$ | $5 \pm 2.5$ |



**Fig. 2** Scatter plots of simulated versus measured groundwater head (left) and simulated *versus* measured contaminant concentrations (right) of the reference model.

Figure 2 summarises the conformity of measured and simulated data sets for both groundwater head and pollutant concentrations. Though deviations from the bisecting line for the

contaminant distribution (Fig. 2 right) are relatively high in comparison to the flow model scatter plot (Fig. 2 left), the implementation of contaminant transport and degradation processes into the model is regarded as successful. Fluctuations in measurement data, e.g. caused by sampling inaccuracies or due to groundwater head oscillations, introduce a huge element of uncertainty which usually cannot be represented by modelling tools in such a complex scenario as described here. Consequently a mathematical optimisation based on the Monte-Carlo (MC) method is presented, which aims to improve model outcomes of the transport and reaction model.

## Optimisation approach using MC techniques

In order to improve the simulation outcomes, an optimisation approach based on the MC technique was performed. Therefore, several flow, transport and reaction parameters (hydraulic conductivity, porosity, diffusion + adsorption coefficients, longitudinal + transversal dispersivity, degradation rates) are varied stochastically and implemented in the model (as described by Hill & Tiedeman 2007). The parameter variation of the reference model is given in Table 1 and Table 2.

A total of ~1200 variants was realised in each of four consecutive MC simulations. For all groundwater wells (see Fig. 1) the quadratic deviation between simulated and measured concentration data of the four compounds (PCE, TCE, cis-DCE and VC) is calculated. As a form of results weighting, the quadratic deviation was normalised on the original reference model as discussed in the previous section. Thus, for the optimisation approach the target function is defined as follows:

$$Err_{norm} = \sum_{species} \frac{\sum_{wells}(C_{meas} - C_{sim})^2}{\sum_{wells}(C_{meas} - C_{org})^2} \tag{1}$$

$Err_{norm}$: cumulated normalised error; $C_{org}$: simulated concentration of CHC compound in the original model; $C_{meas}$: measured concentration of CHC compound; $C_{sim}$: simulated concentration of CHC compound.

The minimisation of this target function delivers a mathematical approach to improve model outcomes. For each of the four successive MC simulations the parameters of the "best" model of the previous simulation was chosen as the originating parameter set. Parameters were varied based on the assumption of a normal distribution with the parameter of the respective reference model as mean value $\mu$. The standard deviation was chosen to be 0.25 $\mu$.

Results showed a significant decrease in error values (calculated according to equation (1)) for the optimisation approach. An overall decrease of the cumulated normalised error by almost 50% was achieved using this technique.

However, while the application of the MC approach was applied successfully in general, distribution of some chloroethene compounds (cis-DCE and VC) could not be optimised. The respective quadratic error remained on a constantly high level. Additionally, reaction rates in the model (see Table 2) appear to be quite low in comparison to literature data (Wiedemeier *et al.*, 1998; Schaerlaekens *et al.*, 1999; Wilson *et al.*, 2001; Clement *et al.*, 2002; Noell, 2009). This observation raises concerns about the suitability of the 1st-order reaction kinetics for description of contaminant degradation at the field study site.

In conclusion an experimental approach is described in the following section and a review of the underlying 1st-order degradation kinetic of chlorinated ethenes is also performed.

## Batch experiment for chlorinated ethene degradation

The experiment was conducted for assessment of degradation rates of chlorinated ethenes under laboratory conditions using addition of degradation-enhancing substances. Additionally, the effects of different inorganic electron acceptors on the degradation kinetics were under evaluation. Four different test batch approaches were conducted, each using different initial conditions (see Table 3). The experiment was performed in 250-ml wide-necked brown glass jars (DIN 55). The components of each test were added and the jar was filled bubble-free with groundwater and

tightly sealed with a Teflon-coated lid. The experiment was conducted at room temperature and in double determination. Five sampling times were chosen at 4, 11, 18, 29 and 38 days. After opening the respective samples, redox potential, dissolved oxygen and electric conductivity were measured and cation and anion concentrations as well as dissolved organic carbon (DOC) were analysed. Chlorinated ethene concentrations were determined via gas chromatography according to DIN EN ISO 15680 (2003).

**Table 3** Set-up of the batch experiment for chlorinated ethene degradation.

| Batch number | Sample name | Mass soil (g) | Mass EHC (mg) | Mass sodium nitrate (mg) |
|---|---|---|---|---|
| 1 | Reference sample | 50 | – | – |
| 2 | EHC experiment* | 50 | 250 | – |
| 3 | Nitrate experiment | 50 | – | 34.3 |
| 4 | EHC-Nitrate experiment* | 50 | 250 | 34.3 |

*EHC: *in situ* chemical reduction compound based on zero-valent iron and an organic component, distributed by Adventus Group Inc.
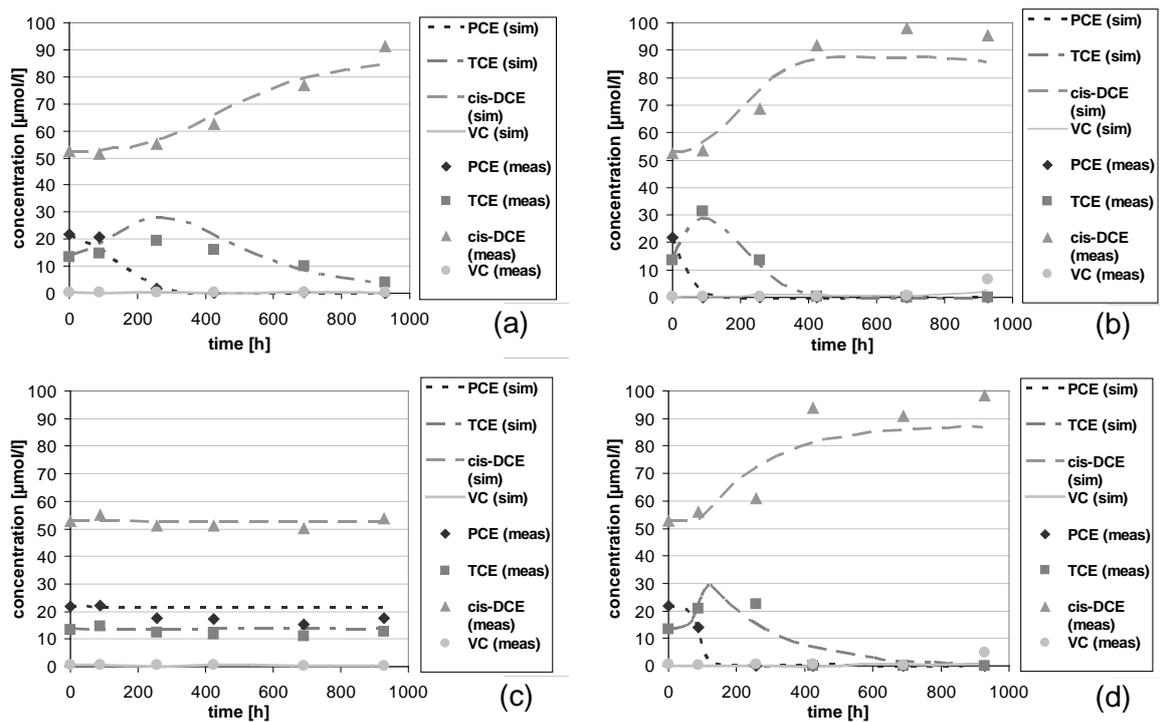


**Fig. 3** Measured and simulated data sets of the batch experiment: (a) reference sample, (b) EHC sample, (c) nitrate sample, (d) EHC-nitrate sample.

The experimental data plotted in Fig. 3 depict the mean concentration data of both the double determinations (index: meas). Due to the extraordinarily high reproducibility of the experiment, only mean values are shown and error bars are omitted. Additionally, measured nitrate and sulphate concentrations are shown in Fig. 4 for the respective experiments.

It becomes obvious that the experiment containing nitrate (experiment 3) shows almost no change in contaminant concentrations (Fig. 3(c)). It can be deducted that nitrate reduction is preferred over the degradation of PCE and thus, the degradation chain of chlorinated ethenes is completely

inhibited until nitrate is depleted. The data for the EHC-nitrate (Figs 3(d) and 4(d)) experiment also confirm this observation: PCE degradation starts after a quick decline of nitrate concentration.

If no nitrate and no further carbon addition are added to the batch (experiment 1), indigenous soil microorganisms are able to convert PCE and TCE at a low rate and in sequential order (Fig. 3(a)). After depletion of TCE the concentration of cis-DCE remains constant on a high level. It can be deduced from the anion concentration development that sulphate is consumed in this phase due to sulphate reduction (see Fig. 4(b) and (d)) and that cis-DCE is dechlorinated only if sulphate concentrations tend to zero. Calculated 1st-order degradation rates for TCE are in the range of $2.3 \times 10^{-3}$ /h (reference sample) to $1.2 \times 10^{-2}$ /h (EHC sample).
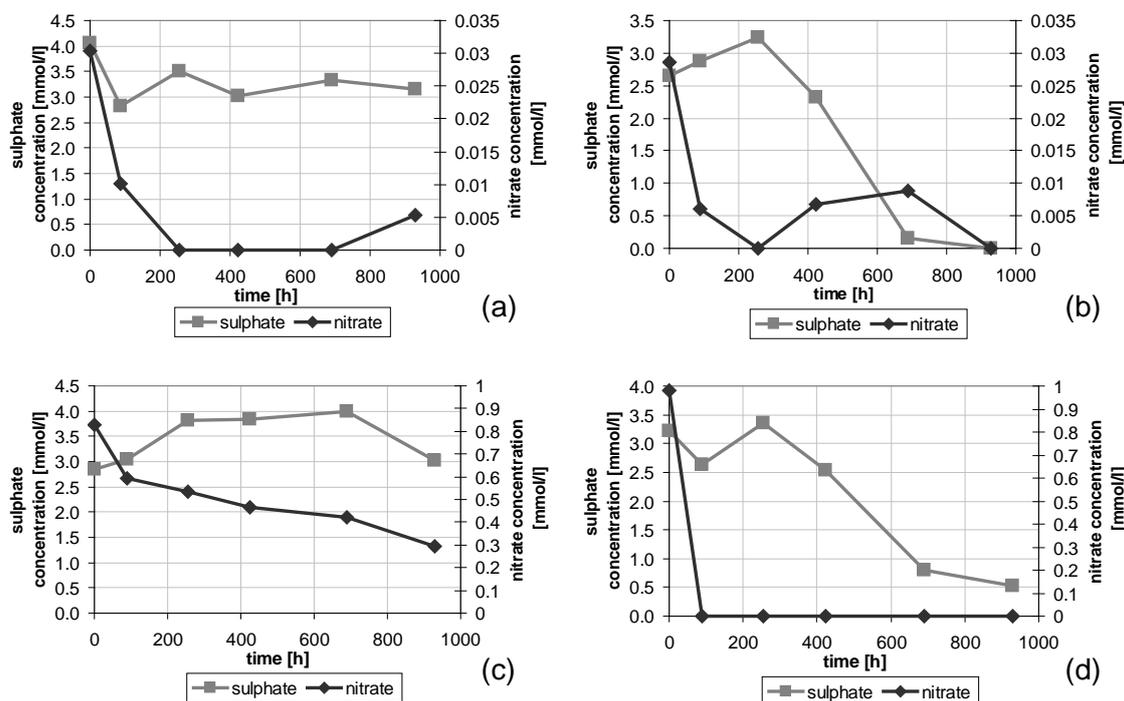


**Fig. 4** Measured nitrate and sulphate concentrations in the batch experiment: (a) reference sample, (b) EHC sample, (c) nitrate sample, (d) EHC-nitrate sample.

The decay sequence deduced from this experiment is given as follows: nitrate reduction → PCE degradation → TCE degradation → sulphate reduction → cis-DCE degradation. Each of these reaction steps seems to inhibit the subsequent reaction to a certain amount. In the case of nitrate, this inhibition can be assumed to be strong due to the observation that no contaminant degradation occurred in the nitrate sample.

To account for the inhibiting effect of inorganic electron acceptors, a formulation was set up using an extended kinetic for the chlorinated ethene degradation (see equation (2)).

$$v = \frac{dC_k}{dt} = -v_{k,max} \cdot C_k \cdot \left[ \left( \frac{C_{NO3}}{K_{I,NO3} + C_{NO3}} \right) \cdot \left( \frac{C_{SO4}}{K_{I,SO4} + C_{SO4}} \right) \right] \tag{2}$$

$v_{k,max}$: 1st-order degradation rate of compound $k$; $C_k$: concentration of compound $k$; $K_{I,NO3}$, $K_{I,SO4}$: inhibition constant of nitrate and sulphate, respectively; $C_{NO3}$, $C_{SO4}$: concentration of nitrate and sulphate, respectively.

Values for the inhibition coefficients $K_I$ and reaction rates $v_{k,max}$ were implemented as given in Table 4. For modelling purposes the simulation software Berkeley Madonna (version 8.3.18) was used. The degradation kinetic is assessed in a 1D approach without the influence of flow and transport processes. The results are shown in Fig. 5 (index: sim).

**Table 4** Parameters used for the simulation of the batch experiments .

| Compound | Range of $1^{st}$-order reaction rate $v_{k,max}$ [1/h] | Nitrate inhibition constants $K_{I,NO3}$ (μmol/L) | Sulphate inhibition constants $K_{I,SO4}$ (μmol/L) |
|---|---|---|---|
| PCE | $1 \cdot \times 10^{-2} - 8 \cdot \times 10^{-1}$ | 0.5 | – |
| TCE | $1.5 \cdot \times 10^{-3} - 3 \cdot \times 10^{-2}$ | 0.5–1 | – |
| cis-DCE | $1 \cdot \times 10^{-4} - 1 \cdot \times 10^{-2}$ | 0.5 | 1–10 |
| VC | $1 \cdot \times 10^{-3} - 1 \cdot \times 10^{-2}$ | 0.5 | 1–10 |
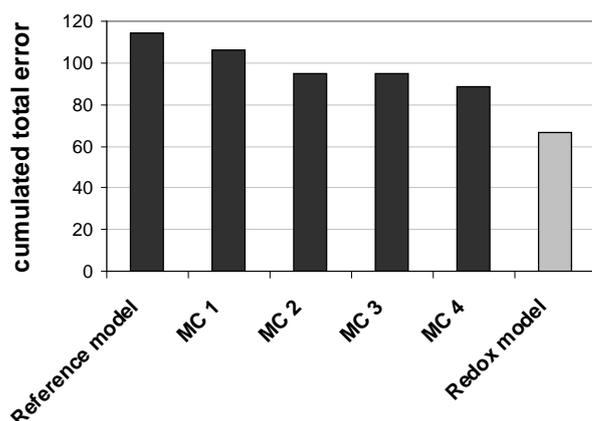


**Fig. 5** Evolution of total error (cumulated over all four chloroethene compounds) of the optimisation approach (black columns) in comparison to the redox model (grey column).

Comparison of the reaction rates given in Table 4 with literature data (e.g. Wiedemeier *et al*., 1998; Schaerlaekens *et al*., 1999; Aziz *et al*., 2000) is possible after application of van't Hoff's law. This law states that an increase in temperature of 10 K approximately doubles to quadruples reaction rates in biological systems. Due to the fact that the experiment described here is conducted at room temperature (~20°C) and the typical aquifer temperature is about 10°C, resulting reaction rates need to be decreased by a factor of two to four.

The comparison with rate constants in aquifers as collected by Wiedemeier *et al*., 1998 shows that both literature and experimental data are in the same range. In his survey Wiedemeier *et al*. reported 1st-order degradation rates between $1 \cdot \times 10^{-5}$ and $1 \cdot \times 10^{-2}$ $h^{-1}$. Application of van't Hoff's law shows results approximately in the range of the values found in the present study ($1 \cdot \times 10^{-4}$ to $3 \cdot \times 10^{-2}$ $h^{-1}$, see Table 4).

**Implementation of parameters into the field-scale groundwater model**

Based on the outcomes presented in the previous section, an enhanced degradation kinetic was implemented in the field scale FE model using the inhibition constants determined in the batch experiment (see equation (2)). The results of the total error calculation are depicted in Fig. 5 in comparison to the error development achieved by the optimisation using MC techniques.

As it becomes obvious from Fig. 5 an improvement of the model results was achieved by utilisation of the inhibition kinetic. In accordance to the experimental results described in the previous section, it could be demonstrated that formation of cis-DCE starts after depletion of nitrate.

**SUMMARY AND OUTLOOK**

In this study a field-scale groundwater model was established to simulate chlorinated ethene decay in the subsurface. In order to further improve the model outcomes an optimisation approach based on the MC method for several flow, transport and reaction parameters was conducted. It became

obvious that parameter optimisation does solve problems originating from parameter uncertainty, but not other model-inherent uncertainties (e.g. resulting from contaminant release boundary conditions).

An extended degradation kinetic was developed which yields useful information by describing reductive dechlorination of chlorinated ethenes. As shown here, inorganic electron acceptors play a crucial role in degradation processes. In particular, it was demonstrated that degradation of cis-DCE only occurs after nitrate and sulphate depletion. This behaviour could be modelled by application of inhibition terms to the degradation equations to account for redox conditions. The respective simulations exhibited plausible results in the batch experiment simulations as well as in the field-scale model. Based on the observations made in this study, *in situ* remediation approaches should aim to carefully evaluate redox conditions at affected sites in order to assess the degradation potential. With respect to the inhibiting properties of nitrate and sulphate, concentrations of both substances should be determined during monitoring campaigns at chlorinated ethene polluted sites. Particularly for MNA measures, the investigations made in this work may help to predict future pollutant plume development.

It is demonstrated that the combination of both laboratory-scale experiments as well as field-scale model development can successfully be applied to predict behaviour of chlorinated ethenes in soil. Although utilisation of inhibition kinetics is commonly used to describe reactions in small-scale systems (e.g. for enzyme kinetics), not many publications of this approach can be found in the field of applied groundwater modelling. Those authors using sophisticated inhibition kinetics for their models (Widdowson, 2004; Rolle *et al.*, 2008) generally lack experimental proof of their model assumptions. Other publications primarily deal with experimental tests, but do not transfer their results to field-scale models (Doong *et al.*, 1996; Shen & Sewell, 2005). Given these considerations the work presented here contributes to a better understanding of contaminant degradation in soil.

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