

## NUMERICAL SIMULATION OF NATURAL AND ENHANCED MICROBIAL TCE DEGRADATION

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### INTRODUCTION

Chlorinated hydrocarbons, particularly tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinylchloride (VC), are widespread contaminants in aquifers of industrialized countries. Diverse in situ techniques are used for decontamination, e.g. pump and treat techniques, surfactant flushing, stimulation of microbial degradation, permeable reactive barrier systems, direct chemical in situ oxidation / reduction, or (enhanced) natural attenuation. The main focus of this paper is on microbial remediation methods, namely natural attenuation and microbial in situ remediation. Natural attenuation of TCE and its degradation products has been studied in the urban area of Hanover, the regional capital of Lower Saxony (Germany). The investigation was funded by the Federal Ministry of Education and Research as part of the funding priority KORA ([www.natural-attenuation.de](http://www.natural-attenuation.de)). In our part of the ongoing joint project, that is the numerical simulation of natural attenuation processes, we modeled the complex microbial degradation reactions and determined the important steps of the reaction chain limiting total degradation of chlorinated hydrocarbons (SCHLENZ *et al.*, 2004).

At a site next to Milano (Italy) a microbial in situ remediation is performed to remove a contaminant source of chlorinated aliphatic hydrocarbons. The microbial dechlorination reactions are the same as at the natural attenuation site in Germany, but degradation is enhanced by injection of lactate. Lactate is an easily degradable electron donor, but it has to be fermented to acetate or hydrogen to be consumed by dechlorinating microorganisms. This fermentation reaction has been investigated in lab experiments (VON GUNTEN & ZOBRIK, 1993) and evaluated using a numerical model (SCHÄFER *et al.*, 1998b). With a slight modification of this existing model for lactate fermentation according to the reaction scheme determined at the site, and by adding the equations for microbial dechlorination from the natural attenuation site, it should be possible to create a numerical model for simulation of microbial in situ remediation of chlorinated hydrocarbons at the Milano site.

**KEY-WORDS:** *model, chlorinated hydrocarbons, natural attenuation, in situ remediation*

### NATURAL ATTENUATION

#### *Site description*

The upper aquifer below the city of Hanover is about 15 m thick and consists of quaternary sand and gravel, separated from deeper aquifers by a Cretaceous mudstone layer. It was contaminated by a chemical wholesaler mainly with 100-500 tons of BTEX, mineral acids, and chlorinated solvents. The developing contaminant plume was dragged into different directions due to a severely changing flow regime, e.g. because of drawdown during construction of a large building in 1970, or during two subway constructions starting in 1978 and 1987. The groundwater flow has been following its natural gradient in about west direction in the last decade only. Starting in 1977 a source remediation was performed, ending in 1987 with the encapsulation of the contaminant source. Hence, the present plume is no longer connected to its original source. Today BTEX are no longer detectable in the groundwater due to natural attenuation and oxidation of contaminants with sulfate, the only electron acceptor present in relevant concentrations. Low pH due to battery acids has been buffered by calcite present in the sediment, only slightly increased  $\text{Ca}^{2+}$  and total inorganic carbon concentrations are evidence from the former contamination. Chlorinated hydrocarbons, namely TCE, cis-DCE, and VC are still detected in the groundwater. Figure 1 shows the 100  $\mu\text{g/l}$  concentration isolines as the outer limitations of contaminant plumes. The interpolated concentrations measured in 1992 and 2001 leave the impression of a spatially nearly stationary, but slightly shrinking plume, giving the hope for natural attenuation taking place. The option to accept natural attenuation instead of an active remediation, because all active measurements are extremely difficult and expensive in the densely populated urban area, is studied in a joint project of the Hanover region, the Lower Saxony Provincial Office for Soil Research, the Federal Institute for Geosciences and Raw Materials, and the University of Kiel, funded by the Federal Ministry of Education and Research.

#### *Model for microbial degradation*

A model for simulation of microbial TCE degradation at the site has been created at the University of Kiel using the model code TBC (SCHÄFER *et al.*, 1998a). Since the aquifer locally contains

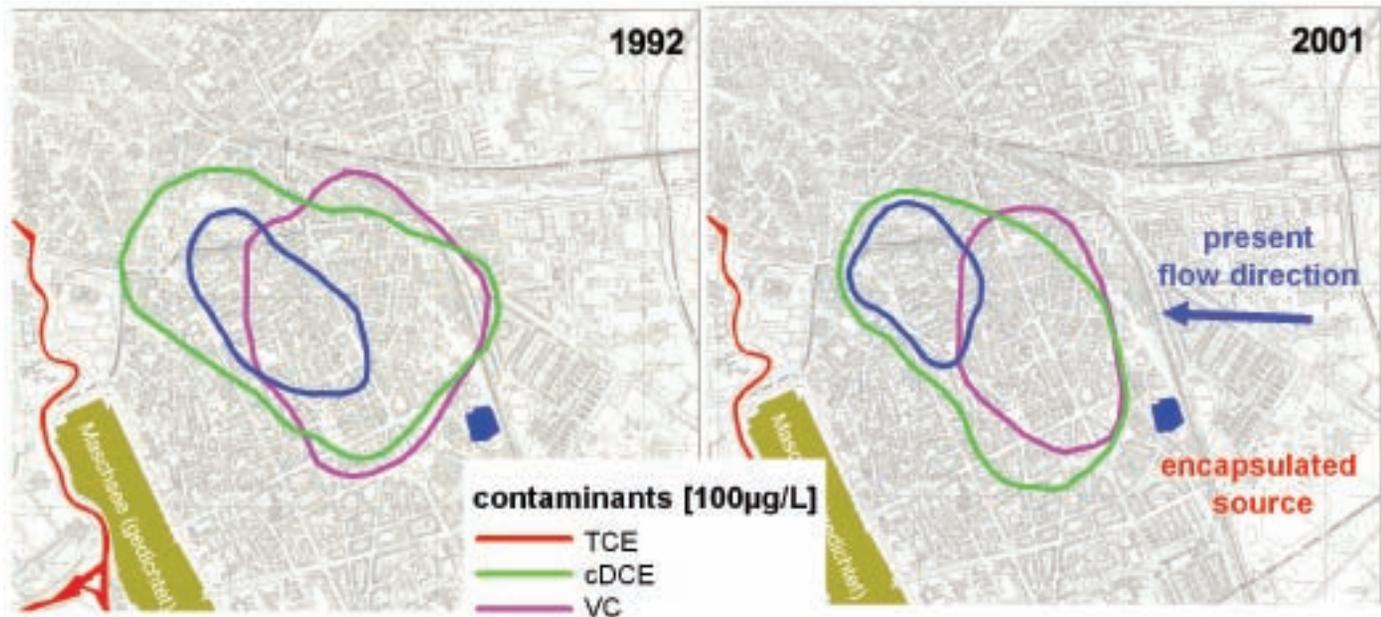


Fig. 1 - Urban area of Hanover with contours of contaminant plumes in 1992 and 2001

some oxygen, direct aerobic degradation of TCE, cis-DCE, and VC is considered in the site model. cis-DCE and VC are also degraded by oxidation with Fe(III)-minerals present in the aquifer sediment. The main degradation pathway, however, is reductive microbial degradation. For the following investigation only this degradation pathway is simulated (Fig. 2).

TCE is stepwise dechlorinated via cis-DCE and VC to ethene. The microorganisms catalyzing this reaction [e.g. Dehalococcoides dehalogenes, MAYMO-GATELL *et al.*, (2001)] require an easily degradable electron donor, like acetate or hydrogen, produced by another bacteria group by fermentation of naturally occurring dissolved organic carbon (e.g. humic substances) or possibly from small amounts of wastewater leaking out of the sewers. Other microorganism groups, like sulfate reducers or methanogens, compete with the dechlorinating bacteria for the easily degradable acetate and hydrogen. Each of the

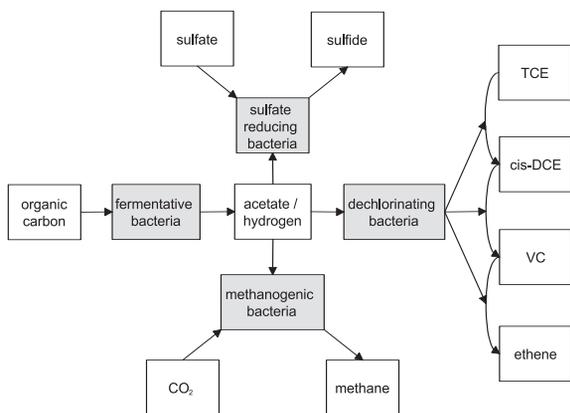


Fig. 2 - Reaction scheme for simulation of natural attenuation of chlorinated hydrocarbons at the Hanover site

six microbial reactions is simulated by a double Monod approach (BAE & RITTMANN, 1996), e.g. for TCE degradation:

$$\frac{\partial C_{TCE}}{\partial t} = -\frac{1}{Y_{TCE}} \cdot \mu_{max} \cdot X_{dechlor} \cdot \frac{C_{TCE}}{K_{S_{TCE}} + C_{TCE}} \cdot \frac{C_{H_2}}{K_{S_{H_2}} + C_{H_2}}$$

Decrease of TCE concentrations ( $C_{TCE}$ ) over time depends on a Yield coefficient ( $Y_{TCE}$ ), the maximum growth velocity ( $\mu_{max}$ ) of dechlorinating microorganisms ( $X_{dechlor}$ ), and two Monod-terms with respect to TCE and hydrogen, including the half velocity constants  $K_{S_{TCE}}$  for TCE and  $K_{S_{H_2}}$  for hydrogen. The required parameters are taken from publications (Tab. 1).

Parameter	Unit	Initial value	Source
$\mu_{max}$	1/d	1.00E+00	SUAREZ & RIFAI, 1999
$\mu_{dec}$	1/d	1.00E-01	SUAREZ & RIFAI, 1999
$K_s$ TCE	M	2.80E-06	HASTON & MCCARTY, 1999
$K_s$ TCE H <sub>2</sub>	M	1.00E-07	SCHÄFER, 2003
$K_s$ cDCE	M	6.60E-06	HASTON & MCCARTY, 1999
$K_s$ cDCE H <sub>2</sub>	M	3.00E-07	SCHÄFER, 2003
$K_s$ VC	M	5.20E-06	HASTON & MCCARTY, 1999
$K_s$ VC H <sub>2</sub>	M	8.00E-07	CUPPLES <i>et al.</i> , 2004
$K_s$ SO <sub>4</sub> <sup>2-</sup>	M	1.05E-05	SCHÄFER, 2003
$K_s$ SO <sub>4</sub> <sup>2-</sup> H <sub>2</sub>	M	3.00E-07	SCHÄFER, 2003
$K_s$ C <sub>org</sub>	M	7.10E-04	SCHÄFER, 2003
$I$ H <sub>2</sub> C <sub>org</sub>	M	1.00E-06	SCHÄFER, 2003
$K_s$ H <sub>2</sub> meth	M	8.50E-07	SCHÄFER, 2003

Tab. 1 - Parameter values for simulation of TCE degradation

*Sensitivity analysis*

Though the degradation pathways and microbial reactions are well known from laboratory experiments, the parameters required to describe microbial kinetics at the site are uncertain. Hence, a sensitivity analysis has been performed to identify the important parameters mainly responsible for total degradation of chlorinated hydrocarbons following a factorial design proposed by MONTGOMERY (2001). Without going into detail three parameters belonging to two processes in the equation system are sensitive, i.e. small changes of these parameters severely influence total degradation. The first two parameters are the half saturation constants for cis-DCE and acetate (or hydrogen) in the equation for cis-DCE degradation. These two parameters affect the velocity of cis-DCE degradation in comparison to TCE and VC degradation. Small changes in these parameters cause an accumulation of cis-DCE during degradation of TCE or its fast dechlorination. The third parameter is the half velocity concentration of organic carbon, responsible for the velocity of organic carbon fermentation and subsequent acetate (or hydrogen) production. If a more easily degradable electron donor is produced, total degradation of chlorinated hydrocarbon proceeds faster. All other parameters are less sensitive, i.e. small changes in parameter values have only little effect on total degradation.

*Simulation results*

Our model can be used to simulate the complex microbial processes of sequential anaerobic TCE degradation. Though the model requires many kinetic parameters which are not determinable at field sites, only three parameters are sensitive with respect to total degradation of chlorinated solvents. These parameters have to be determined or inversely fitted according to site conditions, while the less sensitive parameters can be taken from literature without much consequences on model significance. An important but poorly understood process is the fermentation of natural occurring organic carbon. Until now it is not known which organic substance is fermented and how the chemical stoichiometry of the reaction looks like. For better quantification of natural attenuation of chlorinated solvents a more detailed understanding of this process is required.

Additional investigations have been performed to understand the stationarity of the contaminant plumes over years, despite the present high flow velocities of 100-200 m/a. A conventional  $k_d$ -approach estimates a very low adsorption of TCE and degradation products on the sandy aquifer material with low organic carbon content, hence adsorption was expected not to be responsible for the immobility of the plume. New investigations show that adsorption may be much larger than expected in a sandy aquifer, even for a volatile contaminant like TCE (BALL & ROBERTS, 1991). Studies with site-specific contaminants in columns filled with local aquifer sediment confirm this.

**MICROBIAL IN SITU REMEDIATION**

*Column study*

The previous investigation of natural TCE degradation has shown that total degradation of chlorinated hydrocarbons depends on the availability of easily degradable electron donors. For artificial stimulation of contaminant reduction organic substances like HRC®, molasses or lactate are injected to accelerate this limiting step. At the Milano site dissolved lactate is injected, which is rapidly fermented to acetate and serves as electron donor for degradation of chlorinated solvents. If the reactions are comparable to natural processes, the kinetics of this fermentation step will be responsible for total contaminant dechlorination and should be investigated in detail. VON GUNTEN & ZOBRIST (1993) investigated the redox sequence during natural attenuation of organic substances, with lactate injected into a lab scale column. In this experiment aerobic degradation, denitrification, reduction of solid manganese and iron minerals, and sulfate reduction were observed, as well as fermentation of lactate. The assumed reaction scheme is shown in figure 3. Due to the large number of interfering reactions a numerical model was used to analyze reaction kinetics and quantify reactions (SCHÄFER *et al.*, 1998b).

In the experiment lactate with a concentration of 1.2 mmol/l was injected at a flow rate of 0.72 l/d into a column with a diameter of 5 cm and a length of 29 cm filled with sieved sediment from a natural aquifer. 0.19 mmol/l oxygen and 0.30 mmol/l nitrate in the injected water serve as electron acceptors for lactate oxidation and are rapidly consumed within the first centimeters of the column (Fig. 4). The remaining lactate is fermented to propionate and acetate. Solid manganese or iron mineral reducing microorganisms are assumed to consume better degradable propionate instead of lactate. Both reactions are limited by the slow dissolution of solid electron acceptors. A quantification of the reactions is possible by measured degradation products  $Mn^{2+}$  and  $Fe^{2+}$ , though both substances can react chemically and precipitate as minerals. This is particularly observed for  $Fe^{2+}$ , precipitating as siderite and  $FeS$ . Microbial reduction of 0.23 mmol/l sulfate in

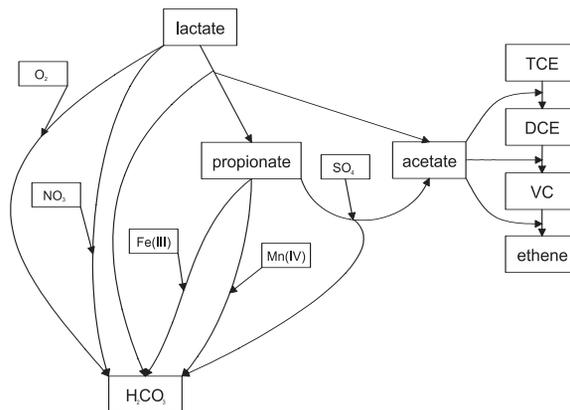


Fig. 3 - Reaction scheme assumed for simulation of lactate degradation in the column experiment with additional reactions for TCE degradation

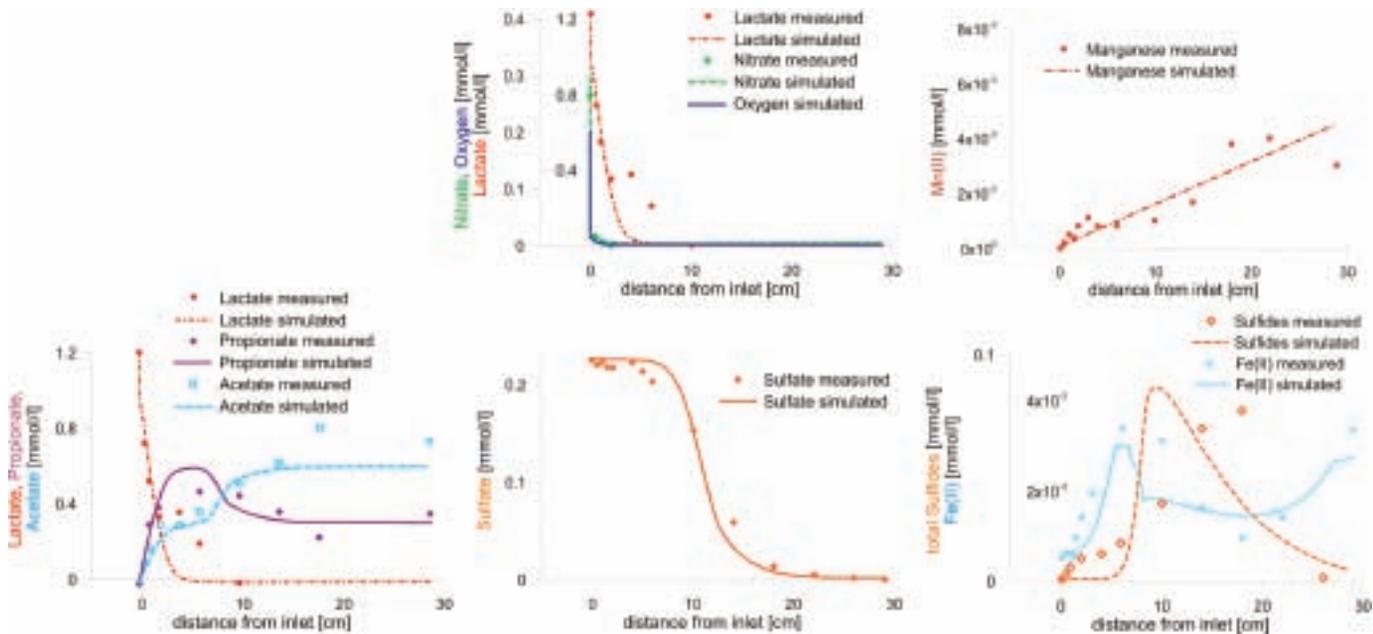


Fig. 4 - Measured and simulated concentration profiles after 48 days of column operation

the injected water and subsequent sulfide production develop slowly in the column system. Due to excess of organic carbon an incomplete oxidation of propionate to acetate is assumed for sulfate reduction.

#### Model set up

For simulation of organic carbon degradation six Monod-type differential equations are assumed, describing the growth of a facultative aerobic or denitrifying microbial group, and the growth of microbes catalyzing manganese, iron, and sulfate reduction or fermentation. The equations are similar, e.g. aerobic microbial growth with oxidation of lactate is simulated by:

$$\frac{\partial X_{O_2}}{\partial t} = v_{max} \cdot X_{O_2} \cdot \frac{C_{lactate}}{K_{S_{lactate}} + C_{lactate}} \cdot \frac{C_{O_2}}{K_{S_{O_2}} + C_{O_2}} - v_{dec} \cdot X_{O_2}$$

If lactate and oxygen are present in sufficient concentrations, the aerobic microorganisms  $X_{O_2}$  replicate and grow exponentially with a maximum growth velocity  $v_{max}$ . Two Monod terms with half velocity concentrations for lactate ( $K_{S_{lactate}}$ ) and oxygen ( $K_{S_{O_2}}$ ) decelerate growth if substrate concentrations decrease. Death of microbes is considered by a constant decay rate  $v_{dec}$ . Growth of anaerobic bacteria is inhibited by the presence of oxygen. The consumption of substrates and the production of degradation products is coupled to the microbial growth by Yield coefficients, which are calculated from energy gain of redox reactions and stoichiometry. Only a simplified set of chemical equilibrium reactions is considered, including dissociation of carbonic acid, hydrogen sulfide, lactic acid, propionic acid, and acetic acid, as well as dissolution / precipitation of calcite. Dissolution / precipitation of iron sulfide and siderite, as well as chemical reoxidation of sul-

fide with Fe(III) minerals is simulated as slow kinetic reactions. Details and parameters are found in SCHÄFER *et al.* (1998b).

#### Simulation results

The numerical model, the assumed reaction scheme and the chosen parameters for kinetic reactions reflect the measured concentration profiles. In the model lactate fermentation starts after 6 days of column operation, when the environment becomes anaerobic. The presence of oxygen inhibits the growth of strictly anaerobic fermentative microorganisms (SCHLEGEL, 1992). Consuming a well-degradable substrate like lactate, fermentative bacteria develop fast and deplete the injected lactate within the first ~6 cm of the column. In the experiment the major lactate degradation is caused by fermentation, but only about 25% of electrons used for oxidation of organic carbon are contributed by fermentation, because the reaction is a disproportionation and not an oxidation.

## CONCLUSIONS

Two complex models have been created to simulate natural TCE degradation at the Hanover site and to simulate lactate degradation in a column experiment. From the reaction scheme assumed for the Hanover site, we learned that natural attenuation of chlorinated solvents is limited by the availability of easily degradable substances. If lactate is used to enhance dechlorination as done at the Milano site, the fermentation of lactate to easily degradable acetate or hydrogen will be an important step for total contaminant reduction. This fermentation reaction, as well as competitive consumption of organic carbon by naturally occurring electron acceptors, have been studied in a column experiment. For simulation of enhanced remediation of

chlorinated solvents at the Milano site these two models can be merged, in order to obtain a better understanding of the reactions at the site, to quantify the proceeding processes and to optimize the remediation scheme. This model should be helpful not only for the Milano site, but also for other sites where active source remediation of chlorinated solvents is performed or planned. But this fusion of models still has to be done, and additional reactions assumed at the

site have to be incorporated to complete microbial and chemical reactions. For a complete model to simulate active source remediation additional processes will also be important, like spreading of injected lactate solution in the heterogeneous subsurface, distribution and dissolution of non aqueous phase liquids, and mixing of contaminants with injected electron donor. Setting up such a model is a challenging, but not impossible task.

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