

Estimation of sequential degradation rates of perchloroethylene by “history matching”

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Abstract Soil and groundwater beneath a chemical laundry site in the Netherlands had been found to be heavily contaminated with tetrachloroethylene (PCE). Additional fieldwork was carried out to determine the extent of the contamination and the potential for natural attenuation. Besides PCE, its degradation products: trichloroethylene (TCE), *cis*-dichloroethylene (DCE) and vinylchloride (VC), were also detected in the groundwater. Modelling of groundwater flow and reactive transport supported the hypothesis that the migration of the contaminants is in balance with the degradation: no further expansion of the plume of contaminants dissolved in groundwater is to be expected. Using history matching with a one-dimensional reactive transport model, the following degradation rates were derived: PCE $0.15\text{--}0.2\text{ day}^{-1}$, TCE $0.003\text{--}0.021\text{ day}^{-1}$, DCE $0.0004\text{--}0.0008\text{ day}^{-1}$ and VC $0.004\text{--}0.008\text{ day}^{-1}$. A more detailed, three-dimensional model was set-up to evaluate remediation alternatives. This model was calibrated using additional measurements of PCE, TCE, DCE and VC concentrations. Modelling showed that hot spot removal will result in complete degradation of the PCE and TCE plumes within 5 years and complete degradation of the DCE and VC plumes between 10 and 20 years. Remedial actions are therefore now focused on the hot spot.

INTRODUCTION

In The Netherlands many (former) textile cleaning industry sites are contaminated with chlorinated solvents. Natural attenuation can reduce the spreading and risks resulting from the contamination to a large extent. A cost-effective remediation approach is to remediate the NAPL phase of the contamination and to rely on natural attenuation for removal of the dissolved chlorinated solvents. This strategy will only be accepted by regulators if some evidence of natural attenuation can be provided. The presence of degradation products in groundwater only provides evidence that natural attenuation is occurring. Degradation *rates* need to be determined if the fate and transport of the contaminant have to be assessed in order to evaluate the acceptability of the strategy. Frequent monitoring of the contaminant and its degradation product over many years is necessary in order to predict the degradation rate based on observations alone (mass balance). When the age of the contamination (moment of spill) and the groundwater

velocity field are known, a transport model can be used to estimate degradation rates by matching a "blue print" of the contaminant situation at a single moment in time.

HISTORY MATCHING

The suitability of natural attenuation as a remedial option is dependent on the combined processes of groundwater flow, degradation and the presence of a source of contamination in the subsurface. The presence of DNAPL within the subsurface, high groundwater velocity and small degradation rates will result in a huge spread of dissolved contaminants. This unfavourable situation will urge the problem owner to focus on the plume of contaminated groundwater as well as on the hot spot (DNAPL).

At the site discussed here, PCE was present as DNAPL within the shallow aquifer. The site is located between the side of an ice pushed ridge and the River Rhine. Groundwater flows from the ridge to the river through a 30 m thick sandy aquifer (transmissivity $1200 \text{ m}^2 \text{ day}^{-1}$). The effective groundwater velocity is 100 m per year and the porosity 0.25. The VC-contamination, a degradation product of PCE, extends 600 m beyond the factory premises (Fig. 1). However, the high concentration of degradation products indicate that the degradation is rather fast. The questions to be answered were: (a) if degradation was fast enough to keep pace with the dissolution and consequent spreading of PCE from the source? and (b) if degradation was complete, which means that no accumulation of toxic degradation products such as VC has occurred.

A one-dimensional transport model in the Modular Computer Code for Reactive Multispecies Transport in 3-D Groundwater Systems (Clement, 1998) was set up to represent a streamtube at the site. The groundwater flow velocity was estimated from a regional, three-dimensional groundwater model and fixed in the one-dimensional streamtube model. The three-dimensional groundwater model proved the flow to be uniform and of constant direction over time, which justifies one-dimensional transport modelling. The fate and reactive transport simulation started at the moment of the spill of PCE 20 years ago. After the pure PCE was spilt, it accumulated within the first 5 m of the subsurface, on top of less permeable clay- and peat layers. PCE is slowly dissolving into the groundwater and therefore causing a long term contamination of the soil and groundwater. The presence of PCE as NAPL was modelled as a continuous flux of contaminant mass into the model. When dissolved PCE spreads with the groundwater flow, it sequentially degrades to TCE, *cis*-DCE, VC and finally ethene and ethane.

The fate and transport of PCE and its degradation products were predicted using a first order sequential decay model, and compared to PCE-, TCE-, DCE- and VC-concentrations measured in 1996 at five wells situated along the direction of the groundwater flow (N201 to N205 and N1 to N3, in Fig. 1). A "blue print" of the measured concentration was compared with the results from the history matching (see Fig. 1 for the blueprint and Fig. 2 for the results history matching). Minimum and maximum degradation rates presented by Wiedemeier *et al.* (1997) were used as starting values. These values are 6.8×10^{-4} – $5.4 \times 10^{-1} \text{ day}^{-1}$ for PCE, 1.0×10^{-4} – $2.1 \times 10^{-2} \text{ day}^{-1}$ for TCE, 1.6×10^{-4} – $2.6 \times 10^{-2} \text{ day}^{-1}$ for DCE, and 3.0×10^{-4} – $1.2 \times 10^{-2} \text{ day}^{-1}$ for VC. Those extreme values were combined in 16 different scenarios. Key to Fig. 2 is the four-digit number above each combination: 1 stands for high degradation rate, 2 for low degradation rate according to Wiedemeier *et al.* (1997).

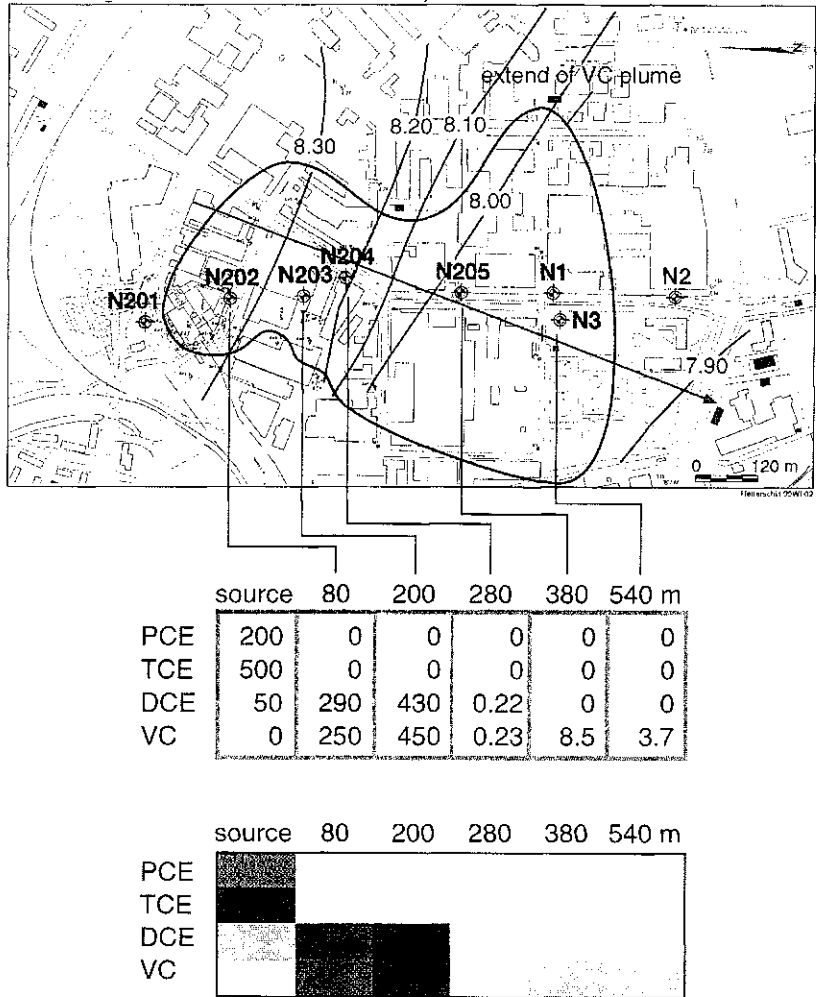


Fig. 1 Extension of VC-contamination at the site, direction of groundwater flow, location of monitoring wells and blueprint of the contamination ($\mu\text{g l}^{-1}$).

The combination of high rates of PCE and TCE degradation and low rates of DCE and VC degradation (right column, second row; 1122) seemed to match best with the measurements. By trial and error using a small range around the rates of this combination, a better fit was acquired (not shown here).

The rates obtained were PCE, 1.5×10^{-1} – $2.0 \times 10^{-1} \text{ day}^{-1}$, TCE, 3.0×10^{-3} – $2.1 \times 10^{-2} \text{ day}^{-1}$, DCE, 4.0×10^{-4} – $8.0 \times 10^{-4} \text{ day}^{-1}$ and VC, 4.0×10^{-3} – $8.0 \times 10^{-3} \text{ day}^{-1}$. These values were used to predict future behaviour of the PCE, TCE, DCE and VC plumes. The plumes have reached steady state: the total mass flux of PCE, TCE, *cis*-DCE and VC provided by dissolution of PCE from the source, is degraded. No further expansion of the plumes was predicted.

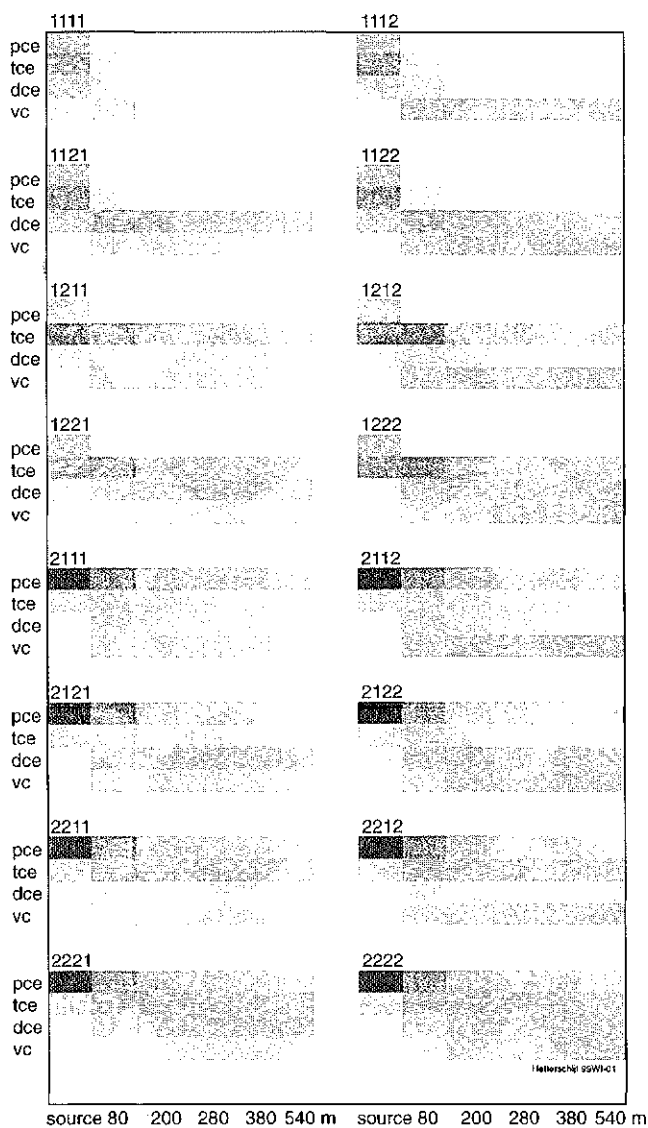


Fig. 2 Results of history matching. 1 = high degradation rate, 2 = low degradation rate, according to Wiedemeier *et al.* (1997)

FUTURE PLUME BEHAVIOUR

Upscaling to a quasi three-dimensional model

Although one-dimensional modelling was sufficient to estimate the degradation rates, a quasi three-dimensional model was required to evaluate the effect of a planned pump-and-treat remediation in the neighbourhood of the chlorinated solvent

contamination. Furthermore the effectiveness of source removal as a remedial option had to be evaluated. The degradation rates of the quasi three-dimensional reactive transport model were calibrated by matching the PCE-, TCE-, DCE- and VC-concentration measured in 1996 at 35 monitoring wells. The one-dimensional model showed the contaminant plumes to be at steady state. The calibration procedure of the three-dimensional model relied on this result; rates were adjusted by trial and error until no change of the present day contaminant situation was predicted. The calibration simulation started with the present day contaminant situation as the initial condition.

The rates derived from one-dimensional modelling were used as starting values for the trial and error calibration procedure. First the rates had to be corrected for retardation due to adsorption of contaminants by the soil, because this process had not been incorporated in the one-dimensional modelling. Retardation factors for PCE, TCE, DCE and VC were calculated from octanol-water partition coefficients and the organic carbon content of the soil. Furthermore the rates had to be corrected for the velocity distribution of the quasi three-dimensional model: the first aquifer of the three-dimensional model consists of two layers with different transmissivities but is represented by just one layer in the one-dimensional model. Rates were derived at an average effective velocity of 100 m day^{-1} , while the effective velocity of the upper and lower part of the aquifer are respectively 40 and 160 m day^{-1} . The original rates of the one-dimensional model, the rates corrected for retardation and different groundwater velocity and the calibrated rates of the three-dimensional model are listed in Table 1.

Table 1 Degradation rates of PCE, TCE, DCE and VC of one- and three-dimensional model (day^{-1}).

Rate	One-dimensional model	Corrected	Three-dimensional model
PCE	0.2000	0.0180	0.0036
TCE	0.0210	0.0040	0.0080
DCE	0.0010	0.0002	0.0012
VC	0.0030	0.0010	0.0060

Scenario: Removal of hot spot

The presence of PCE as DNAPL within and on top of the clay and peat layers at the site will cause long-term groundwater pollution. No remedial effort aimed at the plume of dissolved contaminants will be successful in restoring the aquifer within a few years or decades. The aquifer will be restored only by removal or isolation of the PCE hot spot. Removal of DNAPL at hot spots often requires intensive and expensive techniques.

Therefore the site owner wanted to know if and when the dissolved contaminants would be totally degraded after the removal of the PCE hot spot. Calculations showed that all PCE and TCE are naturally degraded within five years of removal of the hot spot, and DCE and VC are degraded within 10 to 20 years (see Fig. 3 for the progress of the disappearance of DCE between 1 and 10 years).

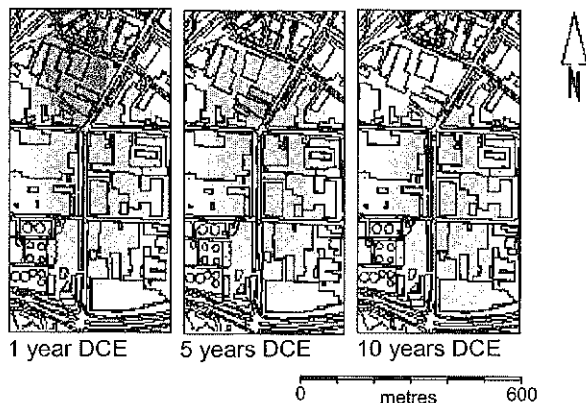


Fig. 3 Degradation of dissolved DCE plume after removal of the PCE hot spot according to the three-dimensional model.

CONCLUSIONS

History matching using a reactive transport model at a site in The Netherlands not only provided convincing evidence of the occurrence of natural attenuation but also provided degradation rates as well. Based upon model predictions, a sound decision on remediation alternatives could be made.

Model calibration by trial and error convincingly showed evidence that a combination of source removal and natural attenuation of the plume of contaminated groundwater will be successful in the cleanup of this site.

REFERENCES

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- Wiedemeier, T. H., Swanson, M. A., Moutoux, D. E., Gordon, E. K., Wilson, J. T., Wilson, B. H., Kampbell, D. H., Hansen, J. E., Haas, P. & Chapelle, F. H. (1997) *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas, USA.