1 Introduction and scope of work

Anthropogenic substances like chlorinated ethenes have been released into the environment in countless sites worldwide, especially in industrialised countries. The release of such contaminants was mainly caused due to the lack of environmental restrictions during 1950-1970 and primarily affects soil and groundwater ecosystems. The European Environmental Agency (EEA) estimates the number of sites requiring cleanup to exceed 100,000 in European countries (European Environment Agency, 2005). In Germany around 320,000 sites have been identified as suspicious areas for soil or groundwater contaminations according to the Bundes-Bodenschutzgesetz (BBodSchG) and are thus catalogued in a register for contaminated sites. The categorisation as brownfield site typically requires an unambiguous prove of contamination occurrence accompanied with an impact on public safety originating from the area of concern. Over 13,500 sites nationwide have already been classified as brownfield sites, meaning that pollutant concentrations have verifiably exceeded regulatory values and hence remediation measures are legally stipulated. However, only around 4,000 are currently subjected to clean-up activities (Umweltbundesamt, 2010).

Typically the low degradation rates of many recalcitrant substances result in a long-term impact on affected groundwater and soil ecosystems: pollutants often persist in soils for decades and pose danger to environment and residents, respectively. Necessary remediation actions conducted at polluted sites often require plenty of time and normally do not completely remove all contaminant substances from the affected site. In particular for wide-spread contamination plumes, financial resources for remediation campaigns often suffice merely for clean-up of the core area, leaving major parts of polluted areas untreated.

During so called Monitored Natural Attenuation (MNA) approaches the future development of affected sites is frequently tried to be modelled in order to assess the fate of contaminants during groundwater transport. The main objective of this approach is to estimate the self-healing potential of the ecosystem of concern and to calculate the potential risks arising from chemical substances in soil and groundwater for different pathways and receptors. However, uncertainties in parameters and inhomogeneities of the system often lead to highly variable model results, which are difficult to interpret for decision makers. In particular, problems with modelling often arise for sites polluted with chlorinated ethenes due to their sequential degradation chain. Their desirable properties (volatile, highly stable, non-flammable, cheap) have led to extensive usage as solvents and degreasing agents in dry-cleaning processes, for instance in laundries, metalworking or automotive industries. Hence, chloroethenes like tetrachloroethene (PCE) are common organic contaminants at many polluted sites. Enquiries estimate that a percentage of over 60% of all brownfield sites are contaminated with this kind of pollutants (Stupp et al., 2007). Generally chlorinated ethenes are subject to degradation processes in aquifer ecosystems leading to a spectrum of conversion products found at contaminated areas. These secondary products besides PCE typically are trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC), which all possess toxic and partially even carcinogenic properties and therefore are of concern for human health if taken up. Health-impairing and carcinogenic effects of these substances have been demonstrated lately and have led to environmental restrictions in usage and disposal.

In consequence, industrial sites contaminated with Dense Non-Aqueous Phase Liquids (DNAPLs) pose a high potential danger for the environment and humans especially in inhabited urban areas. Hence, the improvement of existing risk assessment tools for contaminated sites on the field-scale appears to be of avail in order to predict future development of contaminated aquifers and to lower the risk for affected residents as well as boundary ecosystems. In order to provide an appropriate risk analysis, the construction of a calibrated groundwater flow, transport and reaction model is necessary for demonstration of feasibility of the developed tools.

An experimental area polluted with chlorinated ethenes located in Braunschweig was chosen to evaluate and review the outcomes of the developed groundwater model and to calculate the potential risk for residents exposed to groundwater contaminations in an urban area. This work is targeted on the assessment and the grading of risks associated with groundwater contaminations and to demonstrate the feasibility of the approach for the case study mentioned. Additionally, the area of concern is currently under consideration for a spatially confined in-situ remediation measure.

Further, this work aims to develop modelling tools enabling an improved prediction of contaminant fate in groundwater under spatially varying environmental conditions, e.g. redox potential, which is identified to lead to better understanding and planning of the respective clean-up activities. For all chlorinated ethenes reaction rate constants are generally low and hence, degradation occurs very slowly. In contrast to other problematic organic substances (e.g. PAH and BTEX), adsorption onto soil particles is rather low, resulting in widespread contamination plumes in comparison to the other pollutants (Stupp and Paus, 1999), which turn chlorinated ethene remediation measures into a challenging task. In addition, environmental parameters like redox potential have been proven to show a significant influence on contaminant degradation. However, literature dealing with this topic is not very comprehensive (Widdowson, 2004; Doong et al., 1996). The development of a sophisticated method to predict pollutant decay under spatially varying environmental conditions seems to be advisable and is also substantial in this work.

The work presented here mainly focuses on uncertainties of transport parameters and the establishment of an improved chemical model of chlorinated ethene degradation for a more accurate calculation of environmental risk. The conclusions of these evaluations are used in a risk assessment approach applied to a real-world field-scale scenario in order to calculate health risks arising from groundwater contaminations. Conducted in collaboration of the Technische Universität Braunschweig (Germany) with the University of Florence (Italy), this thesis is embedded in the framework of the International Graduate College 802 “Risk Management of Natural and Civilization Hazards on Buildings and Infrastructures”, which focuses in a multidisciplinary manner on risk assessment and risk management of different hazards.

2 Theoretical background

2.1 *Chlorinated ethenes as groundwater contaminants*

2.1.1 Physical and chemical properties of chlorinated ethenes

Chlorinated ethenes are a group of chemical compounds based on the ethene molecule, which is substituted with a varying number of chlorine atoms. This group consists of the species tetrachloroethene (PCE), trichloroethene (TCE), cis-, trans-, and 1,1-dichloroethene (DCE) and finally vinyl chloride (VC). They all share similar physicochemical properties such as high density, low aqueous solubility and a low degradability in the environment. The degree of substitution defines some of their specific properties: an increasing number of chlorine substituents leads to an increase in density, melting point and boiling point (see Table 2.1).

Table 2.1: Physicochemical properties of chlorinated ethenes (according to Schwarzenbach et al., 2003 and ChemIDplus Database)

Compound	Molar mass $[g \cdot mol^{-1}]$	Density $[g \cdot cm^{-3}]$	Melting point [°C]	Boiling point [°C]	Log K_{OW} [-]	Solubility in water $[mg \cdot l^{-1}]$
PCE	165.83	1.62	-22.4	121.1	3.4	206
TCE	131.39	1.46	-73.0	87.0	2.42	1280
cis-DCE	96.95	1.27	-81.0	60.0	1.86	6410
VC	62.5	0.91*	-153.8	-13.7	1.62	8800

*at boiling point

All chlorinated ethenes are hydrophobic substances, but with decreasing number of chlorine substituents the solubility in water increases. This is also reflected by the octanol-water partition coefficient (Log K_{OW}), which summarises the potential of a substance to dissolve in water or organic solvents (in particular n-octanol). This property leads to a higher mobility of lower-chlorinated ethenes in soil in comparison to higher-substituted ones. Besides their position in the degradation chain (see chapter 2.1.2) this is one reason why cis-DCE and VC are found in the downstream part and PCE and TCE mainly in the upstream part of affected groundwater systems.

The high density of all chlorinated ethenes results in settling of the solvent phase downwards onto impervious soil layers (aquitard) during the source release period. Originating from the solvent phase a delayed dissolution of chloroethene compounds into the groundwater (caused by the low aqueous solubility) often leads to a long-lasting impact onto the aquifer.

Toxicologically all chlorinated ethenes pose harmful effects towards humans. These effects manifest themselves in toxic or carcinogenic properties. Thus, guideline values for environmental occurrence were established which in particular are 10 $\mu g \cdot l^{-1}$ in drinking water according to Trinkwasserverordnung 2001 (cumulated concentration for all chloroethenes), 100 $\mu g \cdot m^3$ for indoor air according to Bundes-Immissionsschutzverordnung 1990 (guideline value for PCE) and 10 $\mu g \cdot l^{-1}$ for soil concentrations according to Bundes-Bodenschutzverordnung 1998 (inspection value for PCE).

2.1.2 Chlorinated ethene degradation in the environment

The main reaction pathway for degradation of chlorinated ethenes is described by a simple consecutive reaction chain. The reaction chain typically starts with the compound tetrachloroethene (PCE) and proceeds with trichloroethene (TCE), cis-1,2-dichlorothene (cis-DCE), vinyl chloride (VC) towards ethene (eth) (see Figure 2.1). In each step of the degradation reaction hydrogen is consumed and hydrochloric acid is released. Although there are other possible isomers for formation of dichloroethene (1,1-DCE; trans-1,2-DCE), mainly cis-1,2-dichloroethene (cis-DCE) is built by microbiologically mediated degradation processes (Bradley, 2000). Each step of the degradation chain is dependant on several environmental conditions like pH-value, temperature and redox conditions and can be described by an own reaction equation (Clement et al., 1998).

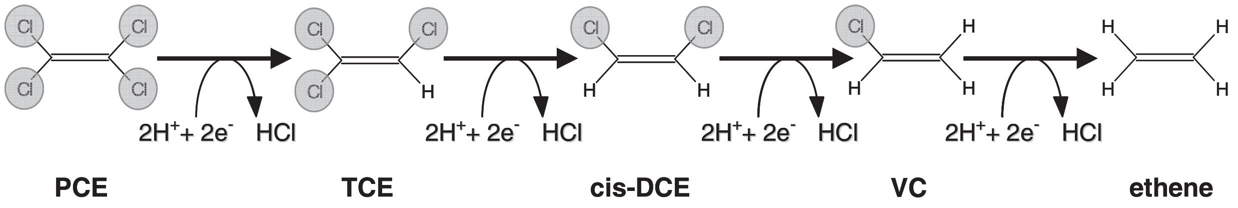

Figure 2.1: Chlorinated ethene degradation pathway

Degradation of chlorinated hydrocarbons typically depends on the environmental conditions predominating in the polluted area and occurs naturally in affected aquifer systems (Mulligan and Yong, 2004). Besides abiotic reactions, two important metabolic pathways are identified for mineralisation of chloroethene pollutants. The first is called “aerobic cometabolisation”, during which dehalogenation occurs as a side-reaction of growth substrate catabolism (Alvarez-Cohen and Speitel, 2001), e.g. toluene (Devlin et al., 2004) or methanol (Yang et al., 2008). Dissolved oxygen is typically used as electron acceptor in this case.

The other important degradation pathway is called “reductive dechlorination” (Bradley and Chapelle, 2010; Olaniran et al., 2004), where electrons are transferred from an organic substrate (e.g. glucose) towards an electron-accepting substance. This pathway is normally used by particular microorganisms to get rid of excess electrons originating from other catabolic reaction pathways (e.g. glycolysis) (Schwarzenbach et al., 2003). On the one hand, inorganic substances like oxygen, nitrate or sulphate might serve as electron acceptors; on the other hand chlorinated ethenes are capable of consuming electrons and are being subjected to dechlorination in this step. In total the average oxidation number of carbon atoms in the chloroethene molecule is reduced in each reaction step (Figure 2.2).

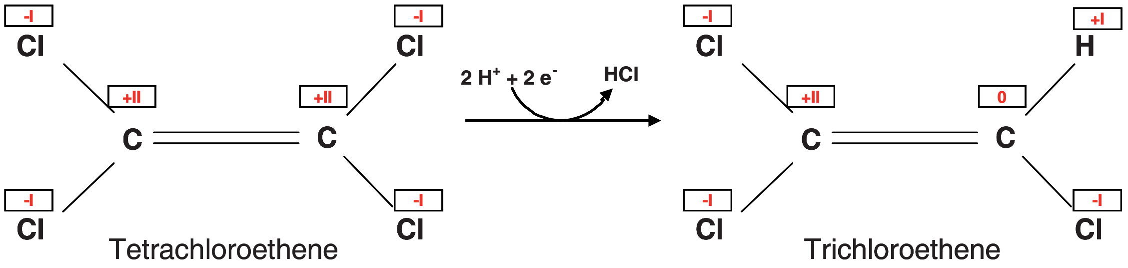

Figure 2.2: Oxidation numbers exemplarily shown for the reaction of PCE to TCE; reduction can be observed at the right-hand carbon-atom

The reductive dechlorination reaction is mediated by a specific group of soil microorganisms, which utilise a set of enzymes called reductive dehalogenases for this task (Maillard et al., 2011). Typically, most of these enzymes are only capable of catalysing the reaction from PCE to cis-DCE. To date, only one species is known to fully degrade PCE to ethene: the strain *Dehalococcoides ethenogenes* 195 (Yan et al., 2009). Polluted sites, where these bacteria are found, normally tend to show a complete mineralisation of chloroethenes, while sites without this specific strain often exhibit an accumulation of cis-DCE, but no further breakdown products (Hendrickson et al., 2002).

From the thermodynamic point of view, reductive dehalogenation in soil and groundwater ecosystems competes with reduction of a variety of inorganic electron acceptors. These electron acceptors are presumed to inhibit dehalogenation of chloroethenes according to their position in the redox chain (see Figure 2.3). The dechlorination reaction does only proceed under thermodynamically favourable conditions. Reactions with higher energy yield, i.e. a more negative Gibbs free energy, are preferred in comparison to those with a lower energy yield or more positive Gibbs free energy, respectively (compare Table 2.2). The redox potential of the groundwater system thus is a crucial indicator for the assessment of the pollutant degradation potential (Christensen et al., 2000).

For each redox couple a standard reduction potential can be calculated by the Nernst equation (equation (2.1)).

$$E = E^0 + \frac{R \cdot T}{z_e \cdot F} \ln \frac{a_{ox}}{a_{red}} \tag{2.1}$$

E: reduction potential

E^0: standard reduction potential

R: universal gas constant ($R = 8.314472\ J \cdot K^{-1} \cdot mol^{-1}$)

T: absolute temperature

z_e: number of transferred electrons

F: Faraday constant ($F = 9.648533 \cdot 10^4\ C \cdot mol^{-1}$)

a_{ox}, a_{red}: activity of relevant species of oxidant and reductant

In aquifer systems temperature differences are assumed to be negligible and thus, the resulting reduction potential of a redox reaction is mainly dependant on the respective standard reduction potential E°and the concentration of oxidised and reduced species.

Additionally, the Gibbs free energy for each reaction is associated with the standard reduction potential by means of the following equation (2.2):

$$\Delta G^0 = -z_e \cdot F \cdot E^0 \tag{2.2}$$

ΔG^0: Gibbs free energy

As a consequence, the redox potential of an aquifer system is supposed to be a mixed potential regarding the participating redox couples, i.e. in unaffected groundwater systems the redox potential is a result of the concentration of inorganic electron acceptors present in the system. Given the fact that sufficient carbon source is available, the electron acceptor with the highest energy yield is favoured to be transformed by microorganisms and hence, reduced by redox reactions during microbial metabolism. This leads to a sequential electron acceptor depletion starting from oxygen and ending with sulphate reduction and methane fermentation (Scheffer et al., 2008). This process is accompanied by a shift in redox potential (Figure 2.3).

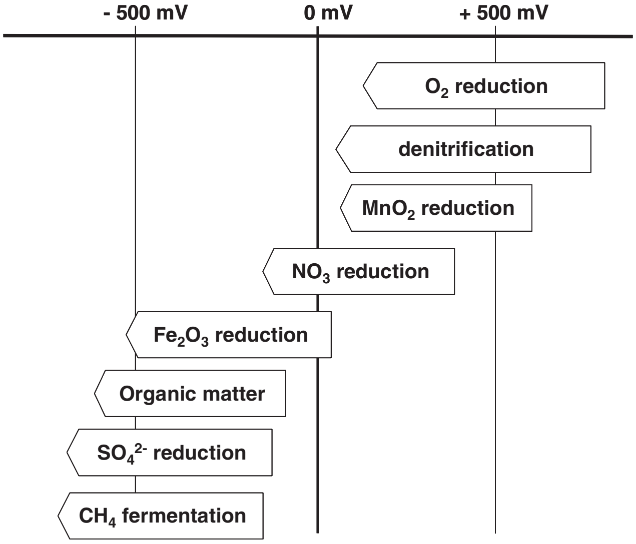

Figure 2.3: Redox reactions catalysed by microorganisms and the associated redox potential at pH 7, redrawn after Schwoerbel (1987)

The corresponding standard reduction potentials for chloroethene degradation are available in literature (Dolfing et al., 2006; Doong et al., 1996). Table 2.2 summarises the Gibbs free energy and standard reduction potential for the reduction of inorganic electron acceptors and chlorinated ethenes. It becomes obvious, that the reductive dehalogenation of chloroethenes is located in the same redox range as the reduction of inorganic electron acceptors and thus, from a thermodynamical point of view a competitive behaviour can be assumed (Widdowson, 2004). The theoretical energy yield from the reduction of chlorinated ethenes increases with their number of substitutes. Referring to Table 2.2 it becomes obvious that different degradation reactions are thermodynamically favoured under certain environmental conditions, e.g. the degradation of cis-DCE is energetically preferred after the depletion of nitrate, while PCE is degraded theoretically also in presence of this substance.

Table 2.2: Redox reactions with corresponding Gibbs free energy ΔG° and standard reduction potential E°(according to Dolfing et al. , 2006)

Reaction	ΔG^0 [kJ/electron]	E^0 [mV]
$O_2 + 4H^+ + 4e^- \rightarrow 2\ H_2O$	-78.7	816
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	-74.4	771
$MnO_2 + HCO_3^- + 3H^+ + 2e^- \rightarrow MnCO_3 + 4H_2O$	-58.9	610
$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$	-41.7	432
$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	+20.9	-217
$PCE + H^+ + 2e^- \rightarrow TCE + Cl^-$	-55.4	574
$TCE + H^+ + 2e^- \rightarrow DCE + Cl^-$	-53.1 to -50.9*	550 to 527*
$DCE + H^+ + 2e^- \rightarrow VC + Cl^-$	-40.6 to -38.3*	420 to 397*
$VC + H^+ + 2e^- \rightarrow ethene + Cl^-$	-43.4	450

*depending on species of DCE involved (cis-, trans-, 1,1-DCE)