



Universiteit Utrecht

**A multifaceted approach to identify and quantify the processes
contributing to chlorinated aliphatic compound attenuation.**

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Abstract

Although chlorinated ethene contamination is one of the most ubiquitous and researched types of groundwater and subsurface contamination, in situ site specific remediation has proven rather difficult due to the nature and the propensity of these contaminants. This thesis addresses the problem through the analysis and quantification of the underlying governing processes, the effect of heterogeneity of the subsurface and the general uncertainty related to groundwater sciences. Based on seminal work, an internship conducted at the municipality Utrecht and groundwater modelling, the limitations of the most often used numerical simulations are identified and adapted in order to properly incorporate the governing processes. The use of degradation rates less sensitive to heterogeneity and uncertainty, such as Michaelis-Menten kinetics, resulted in a more correct approximation of subsurface processes and conditions. Supplementing the numerical outcomes, this thesis proposes a technical guideline and tool to screen and assess chlorinated ethene contaminated sites.

List of Abbreviations/Glossary

To be checked and completed

ATES	Aquifer Thermal Energy Storage
CAH	Chlorinated Aliphatic Hydrocarbon
cDCE	cis-1,2-Dichloroethene
CLRTAP	Convention on Long-Range Transboundary Air Pollution
DNAPL	Dense Non-Aqueous Phase Liquid
DOD	US Department of Defense
DOE	US Department of Energy
EHSP	Environmental Health and Safety Plan
ESTCP	Environmental Security Technology Certification Program
ETH	Ethene
HASP	Health And Safety Plan
HRC®	Hydrogen Releasing Compound
ITRC	Interstate Technology Regulatory Council
NAP	Normaal Amsterdams Pijl/ Amsterdam Ordnance Datum
NAS	National Academy of Science
OSHA	Occupational Safety and Health Administration
PCE	Perchloroethene
QA/QC	Quality Assurance/Quality Control
SATES	Seasonal Aquifer Thermal Energy Storage
SERDP	Strategic Environmental Research and Development Program
TCE	Trichloroethene
tDCE	trans-1,2-Dichloroethene
USEPA	United States Environmental Protection Agency
VC	Vinyl Chloride
VOC	Volatile Organic Compound

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1 INTRODUCTION

Extensive use of chemicals for military and industrial applications combined with poor waste management has resulted in the widespread occurrence of hazardous sites (Aulenta et al., 2010). The resulting chlorinated ethene contamination does not only pose a threat for the environmental quality of the site but it also endangers human health. Unfortunately the awareness for these contaminants and adverse effect on groundwater quality and therefor their harmful nature were only observed in the late 1970's. Several decades later a substantial amount of research has been done in order to investigate, identify and remediate those sites where contaminant levels rose above what was generally considered acceptable and safe.

In the US alone thousands of contaminated sites, related to the historical or ongoing use of these chemicals have been identified. An adequate indication of the severity of this situation is the cost estimation made by the National Research Council (2013), which estimated the cost of the complete clean-up of all of the currently identified sites ranging from \$110 billion to \$127 billion. This estimation however does not include newly discovered legacy sites, or sites that were recently exposed to spills and releases. Not only is the remediation of these sites an expensive undertaking, the long term nature of these remediation projects shows the pressing need and challenges posed to academics and professionals involved with remediation. Taken into account that the characteristics of each contaminated site greatly influences the contaminant propensity and therefore its remediation, it is impossible to come up with an universal solution.

A thorough understanding of the subsurface and the processes involved in contaminant fate and transport is required in order to attend to these contaminated sites. Not only to devise a plan to effectively restore the subsurface and groundwater quality to acceptable levels but also to come up with a way to do it in the shortest amount of time while opting for the most cost effective approach. This thesis will first identify the contaminants and discuss some of the factors that make them the most persistent and ubiquitous threats posed to not only aquifer and groundwater quality but also human wellbeing. Secondly, the processes involved will be examined, differentiating between the various contributing factors, based on the physical, chemical or biological nature of the processes affecting the contaminants. Following the in situ aspect of the contaminants, the study discusses various ways of anthropogenic intervention in the fate and transport of these chlorinated contaminants.

Finally, when the information regarding the contaminant and possible remediation approaches is considered, a straightforward method of incorporating all of the previously discussed

data will be proposed. Introducing a tool that allows both academics and decision makers to quickly identify a specific degradation scenario for a specific contaminated site. Not only will this help in understanding the currently ongoing processes at that site, it will also propose an approach to predict contaminant behaviour, identify the various applicable remediation techniques and determine their expected results.

Chapter 2 discusses the contaminants considered, their historical use, chemical nature, legislation and the resulting contamination as well as express the need for research regarding these compounds and their remediation.

Chapter 3 addresses the physical and chemical aspects of the contaminants that characterize the compounds as harmful to the subsurface and groundwater as well as the difficulty related to their remediation. This is done through the analysis of the factors contributing to the infiltration and contamination of the subsurface.

Chapter 4 focusses on the fate and transport of the contaminants once they get introduced to the subsurface, elaborating on the non-destructive transport processes and the role of the soil characteristics on chlorinated ethene propensity.

Chapter 5 deals with the destructive process of natural attenuation as a means of reducing the contaminant source and plume mass, concentration and fluxes. The important biological, chemical and geochemical aspects of chlorinated ethene degradation will be introduced.

Chapter 6 identifies the influence the subsurface's chemical and geochemical characteristics have on the degradation of the contaminants in question. This will be done by addressing the degradation reactions from a purely chemical perspective.

Chapter 7 introduces the biological importance of the presence of microbial life in the subsurface by discussing the numerous types of microbial cultures involved with natural attenuation, their preferred environment and the various degradation pathways involved with microorganisms facilitated and/or catalysed contaminant destruction.

Chapter 8 is an in-depth analysis of the potential biotic and abiotic degradation mechanisms. An overview of the involved parent and daughter products is given for the various chlorinated ethene degradation pathways, as found in literature.

Chapter 9 offers a variety of methods to kinetically represent and quantify the degradation rates related to the attenuation of chlorinated ethenes in the subsurface. Based on the amount of variables considered different kinetic models are proposed in order to approximate the actual rates.

Chapter 10 lists the various remediation tools and techniques used to reduce mass, concentration and flux of the contaminant source zone and plumes. Most of the chemical, physical, biological, geochemical and hydrogeological alternatives to natural attenuation, used by remediation specialists are briefly discussed.

Chapter 11 proposes a technical protocol, to cope with the uncertainty related to the subsurface and its inherent heterogeneity. Establishing both a thorough understanding of the processes involved as well as sufficient data are required to assess a contaminated site, the potential of natural attenuation or the best suited alternative remedial techniques and to optimize long-term monitoring.

Chapter 12 describes a specific case study, the chlorinated ethene contaminated subsurface of Utrecht. Introducing the problems faced, the parties involved and the numerical visualization of the fate and transport of contaminants using Modflow model and the reactive transport modules MT3DMS and RT3D.

Chapter 13 deliberates on the outcome of the numerical modelling, comparing the solute mass removal for three different degradation reactions and the impact of the presence of pure phase contaminant, slowly dissolving into the groundwater.

Chapter 14 summarizes and reflects on the findings of analytical part of the thesis tested and verified by the numerical simulations of the Utrecht's subsurface. Listing the numerical issues with chlorinated ethene contaminants and their propensity

Chapter 15 elaborates on the difficulties and limitations encountered during the thesis, while indicating specific gaps of knowledge and proposing potential further research related to the multi-disciplinary issue that is chlorinated ethene contamination.

Chapter 16 concludes with a list of all sources used.

2 VOLATILE ORGANIC COMPOUNDS

The term volatile organic compounds (VOC) refers to a large class of carbon-based, anthropogenic and naturally occurring chemical compounds found all over the world. The compounds are referred to as volatile because of their high vapour pressure at room temperature, causing the liquid phased compounds to rapidly evaporate into the surrounding atmosphere. Both gaseous and liquid, VOC are considered an abundant source of groundwater and subsurface pollution.

Excluding methane, an estimated 1.3 pentagrams (10^{12} kg, Pg) of carbon in the form of VOCs is produced annually (Goldstein and Galbally, 2007). The majority, almost 90% comes from biological sources, while only 0,142 Pg is accounted for by anthropogenic sources. To put this massive carbon production into perspective, 1.3 Pg is about one third of the annual global crude oil production (IEA, 2010). In addition these substances are numerous and rather varied in their chemical composition and properties.

We are exposed to a variety of these chemicals on a daily basis, considering most odours and scents are VOCs, one of our five senses is heavily dependent on these chemicals. They also play an important role in nature, for example, by aiding in the exchange of information among plants, or between animals and plants. Yet their applicability outside of nature is just as fascinating, the same group of chemicals can be employed for a variety of functions ranging from dispersants and solvents to fuels and petrochemistry. Although most of the VOC we encounter daily are relatively harmless, quite a large number of these have proven to be harmful to human health and the environment (EPA, 2012). While not acutely toxic, these compounds do exhibit compounding long-term health effects.

Due to their low concentration in the atmosphere and the fact that the symptoms develop over long periods of time, assessing their toxicity is rather difficult. A wide variety of health risks of man-made VOCs have been reported, ranging from headaches, eye, nose and throat irritation to the more extreme damaging of internal organs and the central nervous system. Due to their toxicity, volatility and transboundary nature, all anthropogenic VOC's are regulated by law. Apart from national regulations, there are also international measures taken: *The Volatile Organic Compounds Protocol* for example is an extension of the *Convention on Long-Range Transboundary Air Pollution*. In 1991 this treaty was signed in Geneva, Switzerland and entered into force in 1997. Its prime objective is to regulate emissions of said chemicals, and to reduce and prevent any human exposure to transboundary air pollution and the resulting health risks (UN, 2010).

Figure 1. Countries ratifying the Convention on Long-Range Transboundary Air Pollution.



The main focus of this research will be on a specific group of VOCs, the man-made chlorinated aliphatic hydrocarbons (CAH). They are typically manufactured from methane, ethane, other naturally occurring hydrocarbon constituents and chlorine, through substitution of one or more hydrogen atoms with chlorine atoms. Aliphatic is a term used in organic chemistry to indicate a class of molecules that does not contain an aromatic ring in their molecular structure, as opposed to aromatic compounds such as benzene and toluene (IUPAC, 1997). The term is derived from the Greek word for oil or fat, *aleiphar*, referring to the low miscibility of most of the CAHs with water.

Historical CAH waste management has resulted in contamination of soil and groundwater in almost every industrialized country (Squillace et al., 1999; Wiedemeier et al., 1999; Bradley, 2000). CAHs and their degradation products tend to be persistent in the subsurface and are considered some of the most common and ubiquitous groundwater contaminants (Major et al., 2002). In the past, when the potential pollution and harm these compounds would cause was not yet considered critical. The liquid solvents and degreasers were dumped into landfills or near the industrial facility itself. Expecting that the volatile nature of these compounds would result in rapid evaporation and dispersion into the atmosphere, people were not too worried about subsurface infiltration and the effect on the quality of the soil and groundwater (Westrick et al., 1984)

3 DNAPL INFILTRATION

Unfortunately CAHs also exhibit additional physical properties, apart from a volatile nature these pollutants are characterized by a density higher than water. This is due to the high relative atomic mass of chlorine, amounting to almost twice that of oxygen. Not only does this density combined with the other attributes of CAHs result in facilitating subsurface infiltration, it also results in other phenomena detrimental to groundwater quality. In hydrogeology the term dense non-aqueous phase liquid (DNAPL) is used to describe such immiscible liquids denser than water.

Although DNAPL tend to exist in the saturated subsurface as a separate pure DNAPL phase, it does not mean that they are completely insoluble. If that would be the case, the impact of these contaminants on soil and groundwater quality would be rather limited. Even though their solubility is relatively low, it is still much higher than drinking water limits. Given their high toxicity, any exposure can prove to be detrimental. Therefore any CAH contamination, even in smaller amounts can pose a large long-term threat to groundwater quality and human health (Mayer & Hassanizadeh, 2005).

The pure phase migration of these chlorinated organic liquids is driven by the interaction between three different forces, gravity, viscosity and capillarity. The propensity of CAH DNAPL and their difficult remediation is a result of interaction between these three forces. When released to the subsurface, the contaminants, characterized by a low viscosity tend to infiltrate the unsaturated zone rather quickly. As long as the contaminant is present in the unsaturated zone and exposed to the gaseous phase it will volatilize into the air (Glass et al., 1990; 1991). As a result of residual saturation, DNAPL vapour production can last significantly longer than it takes the contaminants to infiltrate the saturated zone (Wilson et al, 1990). Residual saturation is the term used to indicate the pure phase DNAPL for which the acting capillary force outweighs the effect of gravity. This results in CAH entrapment, defined as the volume of DNAPL trapped in the pores divided by the total volume of pores. As the majority of DNAPL continues the downward migration, the entrapped contaminants will remain stationary in the unsaturated zone resulting in a slow but steady evaporation, releasing DNAPL vapours into the subsurface and the atmosphere.

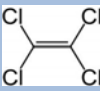
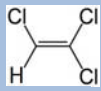
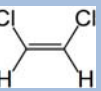
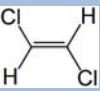
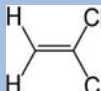
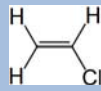
It is in the saturated zone that the density and viscosity difference between water and the chlorinated compounds becomes quite apparent in the propensity of the contaminants. The first saturated zone infiltration process is a result of density driven flow. Due to the superposition of a denser liquid, an interface is created between both liquids. The DNAPL-Water interfacial tension slightly halts the downward migration of contaminants, making it impossible for the DNAPL to submerge below the groundwater table as a single front. DNAPL fingering on the other hand, is the result of perturbations caused by the discrepancies in density and viscosity of DNAPL and water

(Figure 3). Small disturbances in the DNAPL-Water interface result in rapidly downward propagating jets/tendrils of pure phase DNAPL, these fingers actually speed up the infiltration compared to migration behaviour witnessed in the subsurface so far (Zhang & Smith, 2001).

Although these contaminants are referred to as immiscible, they will disperse into the aqueous phase will migrating downwards. Similar to the entrapment in the phreatic zone, residual saturation of DNAPL will also occur in the saturated zone. Where this leads to additional evaporation in the unsaturated zone, the same entrapment below the water table will lead to increased contaminant dissolution (Wilson et al., 1990).

When an impermeable layer is reached and vertical infiltration is halted, the DNAPL have a tendency to form a convex meniscus on top of the layer/aquitard. Here the pure DNAPL will remain relatively unperturbed and slowly dissolve into the surrounding groundwater. All of the above mentioned factors result in the fact that even a small amounts of CAH contaminant can have a huge impact on groundwater quality. At the same time, these small pockets can be hard to locate let alone remediate (Illangasekare et al., 1995). In order to better understand the behaviour of chlorinated ethenes in the subsurface, some of the physical characteristics will be given by Table 1, elaborated on, defined by Figure 2 and finally illustrated using Figure 3.

Table 1: Physical and chemical properties of chlorinated ethenes.

Characteristic/Property	PCE	TCE	cis-DCE	trans-DCE	1,1-DCE	VC
Molecular Formula	C ₂ Cl ₄ 	C ₂ HCl ₃ 	C ₂ H ₂ Cl ₂ 	C ₂ H ₂ Cl ₂ 	C ₂ H ₂ Cl ₂ 	C ₂ H ₃ Cl 
Molecular Weight (g/mol)	165,83	131,39	96,94	96,94	96,94	62,50
Density (g/cm ³)	1,623	1,469	1,284	1,257	1,218	0,911
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Gas
Dynamic Viscosity ⁶ (cp)	0,890	0,570	0,467	0,404	0,330	NA
Boiling Point ¹ (°C)	121	86,7	60,3	47,5	31,9	-13,4
Water Solubility ^{1,3} (g/L at 25° C)	0,21	1,28	6,40	4,50	2,42	2,7
Vapour Pressure ² (mm Hg at 25° C)	18,5	69	200	324	600	2660
Henry's Law Constant ³ (kPa m ³ /mol at 25° C)	1,73	1,03	0,460	0,960	2,62	2,728
Octanol/Water Partition Coefficient ⁴ (Log K _{ow})	2,88	2,53	1,86	1,93	2,13	1,38
Soil-Sorption Coefficient ⁵ (Log K _{oc})	2,37	2,00	1,56-1,69	1,56-1,69	2,18	1,75

¹ChemIdPlus Database; ²Data from EPA, 1986; ³Lide, 2003; ⁴Sangster, 1989; ⁵Data from EPA, 1995; ⁶Data from EPA 1991

Density is the most straightforward property, it is the high density that causes pure phase chlorinated ethenes to not only infiltrate the unsaturated zone but continue downwards once the water table is reached. Viscosity is a measure of the internal resistance of a fluid to flow, mainly determined by the molecular cohesion of the fluid. The lower the viscosity, the less resistance, the easier it is for a fluid to penetrate a porous medium.

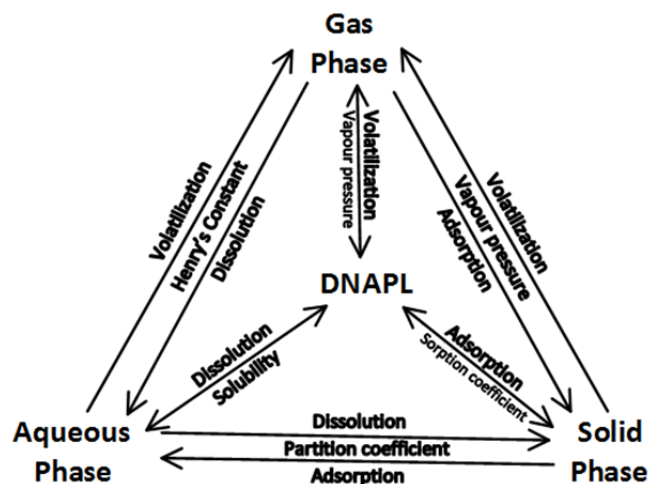
A rather important factor in fluid transport is the hydraulic conductivity of a porous medium, this is a function of the first two properties, density and viscosity as well as the characteristics of the porous medium. Hydraulic conductivity is used to determine the mobility of a fluid in the subsurface.

$$K = \frac{k\rho g}{\mu} \quad (1)$$

From the Equation 1. it is apparent that fluids with either a density greater or a viscosity lower than water have the potential to be more mobile in the subsurface. Where K stands for the hydraulic conductivity, k for the intrinsic permeability, representing the porous medium characteristics, ρ the density, g the gravitational acceleration and μ the viscosity.

The other physical properties listed in Table 1 are related to the transitioning of the CAH contaminants between the different phases. Considering the chlorinated ethenes can be found in up to four distinct phases at contaminated sites, a good understanding of the phase equilibrium relationships shown in Figure 2 is necessary to locate and assess the extent of chlorinated ethene contamination.

Figure 2. Phase equilibrium relationships: processes of interphase mass transfer and rate determining physical properties. (Adapted from Huling and Weaver, 1991)

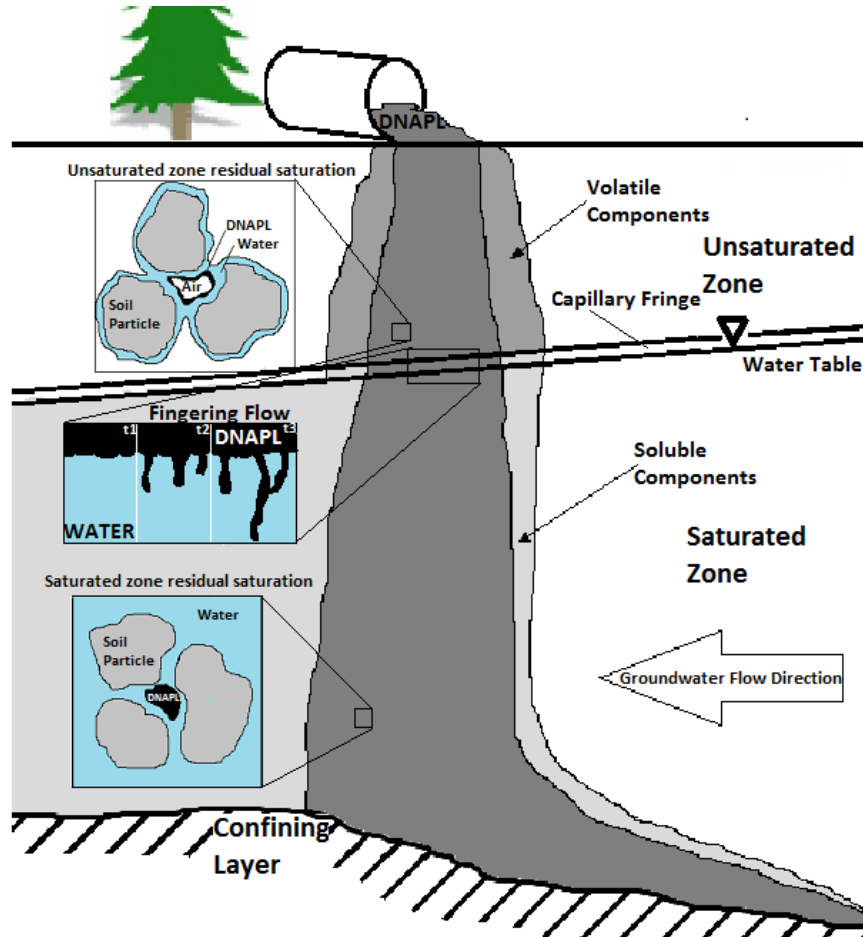


Solubility is used to refer to the equilibrium concentration of the chlorinated ethene in the aqueous phase. It is important to note that organic liquids hardly ever reach this equilibrium concentration in groundwater, they are generally found at concentrations a factor of 10 lower. This difference can be attributed to several dissolution limitations. For instance, the dilution of aqueous contaminants by dispersion, or a reduced solubility due to the presence of other soluble chemicals.

Apart from partitioning into the aqueous phase, the pure phase DNAPL can also volatilize into the air. The before mentioned vapour pressure refers to the partial pressure exerted by the free molecules at the DNAPL surface and is used as an indicator of how readily a compound will evaporate under equilibrium conditions. Henry's law constant is similar yet slightly different than the vapour pressure. Rather than indicating the willingness to transition from the pure DNAPL phase to the air, it relates to the transitioning from the dissolved aqueous phase to the air. Defined as the vapour pressure divided by the aqueous solubility, a higher Henry's law constants results in a greater tendency of the compound to volatilize from the aqueous phase.

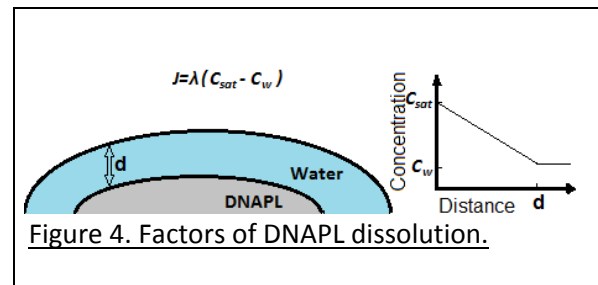
The two last terms in Table 1, octanol/water partition and soil-sorption coefficient relate to the affinity of the chlorinated ethene for organic matter/ lipids and organic matter sorbed to the soil respectively. The first is defined as the ratio of the solubility of a compound in a two phase system, consisting out of a polar and a non-polar solvent, water and octanol. The higher the K_{ow} value is, the more non-polar the chemical compound, making it more soluble in octanol than water. The soil-sorption coefficient is defined as the ratio of the chemical sorbed to the soil and the concentration of that chemical dissolved in water. In general, sorption is referred to as a physical and/or chemical process by which one substance becomes attached to another.

Figure 3. DNAPL infiltration and contamination of the (un)saturated zone.



4 TRANSPORT PROCESSES

Where the previous Section dealt with processes related to the introduction of the CAH contaminants into the subsurface, this Section addresses processes that take place after the DNAPL has been embedded in the saturated zone. Although the pure phase DNAPL remains relatively unaffected



by transport processes, after the initial infiltration it does become subjected to processes such as advection and dispersion when dissolved into the aqueous phase. Dilution, the transfer of contaminant mass to the aqueous phase, is affected by several factors, Figure 4 shows a simplified sketch of an example of a water-DNAPL interface. The mass flux or transfer J is mainly driven by diffusion, creating a concentration gradient, from the concentration C_{sat} at the DNAPL surface to C_w the concentration in water at point d , λ is considered a function of the DNAPL surface area and the groundwater velocity, determining the rate at which the water superimposing the DNAPL droplet will be refreshed.

The equation governing the transport of dissolved CAHs in a three-dimensional porous medium as defined by Bear (1972) with degradation added is given by Equation 2:

$$\frac{\delta nC}{\delta t} = \nabla \left(n \begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{bmatrix} \nabla C \right) - \nabla \cdot \left(n \begin{Bmatrix} v_x \\ v_y \\ v_z \end{Bmatrix} C \right) - \frac{\delta \rho_b S}{\delta t} - \mu (nC + \rho_b S) \quad (2)$$

The equation relates the change in concentration C over time to the spatial changes in concentration caused by hydrological processes such as advection, hydrodynamic dispersion, chemical degradation reactions and specific soil parameters such as porosity n and bulk density ρ_b . The first right hand side term is used to model dispersion, with the matrix representing the second rank dispersion tensor in the three dimensions. The second is the advection term, where the vector is used to indicate the groundwater velocity v in the x , y and z direction. The third term relates to change in time of solute sorbed (S) to the porous medium. Although a first order degradation rate μ is used in Equation 2. to calculate the degradation of both the aqueous and sorbed contaminants, it is just one of the many ways of interpreting/modelling degradation. The del or nabla symbol ∇ refers to a mathematical operator used to determine the gradient, a generalization of the concept of derivation used for functions dependent on several variables. In the case where the function also depends on temporal parameters the gradient generally refers only to the spatial derivatives.

When the operators are replaced by their mathematical function, the velocity, dispersion and soil parameters assumed constant, Equation 2 is simplified to the following Equation 3:

$$R \frac{\delta C}{\delta t} = D_x \frac{\delta^2 C}{\delta x^2} + D_y \frac{\delta^2 C}{\delta y^2} + D_z \frac{\delta^2 C}{\delta z^2} - v_x \frac{\delta C}{\delta x} - v_y \frac{\delta C}{\delta y} - v_z \frac{\delta C}{\delta z} - \mu C \quad (3)$$

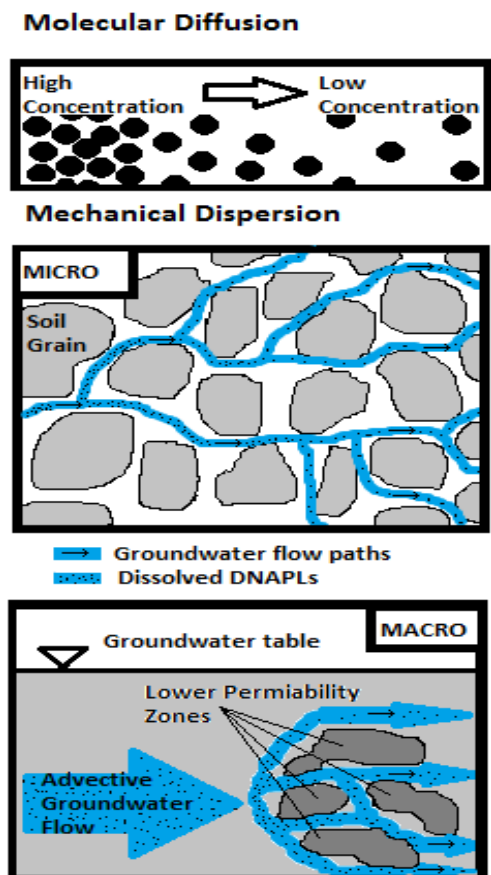
Where R is used to refer to the retardation coefficient, the degree of hindrance experienced by the aqueous contaminants as they are affected by a variety of reversible chemical and physical processes (Eq. 4a). For this particular example the most straight forward absorption was assumed, linear equilibrium sorption. This is done by relating the contaminants sorbed S to the contaminants dissolved in the groundwater C using the partition coefficient K_d as shown by Equation 4b.

$$R = 1 + \frac{\rho_b}{n} K_d \quad S = K_d C \quad (4a,b)$$

Of the various transport mechanisms affecting dissolved CAH transport (Figure 5), advection is the most straightforward. From a hydrological viewpoint, transport of pollutants due to the fluids bulk being transported relates to the displacement of dissolved DNAPL contaminants in the direction of the groundwater flow. Mathematically the fluid's motion can be describes as a vector field. A scalar field (∇ operation) is used to show the spatial distribution of transported material. Out of all the transport processes advection is the only one that does not lower the aqueous concentration.

The dispersion coefficient is somewhat related to advection, considering the term hydrodynamic dispersion is an incorporation of two separate transport mechanisms: molecular diffusion and mechanical dispersion. Diffusion is not affected by fluid bulk motion. Driven by molecular scale concentration differences, it is nothing more than a net movement of molecules from a region of high concentration to one of low concentration. Mechanical dispersion on the other hand is influenced by groundwater flow on both a micro- and a macroscopic pore scale. At the microscopic pore scale, contaminant spreading by transport through a porous medium seems evident, considering the amount of available pathways for the dissolved material to follow. A similar behaviour arises when contaminants travel through the subsurface at a macroscopic scale and subsurface inhomogeneities result in spatial spreading of dissolved CAHs.

Figure 5. Dilution mechanisms.



So far all of these transport processes elaborated on dealt with displacing and spreading the contaminant. However the chemical-physical mechanism of adsorption causes contaminants to be held back. This retardation occurs until the chemical adsorption equilibrium is reached, making adsorption the only transport mechanism that lowers the global average velocity of the dissolved contaminants. The retardation factor is mainly dependent on the chemical nature of the aquifer and the contaminant.

This concludes the list of physical and chemical mechanisms presented in this Chapter, with the caveat that it needs to be taken into account that the concentration reduction processes discussed so far are nothing more than dilution of the maximum concentration of the chlorinated ethene contaminants. Since none of these processes actually contribute to the decrease of contaminant mass spread throughout the aquifer, they are generally referred to as non-destructive processes. Although these processes do not directly contribute to the removal of contaminant mass from the subsurface, they play an important role in the behaviour and transport of contaminants.

No remediation project should be attempted without first understanding the concentration reduction processes. This knowledge is required to track the contaminant plume, its current and future location. Only then can the choice of remediation tools be assessed and the area in which they are to be deployed in order to achieve maximum contaminant mass removal. A good understanding of these processes will not only give insight into the fate of the chlorinated ethenes in the aqueous phase, the contaminant plume can be studied and backtracked to assess and determine the presence of pure phase chlorinated ethenes in the aquifer. Not all remediation techniques target dissolved contaminants, knowing the location of a possible source zone can greatly shorten the remediation process, even prevent potential disasters (Zuurbier et al. 2013).

5 NATURAL ATTENUATION

Most of the processes described in the previous Chapter do result in lower concentrations by simple diluting and spreading of the contaminants, however they do not contribute to a decrease in mass of the contaminant plume. To differentiate between the two types of processes, they are to be defined as either non-destructive (transport and retardation mechanisms) or destructive (any form of contaminant attenuation) processes. The term natural attenuation is used to describe a combination of naturally occurring processes in both soil and groundwater without any form of anthropogenic intervention, affecting the contaminants in the subsurface in a variety of ways: reducing aqueous concentrations, mobility, toxicity, volume or mass of contaminants in those media. These in situ processes include the transport and retardation mechanisms mentioned in the previous section: advection, dispersion, sorption and volatilization (ITRC, 2005). This Section of the thesis will deal with extant knowledge related to a decline in contaminant plume mass, mainly the biological and chemical destruction or stabilization of CAH contaminants.

The implementation of natural degradation as remediation tool has not always been common practice and has come a long way in the last couple of decades (Wang, 2000), it was once viewed as a “no action” or “walk away” approach. Since the nineties it has become increasingly accepted as a viable remediation strategy, especially when combined with contaminant source control and long-term monitoring. Though the process of natural attenuation can technically occur at any site, yet depending on the site’s characteristics the effectiveness of the remediation strategy can vary substantially between sites. Research shows that, as a remediation technique, natural attenuation has several distinct advantages and disadvantages when compared to the more engineered remediation approaches (ITRC, 2008):

Advantages:

1. Destruction or transformation of contaminants to innocuous daughter products.
2. It is a non-intrusive approach to remediation.
3. Can be combined with other remediation techniques and uses of groundwater.
4. Under the right circumstances its costs can be significantly lower than that of alternatives.

Disadvantages:

1. Achieving regulatory action levels might result in long time frames.
2. Best results with site characterization and long term monitoring (expensive and intensive).
3. Change in site conditions over time may result in a decrease of remediation efficiency.
4. Daughter products or by-products may prove more toxic than their parent compound.

In order to differentiate between the different types of CAH degradation two criteria are used, the first is directly related to the reaction undergone by the contaminant, the second relates to the amount of oxygen present at the time of the reaction. From a pure chemical point of view these degradation reactions are nothing more than redox reactions, where the contaminant is either being reduced or oxidized. Based on the nature of the reaction, three types can be identified. First the group of electron accepting reactions, resulting in a reduction or dechlorination of the compounds. Secondly you have the electron donor reactions, whereby the CAH donates its electrons in order to oxidize and consequently degrade. The third type is a bit trickier, rather than only being limited by the availability of electron donors or acceptors in the subsurface these reactions are characterized by the fact that they are facilitated by enzymes or organisms that act as a catalyst. Although the first two types can occur abiotically, they are generally sped up by microbial cultures present in the subsurface. The main difference between the first two and the third type of degradation is that the organisms involved do not benefit from the cometabolic reaction. In addition, the resulting degradation sometimes even proves harmful for the organisms catalysing the reaction.

The second criteria, the presence or absence of oxygen will be elaborated on to prevent any sort of misinterpretation, considering different terms are employed by the different sub-disciplines prevalent in the field of hydrogeology, contaminant transport and degradation. Due to the fact that the propensity of the CAH contaminants is directly linked to the geochemistry and microbiology in the subsurface, each field uses its own jargon to describe the nature of these degradation reactions. Both fields use well established terms to indicate oxygen availability in the subsurface however their usage and range is rather different for the individual sub-disciplines. Figure 6 is used to illustrate the difference between the two commonly employed terms to indicate “oxygen-rich” or “oxygen free” conditions and their usage.

Figure 6. Oxygen usage related terms.

Dashed lines indicate imprecisely defined boundaries between categories.

(a) MDL or minimum detection limit

(b) Theoretical point at which dissolved oxygen content falls to zero.

(Adapted from Bradley, 2008)

Oxygen Conditions		Sub-discipline usage	
		Geochemistry	Microbiology
Practical Anoxic	(a) MDL	Oxic	Aerobic (strictly oxidizing)
	(b) $[O_2]=0$	Post-Oxic	Anaerobic (partially oxidizing or reducing)
	Strict Anoxic	Anoxic	Anaerobic (strictly reducing)

Conceptually the most straightforward term to indicate an “oxygen-free” environment is “anoxic”, indicating a complete absence of oxygen. Due to the difficulty of measuring extremely low concentrations of oxygen in groundwater, this term generally refers to concentrations below 0,1-0,5 milligrams per litre (mg/L). However it needs to be taken into account that usage of the term “anoxic” does not imply that there are no alternative electron accepting processes that potentially could occur in the subsurface. Nevertheless the term is generally used in geochemistry to indicate highly reducing conditions.

The terms used in microbiology, aerobic and anaerobic, are more obscure and ambiguous than the alternative used by geochemists. The term aerobic is mainly used to describe microorganisms that use oxygen as a respiratory electron acceptor. This term can be rather misleading, although the largest component of air is nitrogen at 78%, it is almost solely used to refer to the presence of oxygen. Further confusion can occur due to the fact that the term anaerobic and strictly anaerobic are employed by many microbiologists to refer exclusively to several types of highly reducing conditions. The term anaerobic can apply to variety of reactions occurring under acetogenic, sulphate reducing and/or methanogenic conditions. However it is not used to refer to the more oxidized circumstances such as nitrate, manganese or iron reducing conditions, though these also occur in the absence of air. Similar to the anoxic term, anaerobe conditions refer to oxygen concentrations below 0.1 milligram per litre.

Apart from organisms that thrive in the presence or absence of oxygen there is also a microaerophilic category, organisms that prefer extremely low levels of oxygen, requiring some oxygen for metabolic activity and growth yet hardly preform, or not at all under ambient oxygen concentrations. Indicating oxygen levels between the atmospheric 0-21% oxygen content.

6 REDOX CONDITIONS

Most of the environmental contaminants dealt with in the field of contaminant hydrogeology degrade as a result of redox reactions. This is generally facilitated or catalysed by microorganisms present in the subsurface. The degradation reaction is nothing more than a transformation of the contaminant compound, serving as either an electron acceptor or as an electron donor in a specific biochemical reaction. The importance of in situ redox conditions should be evident and is considered one of the primary determinants of the efficiency of the biodegradation of chlorinated ethenes and many other environmental contaminants (Bradley & Chapelle, 2010).

Any chemical reaction in which atoms have their oxidation state changed is considered a reduction-oxidation reaction, or redox reaction for short. The oxidation state or oxidation number is used to quantify the degree of oxidation of an atom in a chemical compound, typically represented by an integer, which can be positive, negative or zero. The integer refers to the hypothetical charge (electro negativity) of an atom if it were exclusively ionically bonded to atoms of different elements. Reduction and oxidation are two terms used to respectively indicate a decrease and increase in the oxidation state of an atom. Reduction being a net gain in electrons while oxidation refers to a net loss (Figure 7).

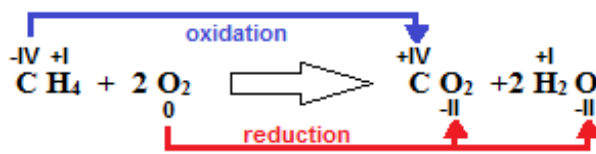
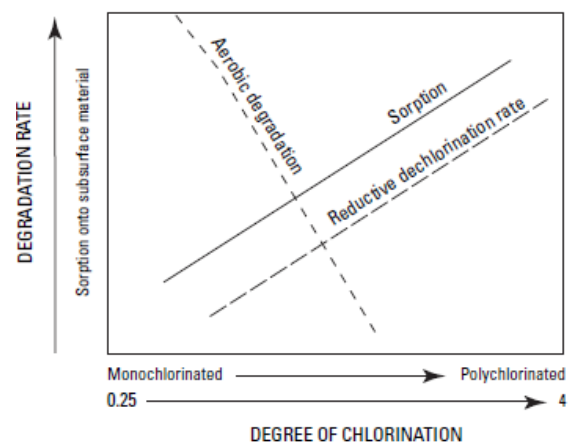


Figure 7. Example of redox reaction.

Roman numbers indicate the oxidation states of the molecules.

Highly oxidized compounds such as PCE and TCE tend to serve as microbial terminal electron acceptors under strongly reducing conditions, meaning the most efficient degradation occurs when there is an in-situ abundance of electron donating compounds (Bradley, 2003; Chambon et al., 2013). As PCE degrades and the number of chlorine atoms bound to carbon decreases so does its state of oxidation. The resulting compounds become less and less oxidized. This loss of chlorine atoms is directly related to the ambient redox conditions required to obtain optimal biodegradation. The less chlorinated ethenes therefore achieve better degradation rates under strongly oxidizing conditions. Although VC has been proven to be able to degrade under reducing conditions, the rate at which it occurs is almost negligible (He et al., 2003b; Bradley and Chapelle, 2011).

Figure 8. Relation between degree of chlorination, sorption and degradation. (Adapted from Norris et al., 1993)



Due to the fact that chlorinated ethenes can serve as both electron acceptor and donor in the subsurface, the in situ redox environment has proven to be significant for CAH biodegradation. This is due to the fact that not only the willingness of the compounds to undergo these degradation reactions but also their role in these reactions is determined by the in-situ redox conditions.

The oxidation reduction potential (ORP) is a measure of the tendency of a compound to gain or transfer electrons and thereby get reduced or oxidized respectively. The redox potential is measured in volts (V) or millivolts (mV) and can be positive or negative based on the affinity of the chemical species for electrons. The higher (positive) the redox potential is, the more inclined the compound is to accept electrons and therefore undergo reduction. A more negative ORP suggests that oxidation is the most likely process affecting the aqueous phase compound. Based on this measure of activity, the reducing and oxidizing substances in the aqueous phase can be analysed, resulting in a better understanding of the possible propensity of any chlorinated ethene contaminants in the subsurface. Table 2 lists the more commonly occurring redox half reactions in chlorinated ethene contaminated aquifers.

Table 2: Redox half-reactions in the subsurface. Redox potential measured at pH 7 and 25°C.
(Compiled from Stumm and Morgan, 1981; Wiedemeier et al., 1997; Bohn et al., 1985)

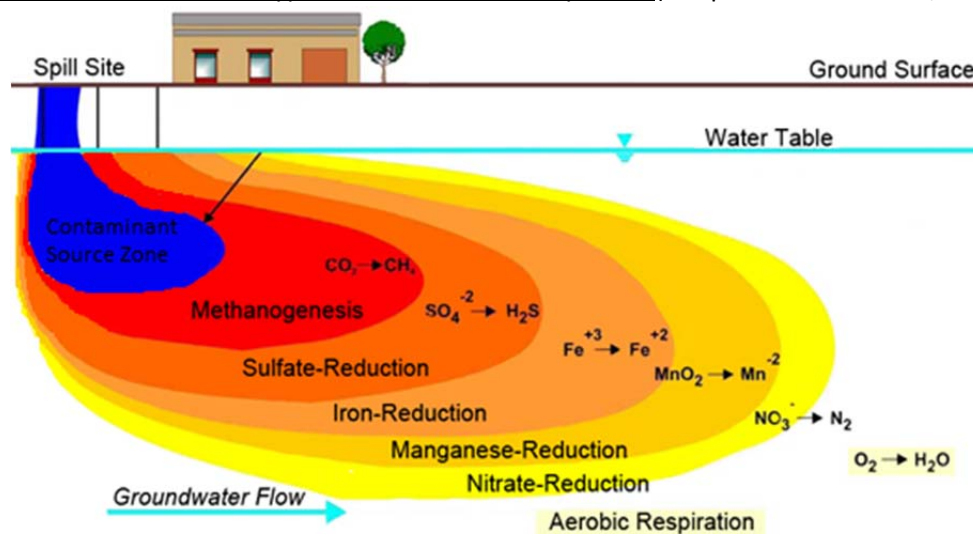
Half-Reactions	Redox Potential E_h (V)
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	0,81
$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$	0,74
$C_2Cl_4 + H^+ + 2e^- \rightarrow C_2HCl_3 + Cl^-$	0,58
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + H_2O$	0,57
$C_2HCl_3 + H^+ + 2e^- \rightarrow C_2H_2Cl_2 + Cl^-$	0,55
$MnO_2 + HCO_3^- + 3H^+ + 2e^- \rightarrow MnCO_3 + 2H_2O$	0,52
$C_2H_3Cl + H^+ + 2e^- \rightarrow C_2H_4 + Cl^-$	0,49
$NO_3^- + 2H^+ + e^- \rightarrow NO_2^- + H_2O$	0,42
$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	0,36
$C_2H_2Cl_2 + H^+ + 2e^- \rightarrow C_2H_3Cl + Cl^-$	0,36
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0,36
$NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$	0,33
$CH_3OH + 2H^+ + 2e^- \rightarrow CH_4 + H_2O$	0,17
$Fe(OH)_3 + 3H^+ + 3e^- \rightarrow Fe^{2+} + 3H_2O$	0,06
$CH_2O + 2H^+ + 2e^- \rightarrow CH_3OH$	-0,18
$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$	-0,21
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0,24
$N_2 + 8H^+ + 6e^- \rightarrow 2NH_4^+$	-0,28
$2H^+ + 2e^- \rightarrow H_2$	-0,41
$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + 2H_2O$	-0,48
$Fe^{2+} + 2e^- \rightarrow Fe$	-0,85

Decreasing Amount of Energy Released During Electron Transfer

Seminal work (Stumm and Morgan, 1970) showed only a few elements considered to be predominant electron acceptors and/or donors in aquatic redox processes, namely hydrogen, carbon, nitrogen, oxygen, sulphur, iron and manganese. In order to obtain the maximum amount of energy from their substrate soil microorganisms attempt to utilize the strongest electron acceptors available (Huber, 1989). The reactions with the highest redox potential will provide the most energy for organisms growth when reduced, with oxygen (O_2) yielding the most, then nitrate (NO_3), manganese (Mn^{2+}), iron (Fe^{2+}), sulphate (SO_4^{2-}) and finally the reduction of CO_2 to methane (CH_4).

Under non-engineered conditions chlorinated ethene reduction is most often the prevailing attenuation mechanism considering the fact that the contaminated sites are generally considered anoxic due to the oxygen depleting nature of the chemical and biological processes involved. Similar to oxygen, the other intrinsic electron acceptors concentrations will sequentially decrease, resulting in a more negative groundwater reduction potential and therefore increasing the tendency of the CAHs to undergo reduction. Leading to the creation of redox zones within the aquifer due to the exposure to the contaminants and electron acceptors depletion, shown by Figure 9.

Figure 9. Redox zones of a typical CAH contaminant plume. (Adapted from Parsons, 2004)



The fact that chlorinated ethenes can be used as both electron acceptors and donors makes the redox potential of the subsurface an important indicator of the viable contaminant degradation pathways. Solely using the groundwater redox potential to identify or quantify the intrinsic processes is difficult, considering it reflects on the mixed potential of multiple reactions mentioned in Table 2. Information on the predominant microbial and geological processes can only be properly deduced when these measurements are combined with data on the availability of electron acceptors throughout the sites domain. It is important to note that by using this type of combined measurement it becomes possible to identify the approximate location and extent of the dissolved chlorinated ethene contaminant plume (Wiedemeier, 1997).

7 MICROBIOLOGY

Prior to 1970, only several dozen naturally-occurring chlorinated organic compounds were reported in scientific literature (Gribble, 1994). The fact that these compounds were considered all but natural components of the biosphere resulted in the consensus that chlorinated ethenes were recalcitrant to biodegradation prior to 1980 (Asplund, 1995; Gribble, 1992, 1994). In the early 1980's the ecological threat that these contaminants posed was clearly established, as numerous sites considered environmental disasters were identified. During the 1980's the necessity of increased CAH related research resulted in the widely reported observation of several PCE and TCE transformation products in anaerobic groundwater systems. By the end of 1980's the important role microorganisms had in the chlorinated ethene degradation became apparent.

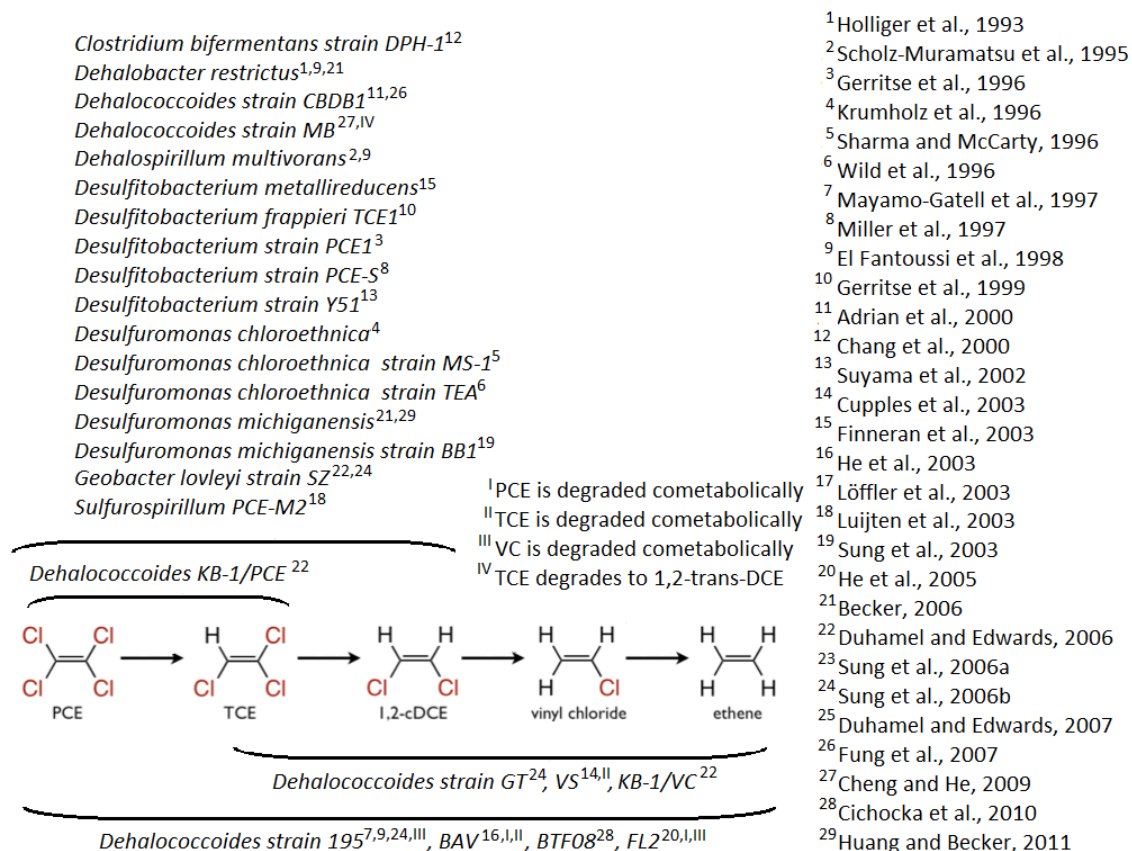
7.1 Reductive dechlorination

According to current literature there are only a few metabolic classifications of microorganisms capable of reductive anaerobic dechlorination (Bhatt et al., 2007; ITRC, 2008). This group of bacteria includes several strains of methanogens, sulphate-reducing and dechlorinating bacteria. Although these bacteria are abundantly found in the subsurface and are able to facilitate a rapid degradation of the more chlorinated ethenes, the research has so far mainly focussed on microorganisms capable of degrading the more toxic DCE isomers and VC to innocuous components such as ethene. However the bacteria able to use DCE and VC as their primary substrates have proven to be far from as abundant as the ones related to PCE and TCE degradation (He et al., 2003a).

When the research submitted to the scientific community, indicated that the *Dehalococcoides* species were able to facilitate the complete sequential degradation of chlorinated ethenes in laboratory studies (Freedman et al. 1989) as well as in the field (Major et al. 1991), the expectation was that eventually many different types of microorganisms capable of the complete degradation of CAHs would be found. More than two decades of field research and intense laboratory studies later have proven that this expectation was most likely incorrect. Nonetheless, several studies have found a correlation between the accumulation/persistence of DCE and VC and the absence of the *Dehalococcoides* species (Fennel et al. 2001, Hendrickson et al. 2002a/b) linking this group of microorganisms directly to the reductive dechlorination of a whole array of CAHs.

Although it is by far the most widely researched genus of bacteria, the *Dehalococcoides* group is just one of many strains of microorganisms capable of facilitating the reductive dechlorination of chlorinated ethene contaminated sites. The other strains of bacteria, their applicability and the related studies are given by Figure 10.

Figure 10. Bacteria strains capable of facilitating reductive dechlorination through dehalorespiration.



It is of importance to note that the presence of one of these strains and an abundance of CAH contaminants does not always result in the complete removal of harmful compounds in the aquifer in question. As mentioned before the cometabolic type of dechlorination requires another suitable co-substrate for the microorganisms catalysing the degradation. Considering H₂ apart from a few exceptions has proven to be the ultimate electron donor for the redox reactions involved with reductive dechlorination (Löffler et al. 2000). Only a few species of bacteria rely on more complex electron donors such as acetate and formate, in order to successfully degrade chlorinated ethenes (Krumholz et al., 1996; Krumholz 1997; Löffler et al., 2000). This additional process depends on the existence of microorganisms or a microbial community capable of fermenting a steady supply of carbon substrates in order to provide the necessary electron donors for dehalogenation.

Indicating that the process of microbial reductive dechlorination appears to be more multifaceted than first anticipated. Making the availability of suitable electron donors as well as the resulting competition for H₂ and acetate/formate between the dechlorinating bacteria and other indigenous microorganisms the principal determinants of intrinsic chloroethene reductive dechlorination efficiency (Yang & McCarty 1998; Löffler et al. 1999). Table 3 and 4 illustrate a number of hydrogen yielding and consuming reactions occurring in the subsurface.

Carbon Substrate	Fermentation Reaction
Methanol	$\text{CH}_4\text{O} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2^- + \text{H}_2\text{O} + 3\text{H}_2$
Ethanol	$\text{C}_2\text{H}_6\text{O} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + 2\text{H}_2 + \text{H}^+$
Acetate	$\text{C}_2\text{H}_3\text{O}_2^- + 4\text{H}_2\text{O} \rightarrow 2\text{CO}_2^- + 2\text{H}_2\text{O} + 4\text{H}_2$
Propionate	$\text{C}_3\text{H}_5\text{O}_2^- + 3\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{CO}_2^- + \text{H}_2\text{O} + 3\text{H}_2$
Lactate	$\text{C}_3\text{H}_5\text{O}_3^- + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{CO}_2^- + \text{H}_2\text{O} + 2\text{H}_2$
Butyrate	$\text{C}_4\text{H}_7\text{O}_2^- + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} + \text{H}^+$

Table 3. Examples of hydrogen yielding fermentation of organic matter.

Table 4. Examples of reactions using hydrogen as electron donor.

Stoichiometrically 1.0 gram of molecular hydrogen is sufficient to dechlorinate 20,6; 21,7; 24,0; 31,0 grams of PCE TCE DCE and VC respectively. Assuming 100% of molecular hydrogen is used by the dechlorinating microorganisms.

Electron Acceptor	Electron Acceptor Reduction
Oxygen	$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
Ferric Iron	$\text{e}^- + 3\text{H}^+ + \text{FeOOH} \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O}$
Sulfate	$4\text{H}_2 + \text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{HS}^- + 4\text{H}_2\text{O}$
Carbon Dioxide	$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
PCE	$\text{H}_2 + \text{C}_2\text{Cl}_4 \rightarrow \text{C}_2\text{HCl}_3 + \text{HCl}$
TCE	$\text{H}_2 + \text{C}_2\text{HCl}_3 \rightarrow \text{C}_2\text{H}_2\text{Cl}_2 + \text{HCl}$
DCE	$\text{H}_2 + \text{C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{HCl}$
VC	$\text{H}_2 + \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$

7.2 Aerobic oxidation

The first report on oxidative bioremediation was by Wilson and Wilson (1985), who found that specific methanotrophic bacteria were capable of oxidizing TCE to CO_2 under oxic conditions. Further research has identified a whole array of microorganisms capable of chlorinated ethene mineralization, the transformation of organic to non-organic compounds. More specifically, aromatic compound oxidizers (BTEX compounds) (Nelson et al. 1986; Fan et al. 1993; Malachowsky et al. 1994; Fuller et al. 1995), methane oxidizers (Baek and Jaffé, 1989; Moore et al. 1989; Tsien et al. 1989; Gerritse et al. 1995; Semprini 1995; Hopkins et al. 1995; Vanelli et al. 1990), ammonium oxidizers (Vanelli et al. 1990) propane oxidizers (Malachowsky et al. 1994), isopropene oxidizers (McCarty and Semprini, 1994), propene oxidizers (Reij et al. 1995), methanol oxidizers (Fitch et al. 1996), ethene oxidizers (Verge et al. 2001) and vinyl chloride oxidizers (Verge et al. 2002).

All these different strains of microorganisms are incapable of using the chlorinated ethenes as a primary substrate, making aerobic cometabolic degradation not only reliant on oxygen content but also the presence of a suitable carbon co-substrate. The potential for oxic cometabolic oxidation of CAHs might not be a reliable long-term degradation mechanisms due to the low oxygen concentrations of the generally anoxic contaminated aquifers (Semprini, 1995). However, they do become viable at the periphery of the contaminant plume, where the oxygen can be introduced through the diffusion from surrounding oxic aquifers as well as the infiltration of oxygenated recharge (Dolan and McCarthy, 1995). Consequently most of the cometabolic oxidation related bacteria, in a non-engineered subsurface can be found at the plume fringes and near the water table.

The two main differences between the microorganisms involved with direct and cometabolic anaerobic oxidation is that direct degradation has a requirement less, since the contaminants themselves can be used for energy and growth of the bacteria involved. The second difference is related to the chlorinated ethenes affected by this microbial facilitated degradation, where cometabolism could result in the mineralization of TCE. The direct approach only affects the least chlorinated contaminants DCE and VC (Hartmans et al. 1985, 1992a/b; Hartmans 1995; Verce et al. 2002; Bradley et al. 2000a; Coleman et al. 2002a/b; Elango et al. 2006). Multiple studies have observed rapid microbial degradation, including mineralization of VC, the least chlorinated CAH under anoxic conditions (Bradley et al. 1996, 1998a, 1998b, 1998c; Davis and Carpenter, 1990; Phelps et al. 1991).

Several strains of *Mycobacterium aurum*, capable of using VC as their sole source of energy and carbon were isolated by Hartmans and his colleagues (1985, 1992a/b). A decade later Verce and co-workers found another organisms, *Pseudomonas aeruginosa* capable of similar feats. (Verce et al. 2002). After collecting and testing soil samples, they retrieved 22 chlorinated ethene contaminated in Europe and the Unites States. Coleman and his team found that 60% of these samples contained strains of bacteria that resulted in the aerobic biodegradation of VC (Coleman et a. 2002a). *Mycobacterium* were found in half of the samples taken as well as one sample with *Nocardioides* bacteria, these observations led the scientists to believe that potential for non-cometabolic aerobic VC degradation is widespread in CAH contaminated environments (Coleman et al. 2002a).

Several studies have also indicated the possibility of DCE degradation under oxic conditions, yet in the absence of an apparent carbon source to be used as a co-substrate for cometabolism (Bradley et al. 1998a/b/c; Klier et al. 1999). Even more interesting is that those studies also found these microorganisms facilitating the direct oxidation of DCE to be prevalent in organic rich sediments, characterized by high amounts of dissolved organic carbon (DOC) (Bradley et al. 2000a). Coleman et al. were able to isolate *strain JS666*, a type of bacteria closely related to the genus *Polaromonas vacuolata* able to use cis-DCE as a primary substrate for metabolism, allowing for the natural attenuation of DCE even under conditions not suitable for aerobic cometabolism (Coleman et al. 2002b).

7.3 Anaerobic oxidation

The capability of microbial oxidation of VC to innocuous products under anaerobic conditions was first described by Bradley and Chapelle (1996), when investigating microorganism facilitated degradation of VC in a Fe(III)-reducing sediment. Although a low, yet significant mineralization rate was reported for non-treated sediment, degradation rates comparable to aerobic oxidation were achieved once the ambient Fe(III) conditions were amended with additional iron (Fe(III)) (Bradley and Chapelle, 1996; Bradley et al., 1998a/b). Subsequent research demonstrated the susceptibility of DCE to anaerobic microbial oxidation (Bradley et al., 1998c/d).

Unfortunately the lack of pure and mixed cultures of microorganisms capable of mineralizing DCE or VC under anoxic or microaerophilic has been rather detrimental to the identification and description of the mechanisms of anaerobic microbial oxidation. The evidence gathered so far indicates a syntrophic relationship between CAH degrading organisms and various respiratory organisms capable of mineralizing the resulting transformation products to harmless gasses such as CO₂ and methane (Bradley and Chapelle 2000b). A variety of mechanisms for chlorinated ethene mineralization under oxic conditions have been proposed:

1. Net oxidation with chloroethanol as an intermediate (Vogel and McCarty, 1985).
2. Syntrophic oxidation with acetate as an intermediate (Bradley and Chapelle, 1999a/b 2000b).
3. Syntrophic oxidation with ethene as an intermediate (Bradley and Chapelle 2002).
4. Microaerophilic mineralization at sub-detection DOC levels (Gossett 2010).
5. Mineralization due to abiotic processes that are wrongfully interpreted as biological activity.

8 REACTION PATHWAYS

A wide variety of degradation pathways can result in CAH attenuation, determined by the chemical and biological characteristics of the domain. The viability of each pathway relies on the redox conditions of the subsurface, as discussed in Chapter 6; the availability of electron donors and acceptors; bioavailability of microorganisms able to catalyse microbial degradation and the presence of a suitable growth substrate for the microorganisms to metabolize. A brief summary of the various reaction pathways, the required conditions and compounds as well as the affected CAH contaminants is given in Table 5.

Table 5. Potential degradation reactions.

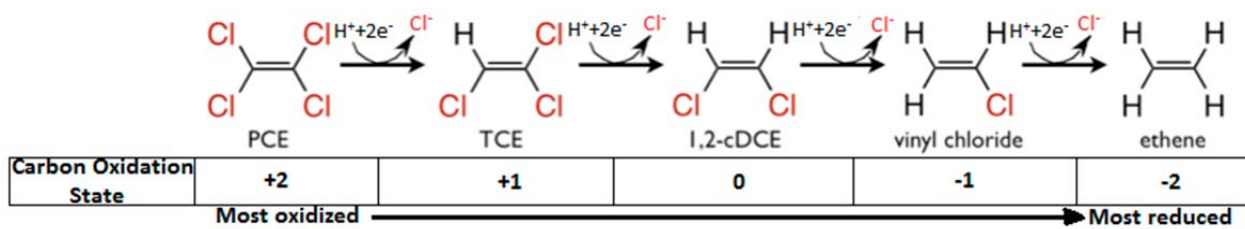
Degradation Mechanism	Carbon Source	Electron Donor (Reducing Agent)	Electron Acceptor (Oxidizing Agent)	Affected CAHs
Aerobic Oxidation (direct)	CAH	CAH	Oxygen	DCE, VC
Aerobic Oxidation (cometabolic)	Organic carbon	Co-substrate	Oxygen	TCE, DCE, VC
Anaerobic/Microaerophilic Oxidation (direct)	CAH	CAH	SO ₄ , NO ₃ ⁻ , NO ₂ ⁻ , metals or O ₂	DCE, VC
Anaerobic/Microaerophilic Oxidation (cometabolic)	Organic carbon	Co-substrate	SO ₄ , NO ₃ ⁻ , NO ₂ ⁻ , metals or O ₂	TCE, DCE, VC
Anaerobic Reductive Dechlorination (direct)	Organic carbon or CO ₂	Hydrogen	CAH	PCE, TCE DCE, VC
Anaerobic Reductive Dechlorination (cometabolic)	Organic carbon or CO ₂	Hydrogen	Cometabolic electron acceptor	PCE, TCE DCE, VC
Anaerobic Reductive Dechlorination (abiotic)	NA	Hydrogen	CAH	PCE, TCE DCE, VC

8.1 Reductive degradation

8.1.1 Biotic anaerobic reductive dechlorination (direct and cometabolic)

Reductive dechlorination is a sequential degradation reaction in which the chlorinated ethenes, serving as electron acceptors are reduced while hydrogen, the most important electron donor for reductive dechlorination gets oxidized (Parson 2004). The process is considered sequential since chlorine atoms are consecutively replaced by hydrogen atoms as the chlorinated ethenes become less and less chlorinated, yielding the completely dechlorinated and harmless end product ethene at the end of the PCE->TCE-> DCE->VC->ETH degradation chain. Initially it was assumed to be a purely cometabolic mechanism, however in the early 1990s its was proven that certain microorganisms were able to dechlorinate these chemicals as part of a respiratory process (Holliger and Schraa, 1994). These organisms are referred to as dehalorespirators and use chlorinated ethenes as a primary growth substrate, meaning microorganisms derive energy as well as growth from the degradation reactions illustrated using Figure 11.

Figure 11. Biotic reductive dechlorination through dehalorespiration



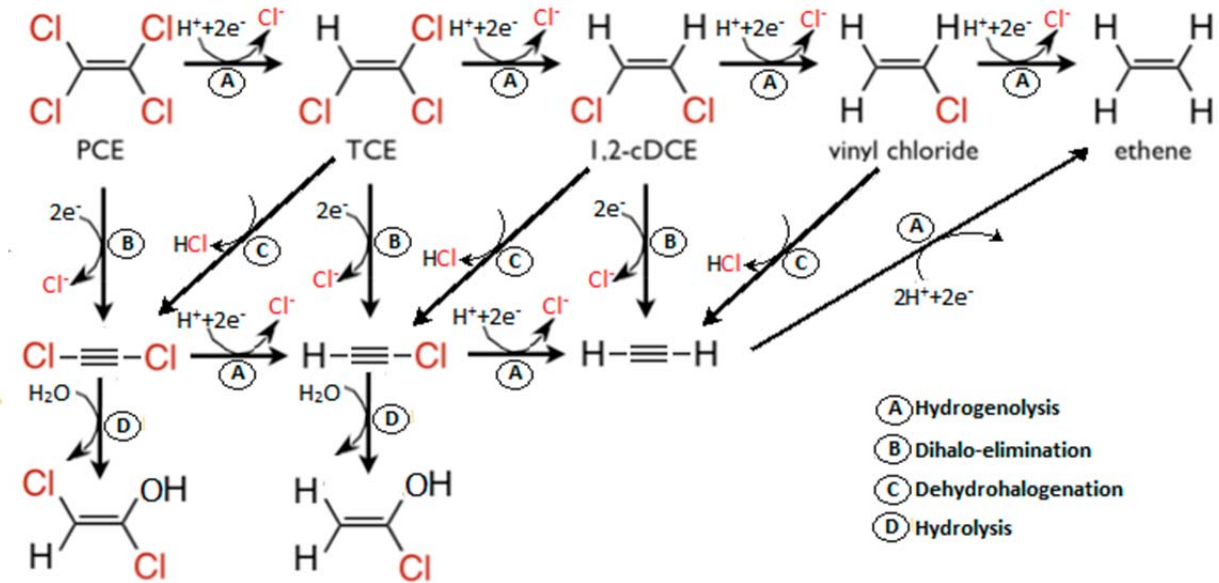
The greater oxidation levels related to the more oxidized nature of PCE and TCE makes them more susceptible to reductive degradation. Although there are several strains of bacteria that can facilitate this degradation there has only been one strain identified that can carry out the complete degradation of the chlorinated ethenes (Cupples et al., 2003; He et al., 2003a/b). Unfortunately this specific strain occurs less often at chlorinated solvent contaminated sites. Resulting in the partial degradation of PCE and TCE and the accumulation of the lesser chlorinated compounds DCE and VC in the subsurface (Weaver et al., 1995; Wilson et al., 1995). This build-up of DCE and VC can be attributed to a number of factors; the depletion of primary nutrients, unfavourable redox circumstances or the lack of microorganisms capable of completely degrading the CAHs to ethene.

Of the three possible DCE isomers mentioned before, cis-1,2 DCE is the most regularly encountered intermediate product of the sequential degradation process. The accumulation of it is a good indicator of the presence of dehalorespirators and the reductive dechlorination potential of the subsurface. Among the presence of PCE daughter compounds other indicators of reductive dechlorination are elevated chloride levels (> twice as high as regular background levels), heightened dissolved hydrogen concentrations (>1nM), low dissolved oxygen (DO) concentrations (<0,5 mg/L) and a low oxidation-reduction potential of the groundwater (<50 mV) (Wiedemeier et al. 1997).

8.1.2 Abiotic reductive dechlorination

Although intrinsic degradation under abiotic circumstances is several times slower than degradation resulting from microbiological activity, it is still significant especially over long periods of time. Little research has been conducted on this phenomena but the lab experiments conducted to investigate this process did manage to characterize the reductive chlorination of chlorinated ethenes as well as predict their fate and transport (Lee & Batchelor, 2004). The researchers' main goal was to evaluate the effect of different electron donating compounds on reductive capacity of the soil and the resulting reaction times. For both electron donors the degradation reaction yielded similar transformation products, namely: ethyne, ethene and ethane (Figure 12). Interestingly, in comparison to the biotic alternative, no sequential degradation products were found, or at least none above the detection limits (Lee and Batchelor, 2004).

Figure 12. Potential abiotic reductive degradation pathways.
(Compiled from Vogel and McCarthy, 1987; Brown et al., 2007)



8.2 Oxidative degradation/mineralization

Multiple studies have indicated that even the most chlorinated ethenes can be subjected to oxidative degradation under the right aerobic conditions (Hartmans et al. 1992a, Hopkins and McCarthy, 1995, Klier et al. 1999, Coleman et al. 2002, Bradley 2003). Several studies have found that apart from direct microbial oxidation, the contaminants can also be cometabolically oxidized under oxic conditions (Murray et al. 1993; McCarty and Semprini, 1994; Vogel 1994; Bradley 2003). The less chlorinated CAHs such as the di-chlorinated DCE and the mono-chlorinated VC can be directly oxidized, while TCE tends to rely on cometabolic processes in order to degrade. Under non-engineered conditions direct oxidation is carried out faster than the cometabolic mechanisms (McCarthy 1994).

8.2.1 Direct aerobic oxidative degradation

Direct aerobic oxidation, is the microbial breakdown of a chemical in which the compound is not only used as an electron donor but also serves as the primary substrate for the microorganisms mediating the process. This type of microbe facilitated oxidation is generally referred to as mineralization, the process in which an organism turns organic matter into an inorganic substance. The resulting electrons generated by the oxidation of the CAH are transferred to an electron acceptor such as oxygen. In conjunction with the reduction of oxygen to water the CAHs are oxidized into carbon dioxide, chlorine, water and electrons. Similar, yet inversely proportional to the behaviour of CAH noticed during reductive dechlorination the tendency of these compounds to undergo oxidation

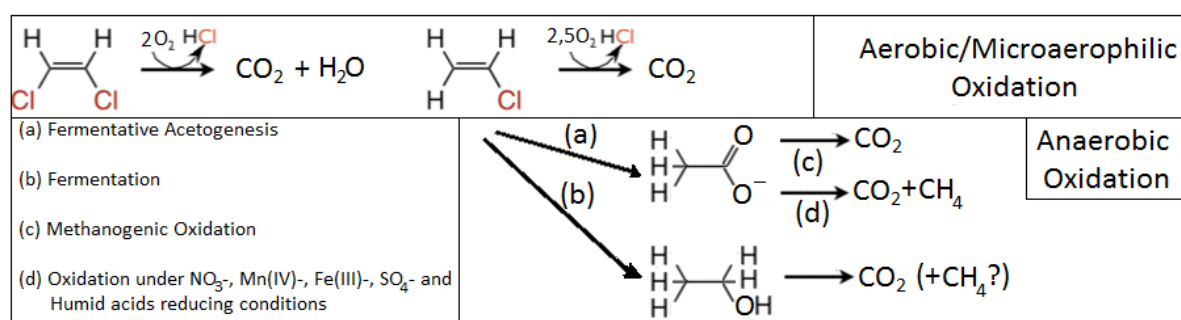
increases as the chlorine substituents decreases (Vogel et al 1997). The highly oxidized nature of PCE and TCE prevents them from being used as primary substrates during aerobic microbial oxidation.

Since the presence of DCE and VC at the majority of the sites is related to the sequential dechlorination of PCE and TCE under reducing conditions. Consequently this type of intrinsic CAH oxidation is generally limited to the fringe of the contamination plume, where dissolved oxygen has not been lowered to sub-oxic levels through microorganism respiration (Bradley et al. 1998; Sorenson et al. 2000; Erwin et al. 2005). In the rather uncommon event of VC getting directly released to oxic aquifers, aerobic VC mineralization by microorganisms has proven to be a significant degradation mechanisms as observed at polyvinyl chloride production sites (Hartmans, 1995).

8.2.2 Cometabolic aerobic oxidative degradation

Although PCE and TCE cannot be directly oxidized, TCE has been demonstrated to undergo cometabolic degradation under oxic conditions, degrading TCE to CO₂ (Wilson & Wilson, 1985; McCarty and Semprini, 1994; Ryoo et al. 2000). Since this type of degradation has received a lot of attention, due to the fact that compared to the other pathways aerobic cometabolism resulted in the destruction of the TCE compound rather than the transformation into other hazardous chemicals. Both the presence of oxygen and a primary carbon substrate are required to induce and maintain oxygenase production necessary for aerobic cometabolism of chlorinated ethenes (McCarty and Semprini, 1994). Although this type of intrinsic degradation is generally not considered as a significant long-term degradation mechanism, it has been rather successful as a degradation pathway for enhanced bioremediation (McCarty and Semprini, 1994; Battelle, 2001).

Figure 13. Proposed reaction pathways for cis-DCE and VC oxidation.



Unfortunately there are two factors that limit the cometabolic oxidation of CAHs, first of all aquifers that contain enough oxygen to support both the direct and cometabolic oxidation of chlorinated ethenes tend to be depleted of oxygen as a result of respiratory oxygen consumption. Thus resulting in anoxic conditions. Secondly the intermediates formed during cometabolic oxidation, mainly epoxides have proven themselves to be toxic to certain strains of microorganisms facilitating the degradation reaction (Battelle, 2001). Making this form of degradation a poorly suited

mechanism for long-term contaminant attenuation under both natural and enhanced conditions (Battelle, 2001).

Historically the potential of microbial degradation was assessed for anoxic conditions. This was done under highly reducing circumstances, consequently the focus lay mainly on microorganism facilitating reductive dechlorination (Vogel et al., 1987; Vogel, 1994, Semprini, 1995; Wiedemeier et al., 1996a/b). However a site could still be considered relatively oxidized even though it is characterized by low dissolved oxygen levels, yet exhibited ongoing iron-reduction, nitrate-reduction and/or manganese-reduction. Even though CAH reduction under these anaerobic, microaerophilic conditions (DO 0,1-0,5 mg/L) is considered the chief contributor to CAH attenuation, oxidation or mineralization of these compounds can still play an important role.

8.2.3 Anaerobic or microaerophilic oxidative degradation

Vogel and McCarty (1985) were the first to report on the potential of chlorinated ethene oxidation in the absence of detectable oxygen, under microaerophilic conditions. Using a bioreactor fed with [1,2-¹⁴C] PCE and acetate the researchers found, through tracking the ¹⁴C isotope, that PCE was primarily transformed to TCE, with lower quantities of DCE and VC, although they recovered approximately 24% as CO₂ after 4 days. The researchers concluded that the chlorinated ethenes would sequentially get reduced until VC was reached, which would then anaerobically oxidize to yield CO₂ (McCarty and Jeminez, 1985). Other studies found that 8% of the initial ¹⁴C was recovered as CO₂ while the majority was sequentially degraded and transformed to TCE, cis-DCE, VC and ethene respectively (Adamson et al. 2001). Other studies (Bradley et al. 1996) using other anoxic, iron(III)-reducing conditions further confirmed the possibility of the lower chlorinated compounds to be degraded through means of oxidation, even under anoxic conditions.

Not only did these observations result in the realization that microbial oxidation of VC under relatively oxidizing, yet anoxic conditions might be a rather relevant mechanism for CAH remediation (Bradley et al. 1996, Bradley et al. 1998b/d) the addition of Fe(III) to an anoxic aquifer would also result in VC oxidation rates comparable to those observed at oxic sites. This potential degradation method demonstrated an alternative to the rather slow reduction of VC to ethene. Not only has the least chlorinated CAH VC been found susceptible to this oxidation process, even the DCE isomers were proven to be affected by net microbial oxidation under anoxic conditions (Bradley et al. 1998c).

This combination of reductive dechlorination of the more chlorinated PCE and TCE followed by the mineralization of DCE and VC under anoxic conditions represents an alternative route and explanation for the complete removal of DCE and VC, yet the insufficient accumulation of the VC dechlorination products such as ethene and ethane.

9 DEGRADATION KINETICS

Chemical or enzyme kinetics, the study of rates at which reactions occur, allow for a better understanding of the degradation processes and the contributing and/or inhibiting factors. Relying on a series of experiments under controlled conditions, a specific behaviour or tendency can be studied. Analysis of the experimental data yields information on the rates of the processes governing the reaction. Once the rates are determined the appropriate rate laws and reaction constants can be derived, the resulting formulae can then be analytically solved or used to construct a mathematical model in order to describe the characteristics of a chemical reaction.

The main factors influencing the reaction rates include: the concentrations of the reactants, the temperature at which the reaction occurs, the physical state the reactants are in and the presence or absence of catalysts (EPA, 2000). These reactions depend on molecular collisions of the reactants involved, the higher the concentration, the more frequent these interactions between reagents will occur. Temperature influences the reaction rates in a similar way, molecules at a higher temperature will exhibit a higher thermal energy, resulting in more collisions, the main contribution of temperature however is the fact that the activation energy required for the reaction is more easily obtained. The physical state or phase the reactants are in determines the amount of contact between the reagents involved, limiting the reaction to the interface between the two phases when the reactants occur in separate phases. Catalysts or enzymes can potentially accelerate the chemical reaction, allowing the reaction to occur at a lower activation energy.

The main focus of this chapter will be on the effect of concentration and presence of catalysts and/or inhibitors, under specific redox conditions on the chlorinated ethene degradation reaction rates. Even though temperature is generally one of the most important contributing factors, the minute temperature differences found in the subsurface hardly impact the chemical or microorganism facilitated reactions occurring in the subsurface (Zuurbier et al., 2013). Several kinetic models have been used to interpret chlorinated ethene degradation, the type of kinetic rate expression is determined by the rate limiting factor of the degradation process.

The following Sections will briefly discuss the most often resorted to methods for quantifying chlorinated ethene degradation. Degradation rates per chlorinated contaminant under specific conditions, are approximated using various kinetic models is discussed in Section 9.4. The main goal is, once the site has been evaluated to quickly identify the correct kinetic expression. Yielding the more complex concentration change over time kinetic models for contaminated sites identified by high degrees of heterogeneity, while more simplified degradation expression can be resorted to when the variance of one or more variables of chlorinated ethene degradation is deemed negligible.

9.1 Zero order kinetics

When the degradation reactions appear to be sediment-limited, completely independent of the contaminant concentrations, the process is generally described using zero order degradation kinetics. The limiting factor for this type of degradation is the degradation capability of the soil, the speed at which the contaminants degrade is influenced by the availability of electron donors and acceptors and/or the presence of microorganisms facilitating the reaction (McCarty, 1997). The equation used to indicate this type of sediment-limited degradation is given by Equation 5:

$$r_i^0 = \frac{dC_i}{dt} = -\mu_i \quad (5)$$

$$C_i(t) = C_0^i - \mu_i t \quad (6)$$

Where the change in concentration C_i (μM) of contaminant i over time equals a constant rate μ_i ($\mu\text{mol day}^{-1}$). When solved for $C_i(t)$, the concentration at time t results in the linear relationship shown in Equation 6, where C_0^i indicates the initial concentration and μ_i the zero order rate constant. Although this reaction simplifies the process of the rather multifaceted natural attenuation, it can result in a good approximation of in situ biodegradation if the subsurface is quite homogenous and the biodegradation capacity does not vary too much throughout the domain.

9.2 First order kinetics

First order degradation kinetics rely on the assumption that there is a sufficient amount of dissolved organic matter available in the subsurface and the only factor limiting the degradation is the concentration of the contaminants. For contaminant limited kinetics, the degradation of the chlorinated ethenes with respect to their concentrations is given by Equation 7:

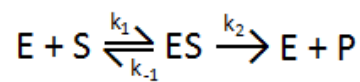
$$r_i^1 = \frac{dC_i}{dt} = -\mu_i C_i \quad (7)$$

$$C_i(t) = C_0^i e^{-\mu_i t} \quad (8)$$

Equation 8 shows the relation between dC/dt , the concentration change over time and the contaminant C (μM) limited first order rate μ ($\mu\text{M day}^{-1}$). When solved for C at a given time, the exponential relationship of the first order degradation kinetics becomes apparent. Although this kinetic rate law has been used in several studies it has several shortcomings. The exponential degradation expression used to describe the contaminant-limited scenario is susceptible to dilution. Subsequently, the direct correlation between contaminant concentration and degradation results in negligible degradation rates once the concentration drops below a certain threshold.

9.3 Michaelis-Menten Enzyme kinetics

Although the zero and first order approach generally result in reasonable results, the methods are vulnerable to heterogeneity, potentially resulting in a misinterpretation of the degradation potential of the subsurface (Zuurbier et al. 2013). The reaction rate μ used in both, zero and first order rate laws is considered constant throughout the model domain, neither of these degradation reactions incorporate the variable conditions or bioactivity in the subsurface. One of the well-known kinetic models, used to evaluate microorganism catalysed reactions or enzyme kinetics is the Michaelis-Menten approach (Suarez and Rifai, 1999). For the standard Michaelis-Menten kinetic model the following reaction between enzyme (E), substrate(S) and product (P) is assumed:



The kinetic model will be used to interpret both direct and cometabolic microbial degradation, therefore several new concentration variables will have to be defined. Where C was used in the zero and first order degradation schemes to indicate the concentration of the contaminant, the assigned variable used in the Michaelis-Menten approach for contaminant concentration depends on its relation to the microorganism. During direct metabolic microbial degradation the contaminant will be used as a substrate, hence its concentration will henceforth be referred to as S . In contrast to cometabolic degradation where other carbon sources are used as substrate and the contaminant is reduced to the role of co-substrate and the variable C , is used to refer to its concentration.

Similar to the first order rate law, Michaelis-Menten kinetics relates the degradation rate to the concentration of the reactant S or C (μM). However the variation in reaction rates is limited by the maximum specific CAH degradation rate ($k_{max} = k_2[E]; \mu\text{M day}^{-1}$) and its half-velocity coefficient ($K_s = (k_2 + k_{-1}) / k_1; \mu\text{M}$), the kinetic relationship, where the contaminant is used as primary substrate, is given by Equation 9:

$$r_i^M = \frac{dS_i}{dt} = -\frac{k_{max}^i S_i}{K_s^i + S_i} \quad (9)$$

In order to incorporate additional mechanics and processes, several adaptations can be made to the kinetic relationship above. The modifications discussed in this thesis will relate to the inhibition processes affecting degradation, the effect of biological activity and toxicity on chlorinated ethene attenuation and the redox nature of the reaction. Although there are multiple methods of adapting the Michaelis-Menten kinetic model only the most straightforward ones will be discussed.

9.3.1 Inhibition:

Most of the degradation processes studied are biological by nature and therefore rely on living organisms, which can be influenced by inhibitory or toxic compounds. Inhibition is a term used to refer to any type of chemical or physical change impacting the effectiveness of microbial degradation. Although there are many factors able to affect the microorganisms such as pH, temperature and redox potential, this thesis will focus on the inhibition caused by the inhibitory and toxic agents present in the subsurface at chlorinated ethene contaminated sites. Figure 14 depicts some of the more commonly occurring inhibition kinetics.

Competitive inhibition assumes that an inhibitor binds to the enzyme in a similar fashion as the substrate. Due to the same site of the enzyme being occupied, the formation of the active complex (ES) and its resulting products decreases (Yu et al., 2005; Christ and Abriola, 2007). Effectively modifying the affinity of the substrate, considering the substrate and inhibitor have to compete for the active sites. Parent-daughter competitive inhibition is illustrated in Figure 15.

Un-competitive inhibition occurs when an inhibitor latches itself to the active complex (ES) formed by the enzyme and the substrate and prevents the product formation/substrate degradation. The assumed mechanism modifies the existing Michaelis-Menten kinetics by scaling k_{max} and K_s based on the concentration of the inhibitor I and the inhibition coefficient K_i .

Non-competitive inhibition is the result of an inhibitor that attaches itself to the active complex (ES), unlike competitive inhibition it does not take up the same space as the substrate would and prevents the product formation through changing the composition of the enzyme. The affinity of the substrate remains constant due to the lack of competition between substrate and inhibitor, resulting in only the k_{max} being decreased.

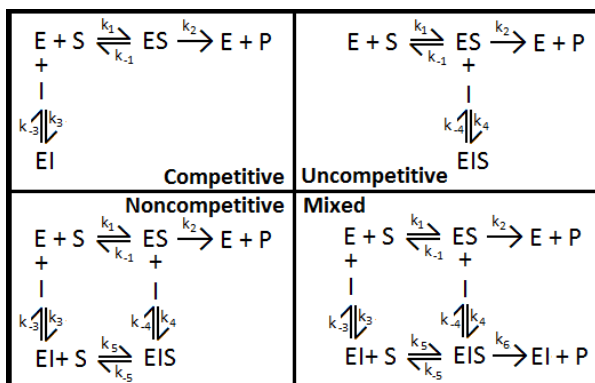


Figure 14: Types of inhibition.

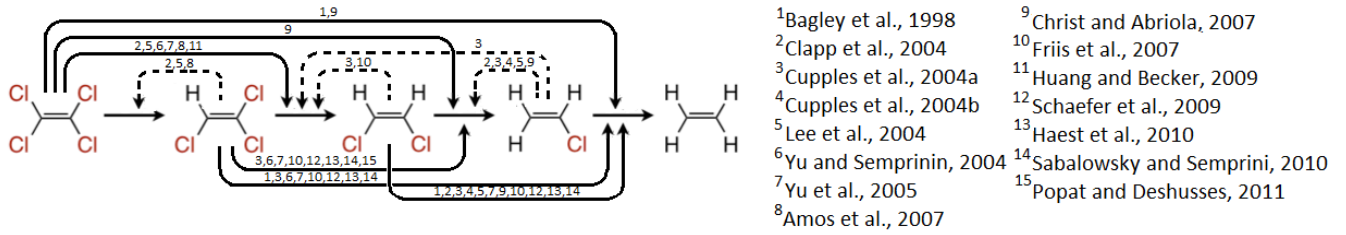
<- Enzyme E, substrate S, product P, inhibitor I, reaction rates k_i

Type of Inhibition	k_{max}^*	K_s^*
Competitive	k_{max}^i	$K_s^i(1 + \frac{I}{K_{ic}})$
Un-competitive	$\frac{k_{max}^i}{1 + \frac{I}{K_{iu}}}$	$\frac{K_s^i}{1 + \frac{I}{K_{iu}}}$
Non-competitive	$\frac{k_{max}^i}{1 + \frac{I}{K_{iu}}}$	K_s^i
Mixed	$\frac{k_{max}^i}{1 + \frac{I}{K_{iu}}}$	$\frac{K_s^i(1 + \frac{I}{K_{ic}})}{1 + \frac{I}{K_{iu}}}$

Table 6: The effect of inhibitors on the Michaelis-Menten parameters k_{max} and K_s .

Inhibitor concentration I (μM), inhibition coefficients K_{iu} and K_{ic} (μM)>

Figure 15. Potential competitive inhibition of parent and daughter compounds during sequential reductive dechlorination as found in literature. (Adapted from Chambon et al. 2013)



9.3.2 Biomass availability and toxicity

The most straightforward adaptation to the Michaelis-Menten kinetic model is based on the assumption that the presence and concentration of the microorganisms aiding in the degradation of the contaminants varies throughout the domain (Maymo-Gatell et al., 1997). In addition to the spatial changes, direct metabolic degradation of the contaminants can result in growth of the organisms, Equation 10 is used to describe the microbial availability.

$$\frac{dX}{dt} = Y \frac{dS}{dt} - k_d X \quad (10)$$

The change in biomass X (cell L^{-1}) over time is related to the microorganisms growth yield Y ($\text{cell } \mu\text{mol}^{-1}$), the concentration of the chlorinated ethene over time dS/dt (assuming it is used as primary substrate, Eq. 9) and the decay rate of the bacteria k_d (day^{-1}). Taking into account that the chlorinated ethene related compounds commonly found in groundwater might not all be used as nourishment for the microorganisms. The above equation gets an additional term added to incorporate the potential toxicity of substrates, co-substrates and degradation products. Alvarez-Cohen and McCarty (1991) introduced a transformation capacity term T_c , a constant relating the amount of degraded compound to the amount of inactivated cells. Assuming the co-substrates toxic effects result in a decrease in overall cellular function, the transformation capacity is shown below in Equation 11, 12:

$$T_c = \frac{dC}{dX} \quad (11)$$

$$\frac{dX}{dt} = Y \frac{dS}{dt} - \frac{1}{T_c} \frac{dC}{dt} - k_d X \quad (12)$$

Now that the degree of biological activity is approximated, the term can be incorporated in the original Michaelis-Menten kinetic model to account for the microbial effect on degradation. Note that k^{s*}_{max} ($\mu\text{mol cell}^{-1} \text{day}^{-1}$) in Equation 13 is different from the previously used ones, the rate was adapted in order to account for the change in units caused by the addition of the biomass term.

$$\frac{dS}{dt} = \frac{k^{s*}_{max} X S}{K_s + S} \quad (13)$$

9.3.3 Availability of electron donors/acceptors and oxidants/reductants.

The final adaption of the Michaelis-Menten kinetic model is related to the reduction and oxidation conditions affecting degradation (Atteia and Guillot, 2007; Christ and Abriola, 2007). Two terms can be added to the equation in order to account for the availability of electron donors and dissolved hydrogen for reductive dechlorination and the availability of electron acceptors and dissolved oxygen for the oxidative degradation process. Equations 14 and 15 incorporate the redox characteristics of reduction and oxidation of chlorinated ethene contaminants respectively.

$$\frac{dS_i}{dt} = \frac{k_{max}^i S_i}{K_s^i + S_i} \frac{[e_d^-]}{K_{e_d^-} + [e_d^-]} \frac{[H_2]}{K_{H_2} + [H_2]} \quad (14)$$

$$\frac{dS_i}{dt} = \frac{k_{max}^i S_i}{K_s^i + S_i} \frac{[e_a^-]}{K_{e_a^-} + [e_a^-]} \frac{[O_2]}{K_{O_2} + [O_2]} \quad (15)$$

Where S_i , k_{max}^i and K_i refer to the concentration, maximum degradation rate and half saturation constants respectively. The square brackets are used to indicate concentrations of the electron donors/acceptors (e_d^-/e_a^-) and the dissolved hydrogen and oxygen respectively.

9.4 Overview and usage of the various kinetic expressions

Depending on the available data, site characteristics and the choice in numerical models any of the previously mentioned kinetic rate expressions can be used to approximate chlorinated ethene degradation in the subsurface. Although the zero and first order kinetic rate laws are more vulnerable to heterogeneity and uncertainty they should always be considered first when assessing a site and the propensity of chlorinated ethene contaminants. However when the inconsistencies between measured data and the numerical simulations are too vast or when the processes involved are studied in a micro scale environment, additional parameters should be included. This thesis opted for the use of Michaelis-Menten kinetics in order to be able to include additional parameters and deal with the limitations of the zero and first order kinetic models.

For illustrative purposes the sequential reductive dechlorination terms per chlorinated compound will be given for the various kinetic approximations. Table 7. will include the zero and first order approach to quantify contaminant degradation as well as the basic Michaelis-Menten method. Additionally, in order to highlight both the versatility and complexity a more extensive Michaelis-Menten kinetic relationship will be given for a single chlorinated ethene compound. Table 8. lists all the partial differentials involved with TCE degradation in a nitrate reducing environment, including competitive inhibition between electron acceptors and between parent and daughter products. Apart from electron donors and acceptors the availability of dissolved organic carbon (DOC) is also included and treated as a potential limiting factor.

Table 7: Sequential reductive dechlorination kinetic relationships.

Degradation	Zero-Order	First-Order	Michaelis-Menten
$\frac{dC_{PCE}}{dt}$	$-\mu_{PCE}^0$	$-\mu_{PCE}^1 C_{PCE}$	$-\frac{k_{max}^{PCE} C_{PCE}}{K_s^{PCE} + C_{PCE}}$
$\frac{dC_{TCE}}{dt}$	$-\mu_{TCE}^0 + \mu_{PCE}^0$	$-\mu_{TCE}^1 C_{TCE} + \mu_{PCE}^1 C_{PCE}$	$-\frac{k_{max}^{TCE} C_{TCE}}{K_s^{TCE} + C_{TCE}} + \frac{k_{max}^{PCE} C_{PCE}}{K_s^{PCE} + C_{PCE}}$
$\frac{dC_{DCE}}{dt}$	$-\mu_{DCE}^0 + \mu_{TCE}^0$	$-\mu_{DCE}^1 C_{DCE} + \mu_{TCE}^1 C_{TCE}$	$-\frac{k_{max}^{DCE} C_{DCE}}{K_s^{DCE} + C_{DCE}} + \frac{k_{max}^{TCE} C_{TCE}}{K_s^{TCE} + C_{TCE}}$
$\frac{dC_{VC}}{dt}$	$-\mu_{VC}^0 + \mu_{DCE}^0$	$-\mu_{VC}^1 C_{VC} + \mu_{DCE}^1 C_{DCE}$	$-\frac{k_{max}^{VC} C_{VC}}{K_s^{VC} + C_{VC}} + \frac{k_{max}^{DCE} C_{DCE}}{K_s^{DCE} + C_{DCE}}$
$\frac{dC_{ETH}}{dt}$	$-\mu_{ETH}^0 + \mu_{VC}^0$	$-\mu_{ETH}^1 C_{ETH} + \mu_{VC}^1 C_{VC}$	$-\frac{k_{max}^{ETH} C_{ETH}}{K_s^{ETH} + C_{ETH}} + \frac{k_{max}^{VC} C_{VC}}{K_s^{VC} + C_{VC}}$

Table 8. Michaelis-Menten kinetics for the sequential reductive dechlorination of TCE.

Redox role	Equation used to quantify
Electron Acceptors	$r_{TCE}^{tot} = \frac{dC_{TCE}}{dt} = -k_{max}^{TCE} \times \min(r_{TCE}^A, r^D) + k_{max}^{PCE} \times \min(r_{PCE}^A, r^D)$
	$r_{TCE}^A = \frac{C_{TCE}}{C_{TCE} + K_s^{TCE} (1 + \frac{I_{NO_3}}{K_{ic}^{NO_3}} + \frac{I_{PCE}}{K_{ic}^{PCE}} + \frac{I_{DCE}}{K_{ic}^{DCE}})}$
	$r_{PCE}^A = \frac{C_{PCE}}{C_{PCE} + K_s^{PCE} (1 + \frac{I_{NO_3}}{K_{ic}^{NO_3}} + \frac{I_{TCE}}{K_{ic}^{TCE}})}$
	$r_{NO_3} = \frac{dC_{NO_3}}{dt} = -k_{max}^{NO_3} \times \min(r_{NO_3}^A, r^D)$
	$r_{NO_3}^A = \frac{C_{NO_3}}{C_{NO_3} + K_s^{NO_3} (1 + \frac{I_{PCE}}{K_{ic}^{PCE}} + \frac{I_{TCE}}{K_{ic}^{TCE}} + \frac{I_{DCE}}{K_{ic}^{DCE}})}$
Electron Donors	$r^D = \frac{C_{DOC}}{K_s^{DOC} + C_{DOC}}$
	$r_{DOC} = \frac{dC_{DOC}}{dt} = \alpha Y_{NO_3}^{DOC} r_{NO_3} + \beta Y_{PCE}^{DOC} r_{PCE} + \gamma Y_{TCE}^{DOC} r_{TCE} + \delta Y_{DCE}^{DOC} r_{DCE}$
Degradation Products	$r_{Cl} = \frac{dC_{Cl}}{dt} = -Y_{PCE}^{Cl} r_{PCE} - Y_{TCE}^{Cl} r_{TCE} - Y_{DCE}^{Cl} r_{DCE}$
	$r_{CO_2} = \frac{dC_{CO_2}}{dt} = -\epsilon Y_{DOC}^{CO_2} r_{DOC}$

The degradation rate for TCE r_{TCE} in Table 8. consists of two terms the first is a degradation term, the second relates to the accumulation of TCE, due to PCE degradation. The term $\min(r_1^A, r^D)$ is used to determine the minimum of two rates, the limiting rate is then used for the actual degradation calculations. The Y terms are growth terms based on a ratio of molar mass between the two compounds involved, scaled using the stoichiometric coefficients α , β , γ , δ and ϵ .

10 REMEDIATION TECHNIQUES, PROCEDURES

As mentioned before, during the last couple of decades a lot of research was done into chlorinated ethene contaminated sites. These studies did not only result in an extensive knowledge database on the contaminants, their behaviour and fate in the subsurface, it also led to the development and application of dozens of remediation techniques. Considering the amount of uncertainty related to the subsurface and its heterogeneous nature, the selection of the right remediation tool is far from straightforward, nor do these remediation techniques come with strict, well established guidelines. In the following section some of the more widely applied in situ remediation techniques will be briefly discussed.

There are two different classifications of enhanced remediation of chlorinated ethenes, closely related to the target of the remediation technique used. The first classification, focusses mainly on treating the area where the contaminants were introduced to the subsurface, or down gradient of this source zone. This type of remediation techniques tries to reduce chlorinated ethene mass in all four phases, whereas the second type of procedures, DNAPL mass removal only has the reduction of aqueous contaminants as primary objective. Depending on the characteristics of the subsurface source zone, plume treatment alone might be sufficient at reducing contaminant levels below regulatory concentrations. This approach has been found to result in relatively long indefinite remediation time periods, especially in the case of enhanced anaerobic microorganisms facilitated remediation (Adamson et al. 2003).

The correct application of a remediation technique does not only rely on the site characteristics or the propensity of the contaminants. The choice of remediation tool used also heavily depends on the remediation goals set. For example, rapid mobilization of contaminants, although it results in extensive mass removal might not always be the best approach, especially if the concentration of the contaminants in the aqueous phase is preferably kept rather low due to the urban nature of the contaminated site. Considering the main goal of any remediation attempt is the protection of the environment and human health the fastest approach might not always be the best.

The four remediation objectives discussed in this thesis are *Mass Removal*, *Mass Concentration/Flux Reduction*, *Plume Life Reduction* and *Life-Cycle Cost Reduction*. The first objective is relatively straightforward, the second and third are slightly different, one focusses on reducing the mass leaving the source area the other solely targets the contaminants in the aqueous phase. The last objective relates to the fact that chlorinated ethene remediation attempts are generally a long term process. Taking into account the costs of multiple treatments or long-term monitoring, this objective mainly comes down to treating the contaminated zone in the most cost effective way.

Further distinction in remediation technologies can be made when analysed how these processes expect to positively affect the removal of chlorinated ethenes from the specific sites. Although these three categories are closely interrelated the following division can be made based on the principal nature of the remediation strategies in question, they either rely on enhancing or limiting physical, chemical or biological aspects underlying CAH transport and degradation.

10.1 Physical approaches to contaminant removal

These approaches attempt to combat chlorinated ethene pollution through altering the transport of contaminants. The clearest example of this type is the pump and treat approach. Although not always terribly effective the induced advection through pumping does result in additional solubilisation of separate phase contaminants as well as removal of dissolved aqueous mass through pumping out contaminated groundwater. However not all remediation concepts are related to increasing the parameters governing the transport of contaminants, other techniques will try and limit the fluxes in the to be treated area, by installing physical barriers in order to prevent any further contaminant spreading. A combination of both of these approaches is when the source area is hydrodynamically isolated using strategically placed extraction and injection wells.

Both of those techniques are related to the aqueous phase, granted most of the time CAH groundwater and subsurface contaminants are found in this phase, they are classified as volatile organic compounds, and as Henry's law dictates this will result in a gaseous phase contaminants. Similar to the pump and treat interception approach for dissolved contaminants, soil vapour extraction (SVE), potentially combined with air sparging are the alternatives for volatile CAH contaminants. Soil vapour extraction is the withdrawal of polluted air from the unsaturated zone and volatilization enhanced through the creation a vacuum in the extraction wells. However this will only affect the aqueous contaminants near the water table, since volatilization can only occur at the water-air interface. By injecting air below the groundwater table the process of air sparging attempts to strip soil and groundwater of the volatile CAH components and transports them to the unsaturated zone, often used in combination with SVE to ensure collection of the harmful volatile CAHs. Additionally air sparging results in a replenishment of groundwater oxygen levels and can promote various types of aerobic and microaerophilic bio degradation reactions.

10.2 Chemical approaches to contaminant removal

There are two different types of chemical intervention possible in the subsurface, the first is the use of chemicals to alter the physical properties of the contaminants, the second focusses on the biochemical degradation of the contaminants. The use of surfactants and solvents belong to the first subcategory of chemically enhanced CAH remediation. Surfactant Enhanced Aquifer Remediation

(SEAR) refers to the addition of special amphiphilic compounds, partially hydrophobic and hydrophilic, resulting in an affinity for both polar water and the nonpolar DNAPL. It is this chemical property that allows surfactants to augment the mobility and recovery of separate phase liquids and residual saturation due to micelle formation. Under certain circumstances they have even proven able to facilitate the desorption of chlorinated ethenes. Solvents, as the name suggest are used to increase the solubility of the contaminants in order to increase the efficiency of groundwater extraction on contaminant removal. Considering the goal of these remediation techniques is to reduce contaminant mass through mobilization it is generally used to increase the effectiveness of the pump and treat approach.

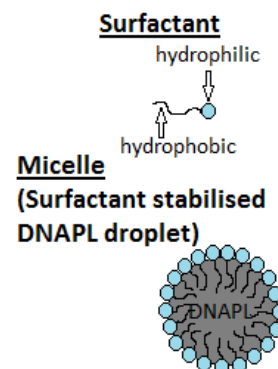


Figure 16. Surfactants and the resulting water soluble micelle

The second type of insitu chemical intervention is used to enhance the redox conditions of the subsurface to enhance the reduction or oxidation of the contaminants in question. A wide range of techniques and reagents have been used in order to chemically treat chlorinated ethene contaminated sites (Gates and Siegrist, 1995; Wickramanayake et al., 2000). This section will discuss some of the more commonly used commercially available chemicals. Although both of these processes can enhance the microbial degradation of the CAH contaminants, they are not dependant on the bioavailability of the subsurface (McGuire et al., 2006). Common in situ oxidants include permanganate, Fenton’s reagent (mixture of hydrogen peroxide and ferrous iron), persulfate and ozone. When dissolved in water most of these chemicals result in the production of hydroxide ions (OH^-), hydrogen peroxide and/or the extremely reactive radical hydroxide hydroxyl ($\text{OH}\bullet$). The hydroxide producing reactions under neutral conditions (3-12 pH) resulting from the addition of these compounds are shown in Table 9.

Table 9. General information of the most commonly used oxidants.

Oxidant	Form	Persistence ⁽¹⁾	Oxidization Reactions ⁽¹⁾
Permanganate	Powder/liquid	>3 months	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- = \text{MnO}_2 + 4\text{OH}^-$
Fenton’s Reagent	Liquid	Minutes-hours	$\text{H}_2\text{O}_2 + \text{Fe(II)} = \text{Fe(III)} + \text{OH}^- + \text{OH}\bullet$
Persulfate	Powder/liquid	Hours-weeks	$\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} + \text{H}^+ = 2\text{HSO}_4^- + \text{H}_2\text{O}_2$
Ozone	Gas	Minutes-hours	$2\text{O}_3 + 3\text{H}_2\text{O}_2 = 4\text{O}_2 + 2\text{OH}\bullet + 2\text{H}_2\text{O}$

⁽¹⁾varies depending on site specific conditions, therefore based on general observations

The occurrence of abiotic reductive dechlorination in the presence of reduced metals (Reynolds et al., 1990) or metallic catalysts in hydrogen rich environments (Lowry & Reinhard, 1999) has been studied for several decades. The beneficial use of zero valence iron particles (ZVI) as a reductant was first demonstrated by Gillhama and O'Hannesin (1994), yet quickly became one of the most applied techniques for chemically treating the subsurface in order to promote reductive dechlorination. There are multiple ways of introducing these compounds to the subsurface from the straightforward source zone injection to the creation of a permeable reactive barrier (PRB) slightly down gradient. Generally micro-scale particles are used, however sometimes nanoscale particles are opted for, apart from being easier to distributed the smaller size results in a large surface area and therefore a higher reactivity (Johnson et al., 1996). Both abiotic oxidation and reduction result in the direct transformation of harmful CAHs into harmless inorganic (CO_2) and inorganic compounds (C_2H_2). Apart from the nature of the reaction the main difference between two types of enhanced degradation is the amount of time the amendments to the subsurface stay active. Where permanganate could persist for several months in the subsurface a properly designed and constructed ZVI utilizing barrier can last an entire decade (Battelle, 2003).

10.3 Biological approaches to contaminant removal

Enhanced bioremediation as the name implies is all about taking advantage of the natural in situ microbial processes. This can be done in a variety of ways, the first and most straightforward is bioaugmentation, the addition of microorganisms to the subsurface in order to initiate or increase the rate and extent of biodegradation. The alternative is the addition of rate-limiting substrate, this way the total amount of biomass and rate at which it degrades chlorinated ethenes increases through growth of the intrinsic and already active microbial cultures. This technique is generally used to target reductive dechlorination processes, by means of direct injection of molecular hydrogen or fermentable substances such as lactate, acetate, ethanol, methanol and glucose. Although this technique has been widely used for the treatment of dissolved plumes, there is an increasing interest in its applicability to source zone treatment (U.S. DOE, 2002). This is due to the fact the addition of electron donors for example to enhance the ongoing reductive dechlorination processes in the subsurface does not only result in affect degradation, the nature of some of these amendments also result in enhanced DNAPL dissolution rates.

11 ASSESSING BIODEGRADATION AND SITE CHARACTERIZATION

Unfortunately it is not feasible to draw conclusions on the fate and behaviour of chlorinated ethene contaminants in the subsurface using laboratory studies only. A shared view on the propensity of the contaminants can only come from both fully understanding the contributing factors and most of all require a comprehensive observations of the subsurface as well as the nature and fate of the actual dissolved chlorinated ethene plumes (Parker et al., 1997).

This thesis presents a technical protocol for both data collection and analysis in order to estimate the potential of natural attenuation as a groundwater and subsurface remediation approach. The protocol is intended to be used as a supplement for the established regulatory framework. The technical course of action, presented in this thesis should allow for the use of converging lines of evidence to be used to scientifically document the occurrence of natural attenuation and to quantify the resulting degradation rates.

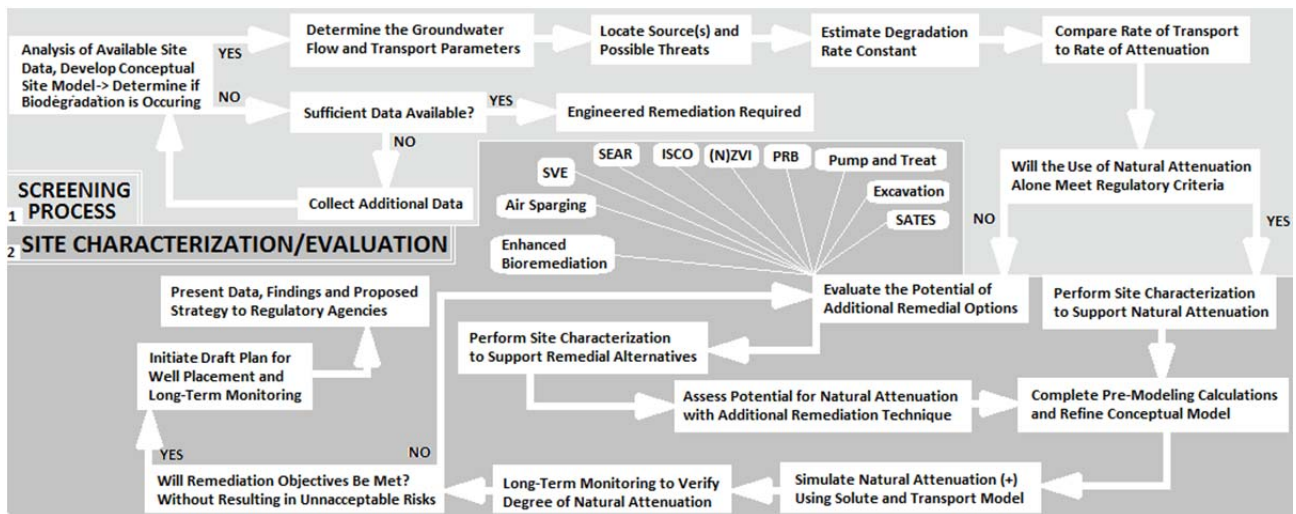
In order to scientifically demonstrate that natural attenuation results in the degradation of site contaminants at sufficiently fast rates, as to be protective of human health and the environment, three lines of evidence are needed. The first is the observed reduction of chlorinated ethene contaminant concentrations down gradient of the contamination source zone. Considering the concentration reduction can be the result of non-destructive transport processes the second line of evidence focusses on the loss of contaminant mass at a field scale. The destructive processes involved are quantified using chemical and geochemical data to monitor the concentration of parent/daughter products, the depletion of electron donors/acceptors and the increase in innocuous metabolic by-products (Walecka-Hutchison and Walworth, 2005). Furthermore a conservative tracer needs to be injected, to assess the residence time along the flow path in order to properly calculate contaminant mass reduction and biological decay rates at the site. The final line of evidence is the microbiological laboratory data required to identify the microorganisms involved and to provide an estimate of the resulting rates of biodegradation.

Due to the inherent uncertainty associated with quantifying and predicting groundwater processes, a sufficient amount of data is required to demonstrate the viability of natural attenuation as a remediation approach. In order to be able to extrapolate the findings relating the hydrogeological nature of the subsurface and the degree of natural attenuation occurring at a specific site, the data related to chlorinated ethene contaminated sites should be gathered under similar conditions. Only then can the cross sites acquired data be compared and contrasted to the fullest extent. The majority of the analytically measurable groundwater and soil parameters used to gain insight into the applicability of various remediation techniques are given in Table 10.

The assessment of the potential concentration and extent of the contaminant plumes at chlorinated ethene contaminated sites is based on both historic variations in, and the current concentrations and size of the dissolved contaminant plume, complemented by the measured attenuation rates. Using this data along with all other available geological, hydrogeological, geochemical, climatological and biological data for the site, a three dimensional representation of the groundwater flow and contaminant transport at the site can be created. The resulting preliminary Conceptual Site Model (CSM) can then be used to identify any shortcomings in the data and allow for the most scientifically advantageous and cost-effective placement of additional data collection points needed.

However due to the previously mentioned uncertainty of the subsurface, these preliminary simulations hardly suffice as an indicator of the viability of natural attenuation as a remediation tool. The weighing of the analytical parameters relevant to biodegradation, is only the first step in analysing and assessing the contaminated site. The proposed screening and site characterization process, from identification of the contaminated site to the suggestion of the most efficient and cost-effective remediation approach, is given by the flowchart displayed in Figure 17.

Figure 17. Natural attenuation of chlorinated ethenes flowchart



Biodegradation can be analytically evaluated based on initial site data, considering chemical and geochemical data was gathered along with contaminant concentrations. The considered analytical parameters are directly related to the requirements for biodegradation mentioned in Chapter 6 - 8. Other than the concentration of potential electron acceptors, pH, dissolved oxygen content, biological parameters such as available dissolved hydrogen and presence of microbial cultures and carbon sources are also weighed with respect to their importance for the natural attenuation rate.

Finally the relevance of degradation indicators such as elevated carbon dioxide and chlorine levels and the presence of degradation daughter products can be evaluated using Table 10.

Table 10. Weighting of analytical parameters for preliminary site assessment.

Analyte	Concentration	Interpretation	Reduction Points	Oxidation Points
PCE	any	Material released	-	-
TCE	any	Material released /daughter product PCE (=2)	2	-
DCE	any	Material released /daughter product TCE (=2)	2	-
VC	any	Material released /daughter product DCE (=2)	2	-
ETH/Ethane	> 0,01 mg/L	Daughter product VC (2 or 3 if > 0,1 mg/L)	2-3	-
Chloride	> 2* background	Degradation product of chlorinated solvents	2	2
Carbon dioxide	> 2* background	Ultimate oxidative daughter product	1	3
Alkalinity	> 2* background	Result of CO ₂ interaction with aquifer minerals	1	1
Elec. Conductivity	>μS/cm	Related to the dissolved chloride ions	2	2
ORP	< 50 mV	Reductive pathway possible (1 or 2 if < -100mV)	1-2	-
ORP	> 750 mV	Oxygen as predominant electron acceptor	-	3
pH	5 < pH < 9	Tolerated pH range (optimally : 6 < pH < 8)	1-2	1-2
Temperature	> 15 °C	Biochemical processes accelerated at T > 15°C	1	1
Oxygen	< 0,5 mg/L	Oxygen threshold for reductive dechlorination	3	-5
Oxygen	> 1 mg/L	Potential VC aerobic oxidation, R.D. improbable	-3	5
Nitrate	< 1 mg/L	Competitive inhibition of R.D. at higher levels	2	-
Iron	> 1 mg/L	Reductive pathway possible	3	-
Sulfate	< 15 mg/L	Competitive inhibition of R.D. at higher levels	2	-
Sulfide	> 1 mg/L	Reductive pathway possible	3	-
Methane	> 0,1 mg/L	Ultimate reductive daughter product	2	-
Methane	< 1 mg/L	VC oxidization possible	-	2
Methane	> 1 mg/L	VC accumulation	3	-1
Hydrogen	> 1 nM	R.D. pathway possible, VC accumulation	3	-3
Hydrogen	< 1 nM	VC oxidation possible	-	3
DOC	> 15 mg/L	Carbon/energy source (natural/anthropogenic)	3	2
Volatile fatty acids	> 0,1 mg/L	Carbon/energy source	2	2
BTEX	> 0,1 mg/L	Carbon/energy source	2	2
-TOTAL-			/48	/30

By using this table the potential of natural attenuation can be easily assessed fulfilling the first step of the screening process. Note that the table should be used to evaluate measurements taken from several monitoring wells downstream of the chlorinated ethene source zone. These separate evaluations can then be juxtaposed to gain insight into the DNAPL contaminated site as a whole. Given the availability of a sufficient amount of data, the total amount of points accumulated will reflect directly on the potential of reductive dehalogenation and aerobic oxidation and can be interpreted using Table 11 and 12 respectively.

Table 11. Interpretation reductive dechlorination screening.

Score / 48	Interpretation
0-8	Insufficient evidence for reductive dechlorination
9-16	Limited evidence for reductive dechlorination
17-25	Sufficient evidence for reductive dechlorination
>25	Strong evidence for reductive dechlorination

Table 12. Interpretation aerobic oxidation screening.

Score / 30	Interpretation
0-5	Insufficient evidence for aerobic oxidation
6-10	Limited evidence for aerobic oxidation
11-15	Sufficient evidence for aerobic oxidation
>16	Strong evidence for aerobic oxidation

After weighing the available chemical and geochemical site data, the groundwater flow and solute transport parameters, discussed in Chapter 4, can be determined. Although hydraulic conductivity, dispersivity and porosity of the subsurface may be estimated, both the groundwater flow direction and gradient need to be quantified. Combined with the retardation coefficients of the chlorinated ethene contaminants in question, the data can be used as input for a solute transport model. The resulting numerical simulations are then used to estimate degradation rates and identify potential source zones as well as areas vulnerable to contamination. Once a degradation rate is chosen that is in accordance with the measured contaminant concentrations and the historical use of these contaminants, the rate of attenuation and transport are to be compared in order to determine if the screening criteria are met.

The result of this comparison will determine if natural attenuation alone will potentially be able to protect human health and the environment, if not, additional engineered remediation approaches should be investigated. A more precise solute and transport model can then be used to evaluate the (enhanced) natural attenuation, resulting in a better understanding of the propensity of the chlorinated ethenes involved. According to these findings a long-term monitoring plan needs to be devised in order to verify the degree and effectiveness of the (engineered) bioremediation. A final analysis of the subsurface, incorporating all the data gathered during the site characterization phase is required before presenting the findings to the problem holders and regulatory agencies.

12 UTRECHT: CASE STUDY

Apart from being one of the oldest, Utrecht is also one of the largest cities in the Netherlands. Its extensive history combined with the urban and industrious nature of the city has led to plenty of contaminants being introduced to the subsurface and groundwater over the years. Like many other industrialized cities, chlorinated ethenes form one of the most threatening and abundant contaminants present in the subsurface.

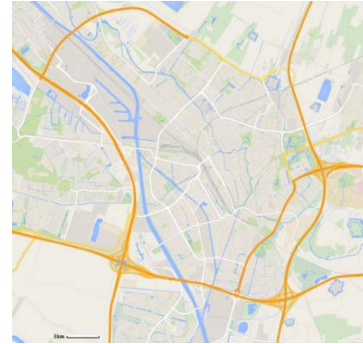


Figure 18. Map of Utrecht (Adapted from Google).

Historical use of these solvents and degreasers in small scale industry such as drycleaners, car garages and metal workshops resulted in multiple source zones in and around the city centre. Although multiple source zones have been successfully identified, they can no longer be traced back to the original separate zones since most of them coalesced over the years (Fennis, 2012). This caused the responsibility to shift from the polluting individuals and companies to the government, in this case the municipality of Utrecht. Far from being aided in their efforts by the dense and urban nature of the polluted city centre, the municipality opted for an area oriented in situ remediation approach. Analysing and treating the city per area rather than as a whole, the municipality of Utrecht combines both the monitored and engineered variety of natural attenuation.

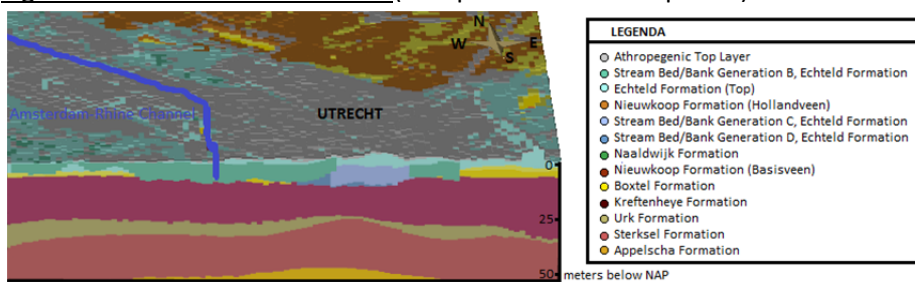
Fortunately the municipality did not have to face these issues alone, by collaborating with the European CityChlor project, the local government gained access to a vast amount of financial, legal, governmental and planning expertise, coupled to knowledge related to soil, energy usage and chlorinated ethene remediation and risk assessment. Whereas most remediation efforts target isolated cases separately, CityChlor assists cities in realizing the overall picture, by focusing on an integrated approach. Combining urban development, sustainable energy use and remediation while incorporating all of the above mentioned expertise and knowledge. Contributing not only to the development of large polluted urban areas but consequently to the future of the city and/or region.

In Utrecht the “Bio-Washing Machine” stimulates/promotes groundwater and soil contaminant degradation while simultaneously opting for a sustainable and environmentally friendly approach to heating and cooling buildings. Aquifer Thermal Energy Storage (ATES) is used to store and collect the thermal energy in the subsurface. By extracting cold water during warm periods, buildings can be effectively cooled, the resulting heated water is then reinjected into the aquifer. When the process is reversed during colder periods, the stored thermal energy can be retrieved, while positively impacting contaminant transport and therefor potentially increasing degradation.

12.1 Hydrogeological setting

The subsurface of Utrecht is known for its heterogeneity, mostly consisting of unconsolidated fluvial and deltaic sediments deposited by multiple river channel deposits of the Rhine river system. The two main aquifers can be found at approximately -5m to -45m +NAP and -70m to -110m +NAP. Although TNO'S GeoTop data provides a nice insight into the subsurface of Utrecht, the relatively large voxel size (100m x 100m x 0,5) results in a more homogeneous/less realistic impression of the subsurface. Figure 19 gives a West to East cross section of the first 50 meters of Utrecht's subsurface, the Amsterdam-Rhine channel was added for reference. The whereabouts of (half) the city can be easily deduced from the contours of the grey anthropogenic top layer.

Figure 19. Subsurface of Utrecht (Compiled from GeoTop data).



Apart from the geological information provided by the GeoTop dataset, the similar Regis II dataset can be consulted to get a more detailed lithography as well as other hydrogeological data related to the composition of these layers. The information was retrieved for the greater Utrecht area and made available by the DINOloket portal of TNO, the Dutch organisation for applied scientific research. Both sets were relied on to define the exact location of the aquifers/aquitards and to estimate the parameters governing contaminant transport in the areas of interest.

The regional groundwater flow is determined by several geophysical and anthropogenic factors, mainly the existence of a large infiltration area to the east of Utrecht and a polder area in the western and north-western direction of the city. Due to the fact that the groundwater levels are kept at a certain level in these polder areas, groundwater tends to flow in a north-western direction. For both modelling domains the groundwater flow was imposed by defining constant head boundaries conditions at the fringes of the model domain. Using measured data made available by DINOloket, numerical simulations executed by Arcadis (2009) and IBU(2010) and meteorological data gathered from the nearby weather station at de Bilt. The resulting regional groundwater flow directions are portrayed by Figure 20.

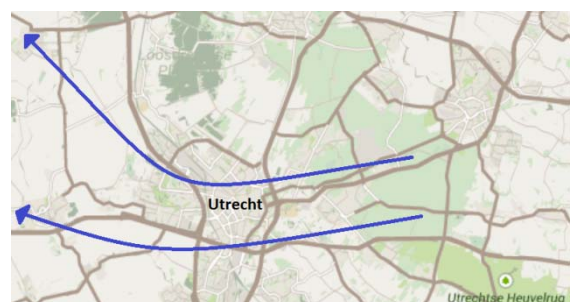


Figure 20. Regional groundwater flow.

12.2 Geochemical setting

The geochemical data used as model input was derived from the Meetnet data, a network of over 300 monitoring wells placed throughout the city of Utrecht. Most of the data, such as contaminant concentrations, oxygen content, pH and redox potential was provided for wells placed on a 250m by 250m grid. However specific parameters, mainly electron donor/acceptor and dissolved organic carbon were measured more sporadically. Making the availability of redox related data one of the key factors in picking the areas of interest. The other two criteria were the presence of ATEs induced groundwater perturbations and potential existence of pure phase DNAPL.

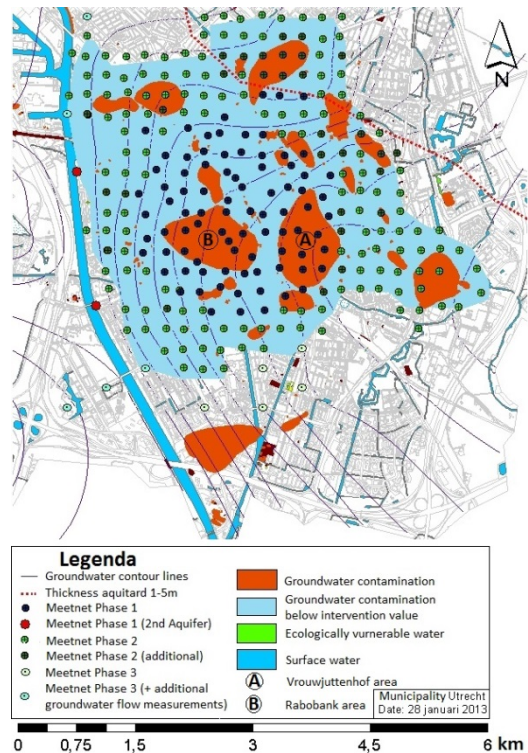


Figure 21. Meetnet and CAH contamination.

For the purpose of this study it was assumed that the subsurface of Utrecht exhibits subtle redox gradients and an overall anoxic nature. Resulting in sequential reductive dechlorination being the main degradation process affecting chlorinated ethene contaminants in the subsurface. Although chlorinated ethene mineralization is bound to occur in the subsurface, the modelled areas were not in the vicinity of dissolved plume fringes or the groundwater table, severely limiting the oxygen needed for the oxidation pathways.

12.3 Areas of interest

Studying the propensity of chlorinated ethenes site per site, results in a better understanding of the effect of the local conditions and the nature of the subsurface on contaminant fate and transport. Similar to CityChlor's area-oriented approach, both modelling domains were selected for their unique characteristics and remediation potential. The two areas chosen are both centred on a separate dissolved chlorinated plume, located on either side of the train tracks. The first is located in the centre of the town, the Vrouwjutenstraat area. The second is centred around the Rabobank building in the Croeselaan. For both areas of interest, the local grids were refined for a 2000m by 2000m domain. Assuming a continuous confining clay layer/aquitard, the depth of the model was set to 45-50m, incorporating the first aquifer in its entirety. This assumption is based on the outcome of the sensitivity analysis of the second aquifer performed during the internship at the municipality, suggesting the risk of aquifer cross contamination was negligible.

12.3.1 Vrouwjuitenstraat

The area of the Vrouwjuitenstraat was chosen as the first modelling domain, considering the most elevated contaminant concentrations were measured in its vicinity. The dissolved chlorinated ethene levels were even high enough to indicate the possibility of pure phase contaminants at the site. It is this potential pure DNAPL presence combined with the area's dense urban nature that forms a bottleneck for most remediation approaches. The main goal of modelling this area was to evaluate natural attenuation as a remediation technique and illustrate the potential danger pure phase DNAPL poses to conventional remediation approaches.

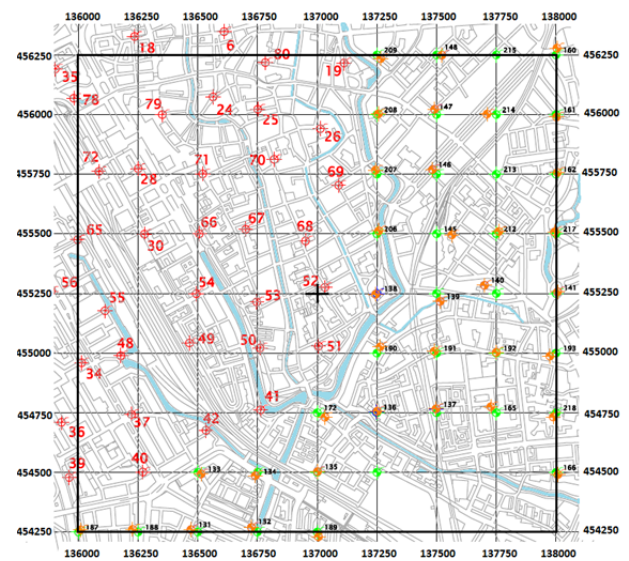
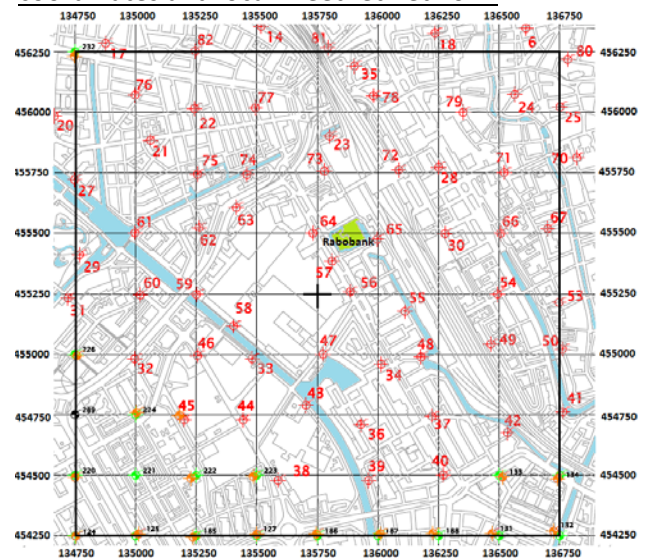


Figure 25. Vrouwjuitenstraat: model domain, coordinates and local Meetnet network.

12.3.2 Croeselaan: Rabobank ATES

Located to the West of Vrouwjuitenstraat, the Rabobank ATES system is a perfect example of combining an environmentally friendly and renewable energy source with groundwater and subsurface remediation. The effect of ATES systems on chlorinated ethene contaminant transport, dispersion and degradation was studied for various degradation kinetics. This was mainly done in order to look into and identify the limitations posed by the use of the conventional zero and first order degradation rates. The ATES wells were spaced 200m apart and were both placed in zones characterized by a high permeability.

Figure 26. Rabobank ATES: model domain, coordinates and local Meetnet network.



Although the annual amount of groundwater extracted for heating and cooling purposes could be found in literature, the amount listed included both wells. Weekly pumping rates per well were deduced from meteorological data gathered at the Bilt, by comparing the outdoors to the desired indoors temperature. By taking this energy deficit into account the required pumping rates did properly reflect on the more intense yet shorted energy demand during winter.

Figure 27 depicts the estimated weekly pumping rates, based on meteorological data gathered in 2011. Note that week 1 does not refer to the beginning of January as one would assume, but rather to the first week of warm water extraction, which was the first week of December (2010).

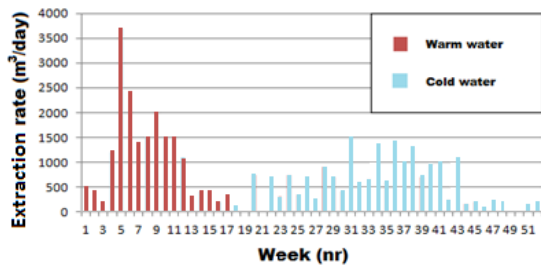


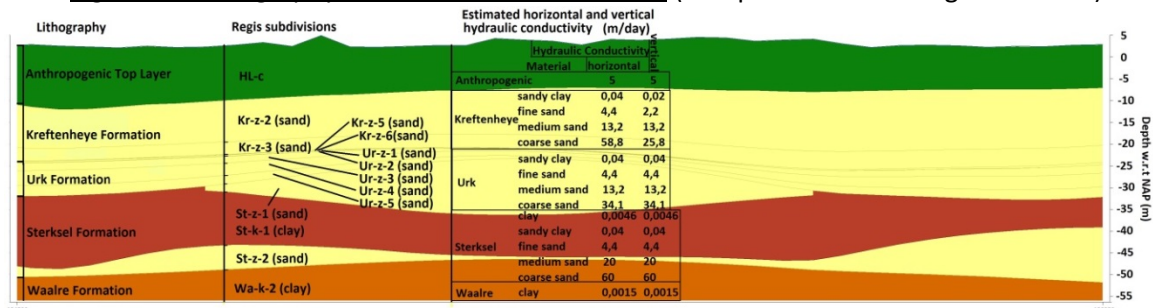
Figure 27. Weekly Rabobank ATEs groundwater extraction rates.

In order to ensure the system was closed, e.g. no contaminants were lost during the ATEs operations, the recirculation of contaminated groundwater was incorporated through a multi-node-well package (MNW) (Halford et al., 2002) further adapted based on seminal work regarding single-node-wells (Zheng, 2006). Effectively making the ATEs system a closed loop, making sure that any contaminant mass extracted from the aquifer was re-injected containing the same amount of chlorinated ethenes.

12.4 Numerical interpretation

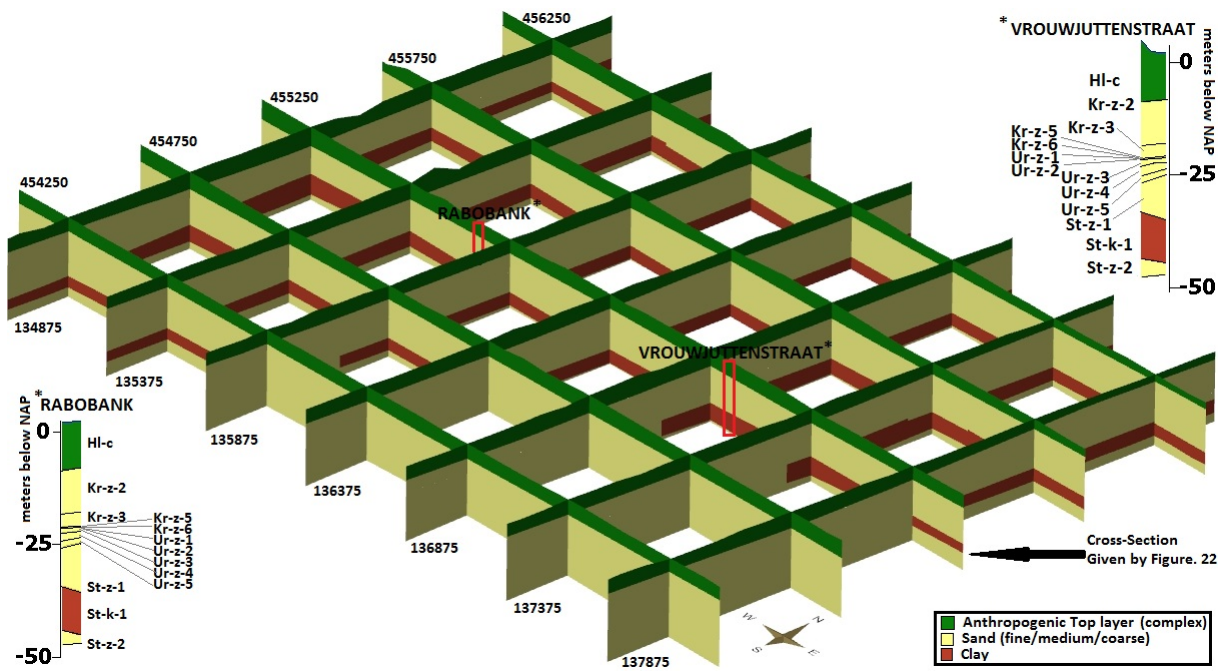
Due to the fact that the centres of both modelling domains are located at the same latitude, a single Regis II (TNO) cross section was used to illustrate a more detailed lithography. Apart from discerning the location of the different layers the Regis II model was also consulted to deduce the specific hydraulic conductivities for each lithographic unit. The regional groundwater flow was simulated by imposing constant head boundary conditions, derived from the Arcadis 2009 model, at the modelled domain’s eastern and north-western boundaries. Groundwater recharge was estimated using meteorological data gathered at the Bilt and the local land-use. Depending on the open/urban nature of the area this generally resulted in a groundwater recharge between 0,5-1,1 mm/day.

Figure 22. Lithography of the Utrecht’s subsurface (Compiled from the Regis II dataset).



Note that the hydraulic conductivity values given by Figure 22, are averages for specific types of porous media composing a variety of lithographic units. By combining this data with the borehole data gathered by Meetnet, the amount of uncertainty regarding the composition of the Utrecht’s subsurface was significantly reduced.

Figure 23. Fence diagram of the two areas of interest (based on adapted Regis II dataset).



The groundwater and solute transport model Modflow was chosen to simulate the propensity of chlorinated ethenes in the Utrecht subsurface. Both the MT3DMS and RT3D solute transport modules were used to simulate reactive transport. The model domain was set to 9 by 5 kilometre, in order to incorporate the entire Meetnet network. The default grid cell size was chosen to be 250m by 250m, in line with the Meetnet well spacing. The grid encompassing the two areas of interest was then refined to 50m by 50 m. Based on Regis II data and bore logs the subsurface was schematized, the deduced Modflow layers are given by Table 13.

Figure 24. Model domain and grid size.

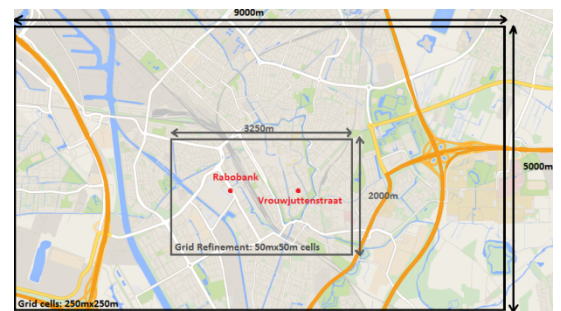


Table 13. Schematization of the subsurface.

Layer	Depth (m)	Description	Composition	Effective porosity (-)	Bulk density (kg/m ³)	Horizontal hydraulic conductivity (m/day)
1	2 - 0,5	Top layer I	Landfill + sand	0,25	1600	3
2	0,5 - 3	Top layer II	Silty/sandy clay + sand	0,15	1550	0,04
3	3 - 17	Kreftenheye I	(medium) coarse sand	0,30	1700	50
4	17 - 23	Kreftenheye II	(medium) coarse sand	0,30	1700	40
5	23 - 30	Urk	Medium sand	0,32	1700	15
6	30 - 40	Sterksel I	Fine sand	0,35	1700	5
7	40 - 47	Sterksel II	Clay	0,06	1400	0,0046
8	47 - 50	Sterksel III	Fine sand	0,35	1700	5

Regional groundwater flow was simulated by specifying constant head boundaries at the edges of the model, mainly the Amsterdam-Rhine channel in the West and an extension of the Utrechtse Heuvelrug in the East. The linear isotherm sorption distribution coefficients were calculated using the specific K_{oc} values as shown in Table 1. and an organic carbon fraction of 0,005. A total of 1300 stress periods, each lasted 7 or 8 days (51 and 1, respectively), resulting in a total period of 25 years. Using Meetnet data two separate dissolved chlorinated ethene plumes were localized and their initial mass calculated based on the sum of CAHs found per measuring well. Contaminant fate and transport was then simulated for zero-, first-order and Michaelis-Menten degradation kinetics for both areas of interest. The expanded Michaelis-Menten kinetics, as described by Eq. 13, were used in order to account for microorganism growth and decay, while assuming limited parent-daughter inhibition. The resulting degradation rates are given by Table 14.

Species	Zero-order ($\text{mg L}^{-1} \text{d}^{-1}$)	First-order (10^{-3}d^{-1})	Michaelis-Menten	
			k_{max} ($\text{mg L}^{-1} \text{d}^{-1}$)	K_s (mg/L)
PCE	$1,86 * 10^{-4}$	0,5 - 5	61,7	0,269
TCE	$1,74 * 10^{-4}$	0,5 - 3	492,8	0,237
DCE	$1,86 * 10^{-4}$	0,25 - 2	40,1	0,170
VC	$1,1 * 10^{-5}$	0,125 - 1	15,2	3,912

Table 14. Degradation rates

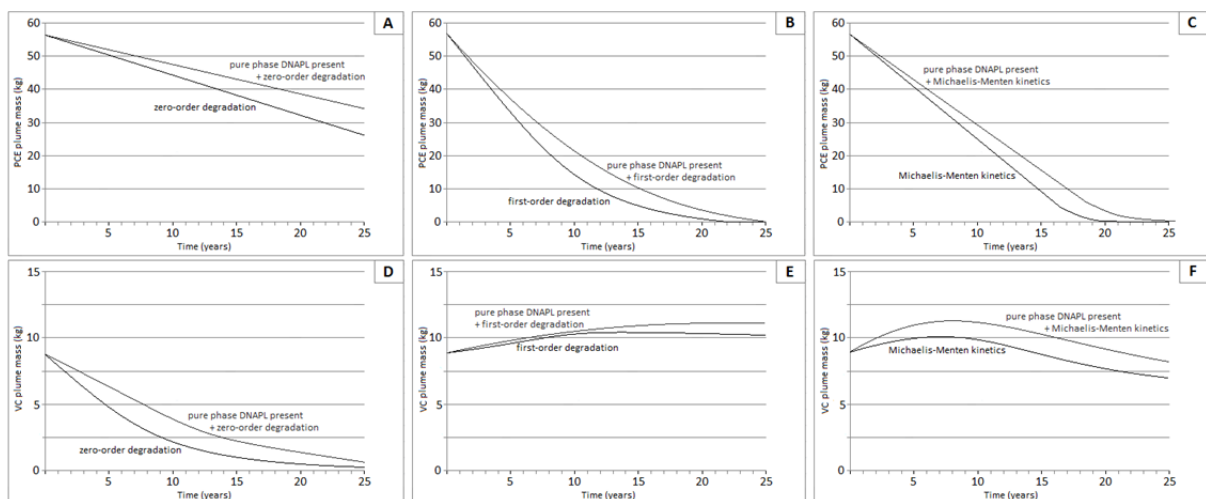
Zero-order and lower first order (Zuurbier et al. 2013) Michaelis-Menten (Yu, 2003, assuming initial 30mg protein/L microorganism concentration).

13 RESULTS AND DISCUSSION

The first goal of the numerical part of this thesis was to contrast and compare several degradation rates under different circumstances. The second goal was to identify the effect and potential risks of the presence of pure phase DNAPL for groundwater and subsurface quality as well as its impact on the chosen remediation attempt, specifically monitored natural attenuation and enhanced dissolution related to an ATEs system. Although the Vrouwjutenstraat and Rabobank dissolved contaminant plumes were slightly coalesced, they were considered separate plumes for the purpose of this study. The main difference between the two areas was that Rabobank zone was exposed to anthropogenic groundwater perturbations due to the presence of the ATEs system. By comparing the three scenarios for the two sites potential strengths and weaknesses of the specific degradation expression chosen were identified. This was done based on a comparison of the ultimate parent product (PCE) and the final chlorinated daughter product (VC) for reductive dechlorination.

13.1 Vrouwjutenstraat

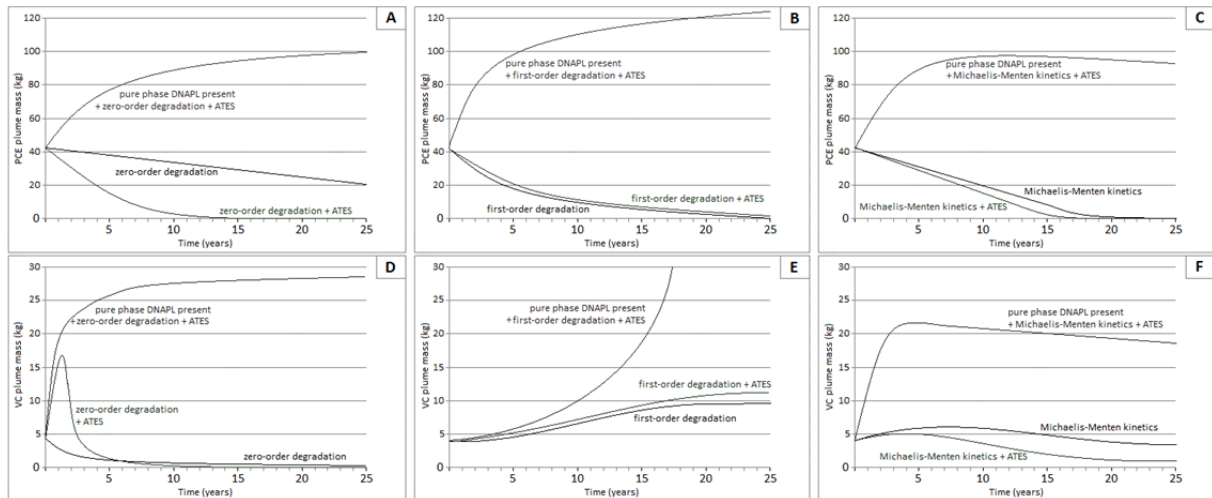
Figure 28. PCE and VC contaminant plume mass for the Vrouwjutenstraat plume.



The effect of the separate phase DNAPL should be clearly visible in the above graphs. Regardless of the degradation kinetics used the dissolution of the pure phase DNAPL results in an increase of plume mass and therefore the remediation time frame. When the only contaminants are either found dissolved in the groundwater or sorbed to the soil, the estimated plume mass reduction after two decades, for zero-, first-order and Michaelis-Menten degradation is 45%, 97% and 100% respectively. The addition of a third phase increases the remediation time required significantly, after 20 years 35%, 92% and 93% for scenario A, B and C respectively. Whereas scenario B, C and D will achieve near complete contaminant removal within 2-3 decades scenario A, E and F will most likely persist for more than 40-50 years.

13.2 Rabobank

Figure 29. PCE and VC contaminant plume mass for the Rabobank plume.



When we compare the effect the groundwater perturbation, caused by the ATEs injection and extraction wells has on the various degradation rates, the effect dilution has become rather evident. Although PCE removal speeds up by a factor of 5 for the zero-order degradation rate, the first-order and Michaelis-Menten scenario are hardly affected, counter-intuitively the first-order degradation even slows down. This is mainly due to the fact that the first-order, contaminant limited attenuation is vulnerable to the induced dissolution and gives a distorted image of reality, as mentioned in Chapter 9. The Michaelis-Menten kinetics result in the best approximation of the actual degradation rates measured by Meetnet. The exact same trend can be seen for scenario D, E and F. Even though the VC plumes mass briefly peaks in the zero-order scenario this is mainly due to the nature of the sequential degradation reactions governing the attenuation.

Whereas the effect of pure phase DNAPL was relatively limited for the Vrouwjutenstraat area, the ATEs induced DNAPL dissolution is clearly visible for the Rabobank site, resulting in a factor 2-3 increase in dissolved PCE mass for scenario A, B and C. The impact on the amount of dissolved VC is even greater, however this was to be expected due to the nature of sequential degradation reactions. The first-order degradation rate discussed for the 29B scenario becomes even more apparent as the enhanced dissolution cause the contaminant limited degradation rate to become negligible, causing the dissolved VC plume mass to skyrocket, resulting in a factor 100 increase over a 20 year timespan. For both the dissolved PCE and VC plumes the Michaelis-Menten kinetics results in the least distorted image and the closest fit to the actual measured concentration values at the Rabobank site.

14 CONCLUSIONS, LIMITATIONS AND FURTHER RESEARCH

Although chlorinated ethene fate and transport is a widely researched topic, the multi-faceted nature of the problem combined with the uncertainty regarding the subsurface makes a one size fits all remedial solution impossible. Only by understanding of all the contributing factors involved, mainly the hydrogeological (Chapter 3,4), geochemical (Chapter 5,6) and microbiological (Chapter 7) processes, the resulting degradation reactions (Chapter 8,9), the potential remediation techniques, natural or enhanced (Chapter 10,11) can this data/knowledge be successfully approximated and processed numerically (Chapter 12).

When numerically estimating current or predicting future chlorinated ethene propensity it is important to take into account the numerical limitations, vulnerabilities and incompatibilities (Chapter 13). Although something might be numerically sound, it does not mean that it reflects perfectly on reality, considering the amount of assumptions and approximations required for a numerical model it is always important to incorporate as much in-situ measured and empirically gathered lab data (if scalable). By following the flowchart proposed in Chapter 11 the amount of numerical distortion can be limited will at the same time gathering extrapolatable information and experience.

The limitations dealt with in this thesis can be categorized into one or multiple of the following classes; gaps in current knowledge, availability of real world data, numerical problems and the influence of heterogeneity and uncertainty. Although some of these can be addressed by simply investing more time and money others are inherent to the nature of the contaminants, specific contaminated sites and the numerical and analytical ways of interpreting remediation.

Although a vast amount of research and time has been invested into the fate and transport of chlorinated ethene contaminants, there still exist numerous gaps of knowledge. The majority of the processes governing CAH degradation and remediation have been identified, unfortunately the total picture has not. There is still much to learn about the various degradation pathways and the physical and chemical conditions under which they prevail. From a biological point of view further research in the microorganisms metabolizing or facilitating will be required to fully understand metabolic degradation and the various ways of enhancing and stimulating this natural attenuation.

Considering the effectiveness of site assessment and remediation approach is directly related to the amount of data gathered, it goes without saying that the availability of relevant data is one of the major limitations in groundwater related studies. Especially when dealing with rather urban contaminated sites it becomes impractical, sometimes even impossible to gather a significant amount of data, not even mentioning the costs. Combined with the extreme spatial variation

exhibited by some of the parameters and ongoing processes it regularly results in a misinterpretation of reality. The presence of pure phase DNAPL is an example of this, although a small amount of the separate phase CAH can be extremely difficult to locate, the impact it can have on groundwater quality and the outcome of a remediation attempt can be totally unforeseen (Zuurbier et al. 2013).

Uncertainty and heterogeneity, as mentioned before can play a huge role in incorrectly interpreting the propensity of chlorinated ethenes. Even though these two aspects are inherent to dealing with the subsurface, they can be minimized by gathering sufficient data. Preferential flow paths or macro pore flow are aspects that can have a massive impact on the transport of contaminants, causing the contaminants to behave in ways never even considered.

The last class of limitations is related to the numerical simulations used to interpret and predict chlorinated ethene behaviour in the subsurface. Although the computing power of modern day devices/setup increases at an incredible pace the vast amount of calculations required can result in rather lengthy simulations. Adding to the complexity of a model does not only add to the computation times required but also the degree of chaotic behaviour exhibited, resulting in a loss of accuracy when simulating for longer periods of time.

The best way to address these limitations is creating a publically accessible knowledge database, considering a lot of the data on the subsurface and the contaminants present in it was made available by the Dutch government and many governments alike, expanding the currently existing (DINOloket) databases should be within the realm of possibilities. Taking into account the complexity of these remediation projects, the ability to compare and contrast a specific site with sites that have already been remediated or are currently undergoing it, should provide insight into the applicability and feasibility of various remediation techniques as well as help predict and anticipate the possible outcomes.

However just data itself will not suffice, at the same time you will need projects such as the European CityChlor initiative. The integrated approach opted for by CityChlor is a perfect example of combining expertise and knowledge of the various parties involved in contaminated groundwater and subsurface clean-up. By combining experience and truly embracing the multidisciplinary nature of the remediation issues faced worldwide, it becomes possible to devise the most resilient approaches to ensuring the quality of living and future of these contaminated regions.

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