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Evaluation of stimulated reductive dechlorination in situ of chlorinated solvents at a site in Huddinge

using principal component analysis, partial least square regression and degradation

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Karin Ljungberg

ABSTRACT

Evaluation of stimulated reductive dechlorination* in situ *of chlorinated solvents at site in Huddinge *using principal component analysis, partial least square and degradation dynamics.*

The method of using stimulated reductive dechlorination when remediating sites contaminated with chlorinated solvents is not unusual, but not many studies have been done on the overall process outside of a controlled environment. In order to investigate the process, principal component analysis (PCA) and partial least square (PLS) regression was used to identify the most important parameters for the degradation of the chlorinated solvents. The most important parameter for all chlorinated compounds turned out to be oxygen, with levels of degradation products increasing with decreasing levels of dissolved oxygen. Dissolved oxygen was deemed the most important variable to measure during a control program on the site.

The degradation dynamics of the process were investigated to examine the behaviour of the chlorinated solvents and their degradation products. The degradation products of the main contaminant TCE were found in all observation points, which indicates an ongoing reductive dechlorination all over the site. A large amount of the mother product, TCE, was found in two observation points, which were believed to be situated close to the sources of the TCE contamination. Over the observation period of 2,5 years the levels of TCE in the source areas decreased significantly to below the remediation goal. However, the levels of TCE increased in another observation point further downstream, with concentrations still increasing at the end of this study. The levels in this point were lower than those measured initially in the source area, but still much higher than the accepted values. Possible reasons for this appearance of TCE could be an isolated sheet of contaminants being pushed into the observation point from a nearby location or transport of the contaminants from the source area in units of higher conductivity such as sand lenses or fractures in the clayey soil.

Keywords: Reductive dechlorination, DNAPL, stimulated bioremediation, chlorinated solvents

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REFERAT

Utvärdering av stimulerad biologisk behandling in situ av klorerade lösningsmedel vid en fastighet i Huddinge med principalkomponentsanalys, partial least square och nedbrytningsdynamik

Karin Ljungberg

Att använda stimulerad reduktiv deklorering som metod för att sanera fastigheter förorenade med klorerade lösningsmedel är inte ovanligt, men få studier har undersökt det övergripande saneringsförloppet utanför de kontrollerade förhållanden i en labbmiljö. För att undersöka nedbrytningsprocessen användes principalkomponentsanalys (PCA) och partial least square (PLS) regression i syfte att identifiera de parametrar som hade störst påverkan på nedbrytningen av de klorerade föroreningarna. Den enskilt viktigaste parametern visade sig vara halten löst syre i grundvattnet, då halterna av nedbrytningsprodukter ökade med minskande syrehalt. Därför ses syre som den viktigaste parametern för att följa förloppet och är den parameter som bör mätas i kontrollprogram över nedbrytningsprocessen.

Nedbrytningsdynamiken analyserades under en observationsperiod på 2,5 år för att studera hur de klorerade föroreningarna betedde sig under nedbrytningsförloppet. Nedbrytningsprodukter hittades i provtagningspunkter över hela fastigheten vilket visar på en pågående reduktiv deklorering. En stor mängd av moderprodukten TCE hittades i två punkter som bedömdes vara källor till TCE-spridningen. Under observationsperioden sjönk halterna av TCE i dessa två punkter till under gränsen för åtgärdsmålet, dock ökade koncentrationen av TCE i en annan provpunkt längre nedströms källområdet. Halterna i provpunkten var inte lika höga som de initiala halterna i källområdet, men de var långt högre än det fastställda åtgärdsmålen och ökade fortfarande när undersökningen avslutades. Möjliga förklaringar till varför halterna ökade i denna provpunkt är att ett sjok av TCE från omkringliggande sediment har transporterats till provpunkten, eller att en föroreningstransport har skett från källområdet via områden med högre konduktivitet i till exempel sandlinser eller sprickor.

Nyckelord: Reduktiv deklorering, DNAPLS, stimulerad biologisk behandling, klorerade lösningsmedel

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PREFACE

This master's thesis corresponds to 30 ECTS, and it concludes my M.Sc. in Environmental and Water Engineering at Uppsala University and the Swedish University of Agricultural Sciences (SLU). The project was carried out at WSP Environmental under the supervision of Karin Tornberg, senior project manager at WSP. John Stenström, professor at the Department of Molecular Sciences at SLU, was the thesis subject reader. Fritjof Fagerlund acted as final examiner. The project is based on an ongoing bioremediation in Huddinge municipality where stimulated reductive dechlorination *in situ* is being used to remediate chlorinated solvents.

I would like to thank Karin Tornberg and John Stenström for guidance during the project, as well as Lars Sonesten for support with PCA and PLS. I also want to thank WSP Environmental for the interesting project and the co-workers for various valuable inputs as well as pleasant coffee breaks.

Finally, I would like to thank my partner, friends and family for their encouragement and support during these months.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Många kemikalier som användes förr i tiden har nu i efterhand upptäckts vara skadliga för både miljön och människor och i den gruppen ingår bland annat de kemikalier som kallas klorerade lösningsmedel. Eftersom klorerade lösningsmedel är ett effektivt avfettningsmedel har de i decennier använts inom många olika typer av industrier såsom kemtvätt, verkstadsindustri och elektronikindustri. Den största användningen i Sverige skedde under mitten av 1970-talet då uppskattningsvis 20 000 ton klorerade lösningsmedel användes varje år. Det är idag förbjudet att använda klorerade lösningsmedel i Sverige och användningen har sedan förbudet infördes sjunkit kraftigt. Trots att användningen av dessa kemikalier har upphört i Sverige så var den tidigare användningen av dem så omfattande att det fortfarande finns många områden som är kraftfullt förorenade runt om i landet. Som del av riksdagens miljömål Giftfri miljö ingår det att sanera förorenade områden så att föroreningar i mark och i grundvatten inte hotar omgivningen. Sanering gör även marken tillgänglig för exploatering så att den kan användas för att skapa samhällsnyttiga fastigheter såsom bostäder, förskolor eller äldreboenden.

På fastigheten som undersöks i den här rapporten användes det klorerade lösningsmedlet trikloreten (TCE) i tillverkningsprocessen för kretskort, vilket lämnade sina spår i området. I början av undersökningen hittades halter av TCE på över 5 000 µg/l i grundvattnet, vilket är 500 gånger högre än projektets åtgärdsmål. Spår av TCE och dess nedbrytningsprodukter hittades i varierande halt i alla provtagningspunkter i området, vilket tyder på att reduktiv deklorering pågår i området. Klorerade lösningsmedel är tyngre än vatten och tenderar därför att lägga sig som ansamlingar på botten av en grundvattenakvifer där de sakta läcker ut i grundvattnet och vidare ut i den omgivande miljön. Föroreningsrester kan även fastna i sprickor eller porer i jorden, vilket bidrar till att föroreningsläckaget kan pågå under lång tid. Flera av de klorerade lösningsmedlen och deras nedbrytningsprodukter är bevisat eller misstänkt cancerogena och dessutom ofta lättflyktiga, vilket gör att de snabbt kan sprida sig till den närliggande miljön. De kan även sprida sig till luften via porerna i marken och utgöra en hälsofara för människor, främst genom risken att få i sig föroreningar genom inandningsluften.

Metoden som används på det förorenade området som studeras i rapporten är reduktiv deklorering *in situ*. Det är en saneringsmetod där man använder sig av mikroorganismer som finns naturligt i marken och som har visat sig vara effektiva för att bryta ner klorerade lösningsmedel. Mikroorganismerna förekommer ofta naturligt i grundvattnet och bryter ner de klorerade ämnena genom att använda dem i sin tillväxt, vilket gör att föroreningen omvandlas till ofarlig eten. Nedbrytningen sker ofta på naturlig väg utan mänsklig påverkan, men för att skynda på nedbrytningsprocessen kan man skapa så bra förhållanden som möjligt för mikroorganismerna. Detta kan göras genom att bland annat injicera stimuli såsom näringsämnen så att mikroorganismerna får alla de ämnen som de behöver för nedbrytningen, vilket gjordes på den undersökta fastigheten. Reduktiv deklorering har en mindre påverkan på omgivningen än många andra saneringsmetoder, dock kan det ta relativ lång tid innan föroreningen har försvunnit från området. Man får ofta räkna med att saneringen måste pågå några år, men markarbeten kan ofta påbörjas på platsen tidigare eftersom själva saneringen främst sker i grundvattnet och inte störs av markarbeten närmare jordytan.

För att ta reda på vilka faktorer som var viktigast för nedbrytningen av de klorerade lösningsmedlen och deras nedbrytningsprodukter utfördes två statistiska analyser, principalkomponentsanalys (PCA) och partial least square (PLS) regressionsanalys. Genom analyserna framgick det att den viktigaste faktorn för nedbrytningen var syrehalten i grundvattnet, där en minskande syrehalt gav ökande halt nedbrytningsprodukter och vice versa. Detta var väntat då mikroorganismerna som står för nedbrytningen är anaeroba vilket innebär att de är som mest aktiva vid låga syrehalter. TCE och dess nedbrytningsprodukter samvarierade ofta i de olika provpunkterna, troligen eftersom höga halter av TCE kan ge en stor bildning av nedbrytningsprodukter. Nedbrytningsprodukterna är förväntade att ha liknande variation, då de bryts ner under samma förhållanden.

När TCE-halterna i de olika provpunkterna studerades kunde man se att det fanns två punktkällor på den förorenade fastigheten där halterna av TCE initialt var mycket högre än i de andra mätpunkterna. Provtagarna misstänkte att stora mängder av TCE hade använts på de platserna i den tidigare industrin och att TCE sedan har trängt ner i jorden, spridits ner i grundvattnet och förorenat stora delar av fastigheten. I denna undersökning visade det sig att den valda saneringsmetoden har medfört att halterna TCE hade minskat betydligt i de två källområdena efter 1,5 år. I en provpunkt längre bort från källområdet hade dock halterna av TCE stigit från låga till mycket höga nivåer. Detta provtagningsrör låg nedströms från källområdet vilket kan tyda på att de höga halterna härrör från förorening som har transporterats iväg från källområdet och förts längre nedströms med grundvattnet. Då den beräknade grundvattenhastigheten i området är alltför låg för att föroreningen skulle kunna transporteras så långt på så kort tid måste istället den eventuella transporten ha skett i områden med högre konduktivitet såsom sandlinser eller sprickor i marken. Den ökade koncentrationen kan även bero på att ett sjok av förorening har transporterats till provpunkten från närliggande sediment. Nedbrytningsprodukter hittades i alla mätpunkter under hela observationsperioden, vilket tyder på att nedbrytningen fortfarande pågår i hela området. Därför bör sannolikt åtgärdsmålen nås om saneringen får fortsätta pågå, men man kan dock överväga att på nytt injicera stimuli i punkten med högst halt TCE för att påskynda nedbrytningen. Om man tolkar föroreningsbilden som att en transport har skett från källområdet kan preventiva åtgärder såsom en barriär eller liknande övervägas för att motverka fortsatt föroreningstransport.

GLOSSARY

DNAPL - Dense non-aqueous phase liquids

PCE – Tetrachloroethene/Perchloroethylene

TCE – Trichloroethene/Trichloroethylene

DCE – 1,2-dichloroethene, present as the isomers *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene

VC – Vinyl chloride

Degree of dechlorination [%] – The degree to which chloride is removed from a compound.

DOC – Dissolved organic carbon.

ORP - Oxidation-reduction potential [mV]

SPC - Specific conductivity [S/m]. A measure of a solutions ability to conduct electricity.

Content

1. INTRODUCTION

1.1 BACKGROUND

The Swedish parliament have decided to include an objective that states: "*The occurrence of man-made or extracted substances in the environment must not represent a threat to human health or biological diversity*" in their Environmental Objective number 4, "A Non-Toxic Environment" which is to be fulfilled by the year 2020 (SOU 200:52). Chlorinated solvents, in particular trichloroethene (TCE) but also tetrachloroethene (PCE), have historically been used both in Swedish industry and all over the world for a long period of time (Naturvårdsverket, 2007). In 2002 it was estimated that the total amount of chlorinated solvents used in industries worldwide was 764,000 metric tons (Löffler et. al., 2012). They have above all been used as industrial solvents and degreasers as well as within the dry-cleaning business.

Chlorinated solvents and their daughter products are volatile, toxic and cancerogenic to various extents (Naturvårdsverket, 2007). They do not stay confined to the contaminated soil but can spread further into the environment by air and water, which makes them a threat to both human health and the environment.

An effective method to remediate soil and groundwater contaminated by chlorinated compounds is anaerobic reductive dechlorination *in situ* (Åtgärdsportalen, 2015). The method is cheap compared to other remediation techniques and as it is done *in situ (*i.e. the remediation is done on site and in the soil), it is often possible to begin development on the site parallel to the remediation. This is an advantage as bioremediation may take several years depending on the conditions of the site. This technique is being used by WSP at a site in Huddinge municipality where chlorinated solvents are present in both soil and groundwater. The remediation of the site started in September 2016.

The contamination present at the site in Huddinge municipality was left in the soil and groundwater by earlier industry on the site. As the contaminants are volatile, the largest threat to human health is inhalation of the contaminants in the buildings planned on the site. As the planned projects includes a kindergarten and a retirement home, the land usage is classed as sensitive land use (KM) by Naturvårdsverket. The pollutant found in amounts exceeding Naturvårdsverket's guideline values for acceptable levels in indoor air during sensitive land use was 1,1,2-trichloroethene (TCE). Tetrachloroethene (PCE) was found on site, but only in low concentrations, indicating that the principal chlorinated solvent used was TCE. The degradation products of PCE and TCE were also found: 1,2-dichloroethene (DCE), present as mainly *cis*-DCE but also in small amounts as *trans*-DCE, and vinyl chloride (VC). Trichloroethane (TCA) was also found on the site but not in amounts exceeding Naturvårdsverket's guideline values, which is why no focus is given to TCA in this project.

1.2 AIM AND OBJECTIVES

The aim of this work is to analyse the process of reductive dechlorination at the site in Huddinge and assess its success, as well as to compare the process with earlier studies in order to contribute to the knowledge of field studies on the subject.

The following objectives will be examined:

- Is the remediation process as could be expected from earlier studies?
- Which parameters in the surrounding environment affect each individual contaminant the most?
- Which parameters are most relevant to measure during a control program for stimulated reductive dechlorination?
- Will the goals of the remediation be fulfilled? Is it possible to calculate when the goals will be met?
- Can any suggestions or improvements of the remediation strategy be found?

2. THEORY AND METHODS

The source contamination at the site is TCE, with traces of PCE. The daughter products *cis*-DCE, *trans*-DCE and VC are also found on site, indicating an ongoing natural degradation. PCE and *trans*-DCE are found in very low concentrations throughout the observation period. The remediation technique used in the project was stimulated anaerobic reductive dechlorination *in situ*.

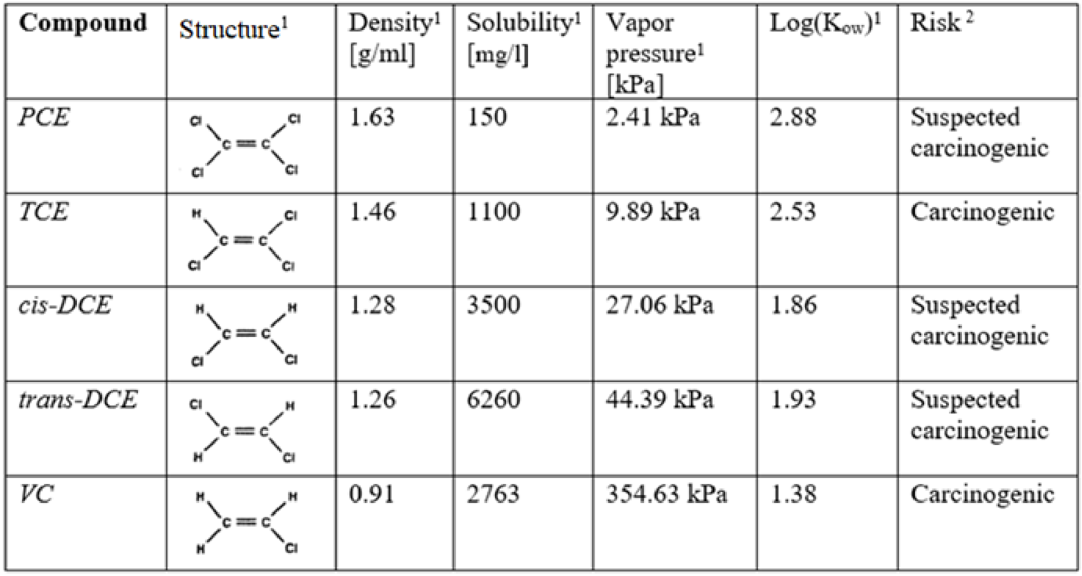
2.1 CHLORINATED SOLVENTS

Chlorinated solvents have been used in industries all around the world. These compounds do not occur naturally, they are all man-made and are as such part of the group xenobiotics (Skladany et. al., 1993). In the Swedish industry, the use of chlorinated aliphatic compounds, especially trichloroethene (TCE), as an industrial solvent was common because of their ability to dissolve fat. This practice was forbidden in Sweden in January 1996 and as a result the use of chlorinated organic solvents has dropped significantly (Kemikalieinspektionen, 2018a).

According to Kemikalieinspektionen (2018a), chlorinated aliphatic compounds are hazardous to human health and are classed as cancerogenic and/or suspected cancerogenic. The amount of chlorinated solvents still present in the soil across Sweden is unknown. The widespread usage of them in different industries has had consequences, it has for instance led to groundwater aquifers being rendered unsuitable as sources of drinking water as well as unsuitable for agricultural and industrial purposes (Mercer, 1990). The most common way for exposure by the chlorinated solvents and their degradation products is through inhalation of gas, which is emitted not only at the source of pollution but also along the contamination plumes (Naturvårdsverket, 2007).

Chlorinated solvents are moderately hydrophobic with a limited water solubility, partly volatile and with a high density compared to water. The properties of them and the degradation products are listed below in Table 1.

Table 1. The chlorinated solvents and their properties.



Compound	Structure[1]	Density[1] [g/ml]	Solubility[1] [mg/l]	Vapor pressure[1] [kPa]	Log(K_{ow})[1]	Risk [2]
PCE		1.63	150	2.41 kPa	2.88	Suspected carcinogenic
TCE		1.46	1100	9.89 kPa	2.53	Carcinogenic
cis-DCE		1.28	3500	27.06 kPa	1.86	Suspected carcinogenic
trans-DCE		1.26	6260	44.39 kPa	1.93	Suspected carcinogenic
VC		0.91	2763	354.63 kPa	1.38	Carcinogenic

[1] Reported by Cwiertny et. al., 2010
[2] Classification towards human health according to according to Kemikalieinspektionen

As seen in Table 1, the less amount of chlorine the compounds have the lighter and more volatile they are as the density, solubility and vapor pressure decrease vertically. When studying the partition coefficient between octanol and water it is seen that the smaller compounds have a higher solubility in water. As seen all compounds are considered cancerogenic/suspected carcinogenic to humans by Kemikalieinspektionen.

The high density and low aqueous solubility of the chlorinated solvents has given them the name "dense non-aqueous phase liquids" (DNAPLs) when present as a free phase (Naturvårdsverket, 2007). As DNAPLs, chlorinated solvents tend to sink though permeable groundwater aquifers and form a layer at the bottom of the aquifer or at other places of low permeability (Matteucci et al., 2015). As DNAPLs moves through the earth matrix, it moves along low-permeability layers until a window into a layer with higher permeability is found, taking the path of least resistance (Puigserver, 2014). When chlorinated solvents are released into the environment they are transported as a free phase through the soil and groundwater, only to be slowed down by layers of low permeability or by capillary forces (Naturvårdsverket, 2007). This transport can be fast and reach large depths and along the way residues may be left behind in pores or cracks. The pollutants tend to slowly be degraded over time in the aquifers as a result of natural microbial degradation, which makes them long-term contaminators of the groundwater and surrounding environment (Matteucci et al., 2015). Natural degradation is possible depending on the site-specific conditions but is often slow and might also be incomplete, which may lead to accumulation of toxic degradation products (Naturvårdsverket, 2007). The degree of threat towards human as well as animal health varies from moderate to very high, from some contaminants being suspected carcinogenics to others being established carcinogenic (Naturvårdsverket, 2007).

2.2 BIOREMEDIATION *IN SITU* – REDUCTIVE DECHLORINATION

Bioremediation *in situ* can be used on all contaminants that are biologically degradable but is most effective when used against hydrocarbons that are relatively easy to degrade (Åtgärdsportalen, 2015). Chlorinated solvents such as PCE, TCE and DCE are relatively easily degradable (Åtgärdsportalen, 2015). When using bioremediation *in situ* to remediate chlorinated organic compounds, reductive dechlorination in an anaerobic environment is most commonly used. When chlorinated solvents are biodegraded anaerobically, the chloride atoms are replaced with hydrogen (Parsons, 2004), a process called reductive dechlorination. The degradation pathway of PCE and the general process of removal of chloride atoms from the chlorinated solvents is described below in Figure 1.

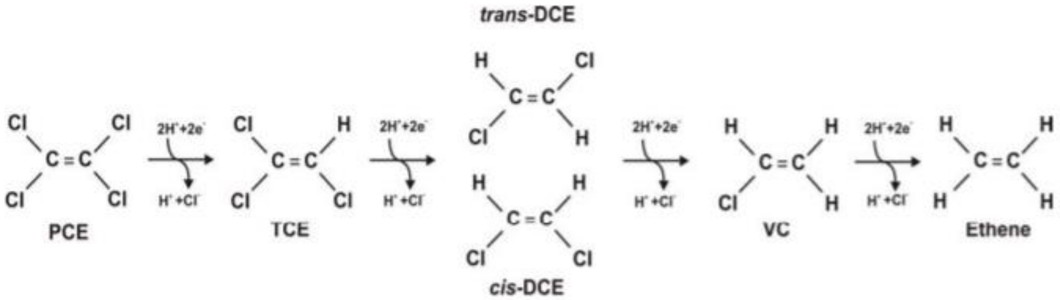


Figure 1. Reductive dechlorination of PCE to ethene. (Parsons, 2004).

As seen in Figure 1, the goal of the process is to transform PCE and other chlorinated ethenes into non-toxic molecules such as ethene. Chlorinated ethenes are degraded sequentially based on the number of chlorine substituents in the molecule, with the molecule with the largest amounts of chlorine atoms being degraded first Alexander, 1999). The higher the number of chlorides in the compound, the higher the oxidation state (Vogel, 1994), which means that compounds such as tetrachloroethene (PCE) and trichloroethene (TCE) are reduced faster than for example vinyl chloride (VC). This affects the biodegradation speed, with the rate decreasing with decreasing amount of chlorine atoms in the molecules (Puigserver, 2014). As a result, the lower order chlorinated compounds such as DCE and VC may accumulate in PCE and TCE plumes.

The redox potential at which different substances are reduced, including the optimal range for reductive dechlorination, can be seen below in Figure 2.

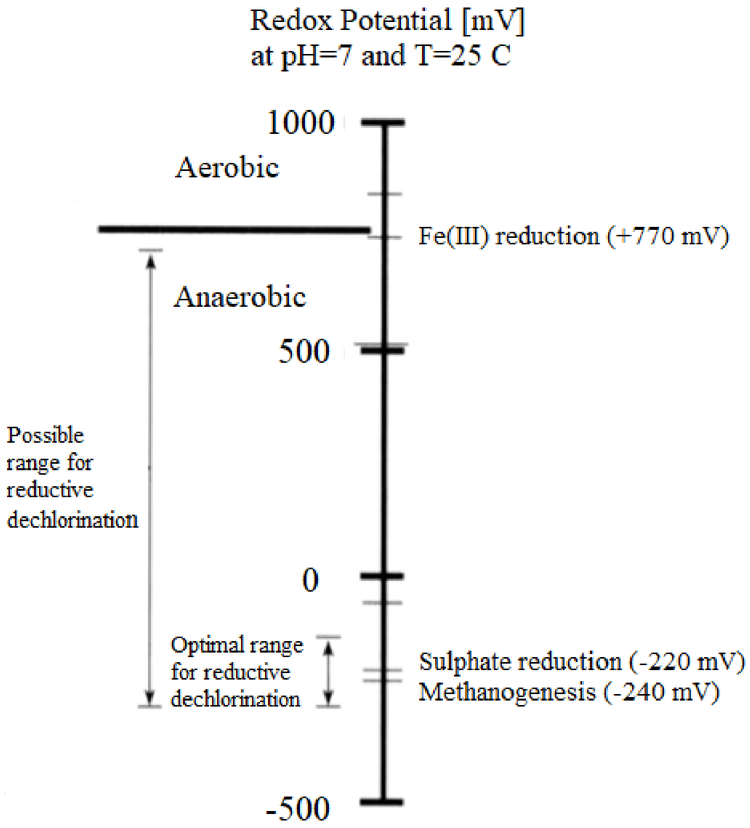


Figure 2. Oxidation-reduction potential ranges for some reactions including reductive dechlorination. Picture based on Wiedemeier et al. (1999) and Löffler et. al. (1999).

As seen in Figure 2, conditions that are sufficiently reducing for dechlorination can be indicated by the reduction of sulphate and the creation of methane on the site.

Reductive dechlorination can be stimulated by introducing dechlorinating bacteria (bioaugmentation) and/or compatible organic substances (biostimulation) (Rabah, 2002). According to David et. al. (2014), the introduction of an organic substrate serves a double purpose – firstly, it provides an organic substrate from which the anaerobic microbial community can release hydrogen, which is necessary for reductive dechlorination to occur. Secondly, it creates an anaerobic environment because of the nutrients and oxygen being used by respiring aerobic microbes.

According to Alexander (1999), the success of a bioremediation is further dependent on the bioavailability of the substances, which is dependent on several factors. Site-specific parameters can contribute greatly to the bioavailability of the targeted pollutant, such as the size and distribution of the pores and the type of soil. Processes such as diffusion and sorption can both affect the concentration of the substrate greatly and therefore also the bioavailability. A further factor that can limit the bioavailability of particularly DNAPLs comes from their unwillingness to mix with water, as dissolved contaminates are more easily degraded (Alexander, 1999).

Normally halogenated compounds such as PCE and TCE are not intentionally degraded to supply bacteria with energy or carbon to support metabolism but have instead been shown to be cometabolically biodegraded by a number of bacteria (Skladany et. al, 1993). There are however several groups of anaerobic dechlorinating microorganisms such as *Desulfomonile, Dehalobacter, Desulfitobacterium* that have been shown to metabolically reduce PCE and TCE to DCE, but not further (Mattes et. al., 2010). According to Volpe (2007), there is only one type of bacteria that has been shown to completely reduce PCE to ethene, and these are the anaerobic dechlorinators *Dehalococcoides ethenogenes*.

Cis- and *trans*-DCE have been shown to be cometabolically degraded by some bacteria (Alexander, 1999) and even by aerobic microorganisms. In an aerobic environment, the tendency of chlorinated compounds to be biodegraded by oxidation increases with the decreasing number of chlorine in the compound (Tiehm, 2011). There are several microorganisms that can reduce VC to ethene to gain energy, and studies indicate that aerobic oxidation of VC is relatively common. On the other hand, aerobic oxidation of cDCE with cDCE as the sole source of energy and carbon seems to be rare and has only been shown to happen when the bacteria *Polaromonas* sp. strain JS666 is present (Schmidt et.al., 2010). It has however been shown that aerobic bacterial cultures grown on VC has cometabolized *cis*-DCE and *trans*-DCE (the later to a lesser extent) in the absence of VC (Verce et. al., 2002

As many microorganisms in anaerobic environments are able to degrade PCE and TCE to DCE, but fewer are able to degrade the lower chloroethenes, it is common for cDCE and VC to accumulate at contaminated sites, as the larger chlorinated compound are more easily reduced, which is often remedied by either improving the environment (biostimulation) or by adding microorganisms to perform reductive dechlorination (bioaugmentation) (Mattes et. al., 2010).

Because of their ability to degrade PCE all the way to ethene under anaerobic conditions, *Dehalococcoides ethenogenes* are the microorganisms most commonly used when performing reductive dechlorination. *Dehalococcoides* use the halogenated hydrocarbons as an elector acceptor, not as a carbon source, which is why biostimulation often needs to be used to promote microbial growth (Baker et. al., 1994). The process of using the halogenated hydrocarbons as electron acceptors is known as halorespiration (Volpe et al., 2007). If the existing population of dechlorinating bacteria is too small, bioaugmentation might have to be done to achieve the intended result (Naturvårdsverket, 2007). For the remediation to be successful, reductive conditions need to be present or created. An example of bioremediation *in situ* and the conditions created when injecting a carbon source is seen in Figure 3 below.

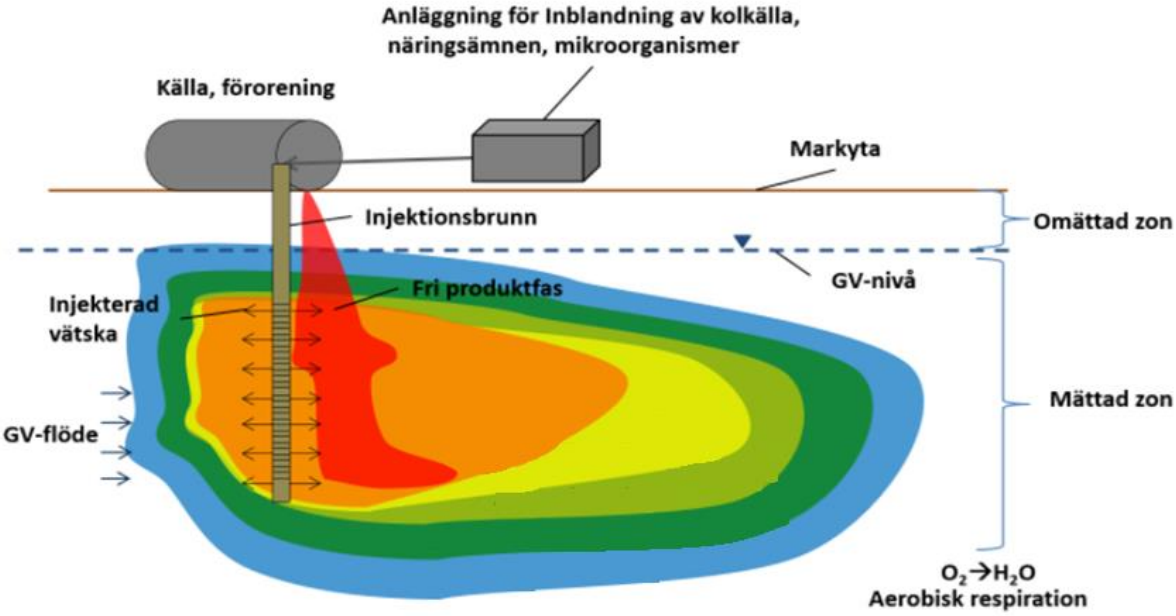


Figure 3. An example of the setup for bioremediation in situ. The figure shows the reductions that often are the results of creating a reductive environment by injecting a carbon source. Based on Åtgärdsportalen (2015).

As seen in Figure 3, several processes occur under reducing conditions, and these can be measured to assess if the conditions are favourable to reductive dechlorination or not. The reducing microorganisms compete for the same resources, which can lead to a temporary inhibition of a product being formed because of the competition and one group thriving at the expense of another (Lu et. al., 2001).

Bioremediation is often associated with long remediation times, but thanks to extensive studies concerning halorespiration to treat chlorinated compounds in groundwater the treatment time can in certain cases be shortened (Åtgärdsportalen, 2015). As the treatment time can vary greatly, so does the cost, but it is seen as one of the cheaper remediation methods. According to Åtgärdsportalen (2015) the method can be used both at pollution sources as well as in contamination plumes. A way to confirm that biodegradation is taking place is to measure the concentrations of the daughter products (Alexander, 1999).

Optimal conditions for the bioremediation process is when all environmental requirements are satisfied, and the only factor limiting the growth of the bacteria is the targeted contamination (Skladany et. al., 1993). If daughter products are present at the site, reductive dechlorination is probably ongoing (Puigserver, 2014). Some important factors include temperature (optimally between 25 - 35 ^{o}C), pH (optimally between 6,5-7,5), the level of dissolved oxygen, and available nutrients (Åtgärdsportalen, 2015). According to Puigserver (2014), positive indicators for conditions suitable for reductive dechlorination is a concentration of methane, ferrous iron and sulphide above 1 mg/l. The concentration of dissolved oxygen should be low, preferably below 1 mg/l, and the oxidation-reduction potential should preferably be below -50 mV (USGS, 2006).

2.3 EARLIER STUDIES

It has been proved in multiple studies that reductive dechlorination in the presence of *Dehalococcoides* is a successful way to remediate sites contaminated with chlorinated ethenes (Matteucci et al., 2015., Vogel, 1994., Volpe et al., 2007 etc.). Instead of further discussing this, focus has been on finding studies investigating sites with similar conditions to the site studied in this project, as well as studies discussing factors that could be relevant to the bioremediation of the site. It was difficult to find studies investigating the process of reductive dechlorination outside of a controlled environment. It was also difficult to find studies investigating the general process rather than merely a specific part of the remediation.

As further discussed in section 3.1 the site in Huddinge was situated in an area of low permeability. The main contaminant at the site was TCE. The chlorinated ethenes present in the highest concentrations were TCE, cDCE and partly VC. The levels of dissolved oxygen on the site are generally low but are at times higher than what is normally used to describe anaerobic conditions. These are the conditions whose impact will be researched in earlier studies.

2.3.1 Site contaminated with PCE in Manhattan, Kansas (Eriksson et. al., 2011)

In this pilot field study, a site contaminated with PCE was studied. The soil on the site was alluvial silty sand soil with less than 10 % silt. A nutrient solution was added to stimulate the reductive dechlorination, which led to significant decreases in oxidation-reduction potential as well as in the levels of dissolved oxygen. An increase in the levels of DCE was observed after 34 days. It was observed that the conversion of TCE to DCE was much faster than that of DCE to VC. On the studied site, the concentration of chlorinated ethenes were seen to vary partly with periods of large precipitation, often with a certain lag period that seems to depend on the site-specific conditions.

2.3.2 Enhanced reductive dechlorination in clay till (Bjerg et. al., 2013)

This study investigated reductive dechlorination on a site with 2-3 m of top fill on the top, with clay till mixed with sand lenses underneath. The clay till had a low permeability compared to the sand lenses. TCE was the principal compound of contamination with an initial concentration of 740 000 µg/l in the groundwater. The degradation was initially occurring mainly in the high permeable areas in the soil, namely the sand lenses, but was later observed in the clay till matrix as well. The complete degradation was faster in the areas of higher permeability. Within 4 years the degradation was occurring everywhere in the observed area and the mass reduction was 24%.

All TCE in the source area was completely degraded into cDCE after 4 years. Degradation of cDCE into VC and ethene was observed in both the plume and source area. The total levels of all chlorinated solvents increase by a factor of 2-4 from the initial observations to day 1331, which the authors suggest might be due to TCE being degraded into the less sorbing compounds of cDCE and VC. In one borehole in the investigated area, the observed levels of TCE and cDCE are similar, which the authors suggest might be due to desorption of TCE from sediments or concurrent dissolution from a solvent phase.

2.3.3 Study of sorption and diffusion of chlorinated ethenes in clayey till (Lu et. al., 2011)

The study examined the behaviour of chlorinated ethenes in natural clayey tills and discovered that the more chlorinated the compound the more strongly it sorbed to the clay samples. It was also found that if the concentrations of the chlorinated ethenes in fractures in the clay matrix were reduced to below that of the matrix, diffusion of the chlorinated ethenes from the clay matrix to the groundwater was caused.

2.3.4 Remediation of chloroethenes in fractured clay till (Manoli et. al., 2012 and Chambon et. al., 2010)

Clayey tills are commonly heterogenous with low permeability zones (the clay) and high permeability zones (sand lenses and/or fractures). The zones of higher permeability largely affect the transportation times in the soil, with especially fractures increasing the speed of the transport. In low permeability soil, the transport of both chloroethenes and injected stimuli is strongly influenced by diffusion and sorption processes in the clay matrix, so the bioremediation in the clay matrix may be limited to areas around the fractures and/or sand units. As the diffusion process is slow, this greatly affects the time to complete remediation. Complete remediation can be difficult and rebounds of chloroethenes can occur during or after the treatment. Re-injecting stimuli may limit the effects of the rebound. Tests with tracers have confirmed the large influence on the transport by fractures in the clay, in which an increased velocity can be seen.

Diffusion limited-transport mainly applies to PCE and TCE, as the daughter products cDCE and VC are more mobile. During the remediation the total concentration of the chloroethenes in the sampled water increased, which was hypothesized to be due to higher mobility of cDCE and VC compared to TCE and PCE.

2.3.5 Migration of TCE through fractured clay with interbedded sand lenses (Reynolds et. al., 2001)

Historically, low permeability soils such as silts, clays etc. have been seen as barriers limiting migration of DNAPLs. It has however been shown that fractures in the low permeability areas are very common, which removes their ability as barriers. The number of fractures normally decreases with the depth of the soil. As the fractures are of very limited volume, DNAPLs have been found to travel large distances through the pathways formed by interconnected fractures. It is however hard to predict the transport as clays commonly are very heterogenous. If the DNAPL migration is fast, the process of diffusion has little effect on the change in mass, but if the migration is slow the opposite can be expected.

Sand lenses have been shown to increase the time of vertical transport in clayey soils, which is thought to be due to the sand lenses blocking the fractures. The sand lenses have a much larger retention capacity than the fractures, which can lead to an increase in the time of transport from the order of days to years. The direction of the groundwater significantly affects the time of transport, with a downward gradient decreasing the transport time.

2.3.6 Competition for hydrogen between methanogens and dechlorinating bacteria (Aulenta et. al., 2007 and Lu et. al., 2001)

In the field study by Aulenta et. al. (2007), a decrease in the formation of DCEs was observed during the remediation process, which was hypothesised to be due to an increased competition between iron-reducers and/or methanogens and dechlorinating bacteria for hydrogen. According to Lu et. al. (2001), dechlorinators of TCE were observed to thrive at low concentrations of hydrogen (in the order of 0.6-0.9 nmol/l) but the dechlorinators of DCE and VC needed a higher concentration of hydrogen (0.1-2.5 and 2-24 nmol/l respectively). Reduction of sulphate and methanogenesis both happened at a hydrogen concentration of above 1.5 nmol/l. This means that they may compete with dechlorinators inside that interval, which is mainly with the dechlorinators of DCE and VC.

2.4 METHODS OF STATISTICAL ANALYSIS

To examine how the chlorinated solvents and their degradation products coexist and possibly affect each other, a correlation analysis was done using principal component analysis (PCA) and a Partial Least Square (PLS) regression. Relevant parameters such as water chemical parameters are measured regularly in the area and will also be part of the analysis.

2.4.1 Principal component analysis

Principal component analysis (PCA) is a method sprung from linear algebra and used in various fields to analyse data (Shlens, 2005). The data set is organized as a matrix, where the rows describe the objects (i.e. what is being measured, for example different groundwater pipes) and the columns describe the variables (i.e. the measured values, for example of TCE) (Shlens, 2005). When many variables are present in a data set, it can be challenging to detect trends and/or other structures within the data set. To make the assessment easier, PCA can be used to reduce the dimensions of a complex set of data while still maintaining most of the variation within the data set (Ringnér, 2008).

According to Shlens (2005), there are four assumptions that have to be made in order to use PCA:

1. The data set is linear.
2. The principal components are orthogonal.
3. The large variances in the data set contains important information.
4. The data set can be described sufficiently using only the mean and the variance.

By assuming number 3, that large variances represent important information and dynamics in the data set, the dimensionality of the data set can be reduced to a few representative components – these are called the principal components (Ringnér, 2008). These new principal components are linear combinations based on the original data set (Abdi, 2010). According to Abdi (2010), the first component (PC1) is essentially a vector in the direction of the largest possible variance in the data set. The second component (PC2) is likewise a vector in the direction of the largest possible variation, with the added constraint that it has to be orthogonal to the first component. A visual example with two principal components is shown below in Figure 4.

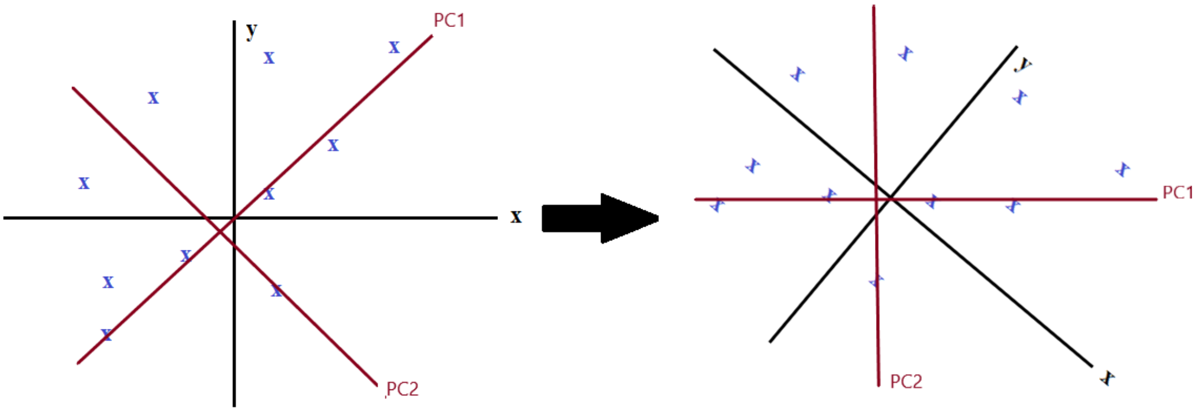


Figure 4. A visual example of the original data set (left) being adjusted to their principal components PC1 and PC2 (right).

The number of principal components used depends on the eigenvalue of the created vectors (Shlens, 2005). According to Shlens (2005), the eigenvalue of the vector describes how much variance (and therefore information) there is in the data set in that direction. For example, if the eigenvalue of PC1 and PC2 are much higher than the rest, there is a lot more information in these directions than in the other and as so only these two are needed to describe the data set in an adequate way.

When the principal components are chosen, the matrix of data from the original data set is changed to fit this created set of vector bases in the direction of PC1&PC2 (Vidal et al., 2016). This new matrix can be understood by studying equation 1 below, based on Esbensen, (1987). The original matrix is called X.

$$X = P * Q^T + E = M + E \tag{1}$$

where
X = The original, complex matrix
M = the PC- model, the underlying structure, which can be split up in P and Q^T
E = Noise
P = The created (new) matrix, with reduced complexity
Q^T = The principal components

According to Ramette (2007), the data set needs to be prepared before performing a PCA, if it doesn't already have a uniform scale or an adequate format. This is normally done automatically if a statistical package is being used. First, the data set needs to be auto scaled. This is usually done by dividing all variables with their standard deviation to make sure all variables affect the model equally. The data set might also need to be centered, which is done by subtracting the mean of every variable to keep the disparity of the objects. The variables are then weighted in a process called *loading*, where the variables with the highest variance (i.e. the highest influence on the principal components) get the highest loading. Outliers might have to be deleted from the data set to be able to make trends clearer. When the principal components have been found, the data set is projected on the new axes, where the length of the projections on the axes is called *scores* (Abdi, 2010). This translates the values of the objects to the new coordinate system. All scores are a linear combination of the original matrix.

When analysing the result of the PCA the graphs of PC1 plotted against PC2 are studied. Extreme values are detected and if necessary deleted, and the plots are studied to find eventual correlation or grouping (Shlens, 2005). Variables that are strongly correlated can be identified by the fact that they group together (Shlens, 2005).

The loadings plot and the scores plot are also studied. According to Eriksson (2006) the loading plot (which is also called the correlation plot) can be interpreted in the following way:

- Two variables placed closed to each other in the same quadrant are positively correlated.
- Two variables placed in the quadrants diagonally opposite each other are negatively correlated.
- Two variables placed orthogonally in reference to each other are not correlated.
- The closer the variables are to the origin, the lesser impact they have on the principal components.

In this project, PCA will be used to analyse data of the degradation resulting from the reductive dechlorination, together with data of the site's water chemical data (pH, nitrate, oxygen levels, conductivity etc.). It will be studied how the variables relate to each other and to the other parameters, as well as to study similarities and dissimilarities between the observed pollutant concentrations. Eventual outliers will be identified and analysed. PCA will be used as an overview of the data set, and strong groupings and outliers in the graphs will be studied, as well as any correlations found within the data set.

PCA was performed using both the tool SIMCA and XLSTAT.

2.4.2 PLS

When PCA has been used to get an overview of the data and eventual correlations/outliers within the original data set, Partial Least Square (PLS), or Projection to Latent Structures as it also is known as, can be used to further identify and analyse these correlations. The explanatory power of the different variables will be studied in order to gain an understanding of the relationship between the variables and the responses. The responses are in this case the measured concentration of the pollutants in the groundwater pipes.

When using PLS regression the main goal is to find relationships between the descriptor matrix (X) and the response matrix (Y) (Ericsson, 1995). A further goal is to simplify the data set, as is done in PCA and for the same reasons, by finding the most important information though a reduction of dimensions (Trygg, 2002). When using PLS, it becomes possible to compare and plot one or several variables at a time (Ericsson, 1995). This makes PLS a useful tool in analysing complex data sets visually.

In PLS, the matrices X and Y are decomposed into new matrices, as can be seen in equation 2 and 3, based on Maitra et al. (2008).

$$X = T * P^T + E, \qquad (2)$$

where T is the scores of X, P^T is the loadings of X and E is the residuals of X.

and

$$Y = U * Q^T + F, \qquad (3)$$

where U is the scores of Y, Q^T is the loadings of Y and F is the residuals of Y.

The meaning of *loadings* and *scores* are the same as for PCA. The decomposition described in equation 2 and 3 is made to maximize the covariance between T and U (Maitra, 2008). This is done by combining the scores of U and T with the variables in Y and X with weights (c and w) chosen to maximise the correlation with the other matrix (MKS Umetrics, 2012). This is a difference from PCA, when only the variance in the matrix X is maximised. In PCA the correlations are sought only in the matrix X, in PLS the correlations between the matrices X and Y are studied (Ericsson, 1995). The data set is normally automatically adjusted in the same way as for PCA, i.e. it is auto scaled and centered.

What PLS does is essentially to act as a tool that forms new variables (the t-variables in the matrix T), which are linear combinations of X, and predicts Y using these new variables. A useful tool to investigate the relevance of each X-variable in all dimensions and compared to all Y-variables, is to use the Variable Influence on Projection (VIP) table (Eriksson, 1995). It shows us what variables are important for explaining the matrix X and its correlation with the matrix Y and is a weighted sum of squares for weights used in PLS (w), taking the amount of explained variance into account (Umetrics, 2012). A VIP-value larger than 1 shows that the variable is important to the model, and that the correlation is significant (MKS Umetrics, 2012). As the VIP-value sinks towards 0,5 the correlation becomes less significant.

If the Y-variables are correlated, it can be useful to analyse them together to get an easier overview (Ericsson, 1995). To investigate this, a PCA on the Y-variables can be used before computing the PLS. Linearity between the X and Y-variables is important to obtain a good model (Eriksson, 2006), which can be tested by plotting the first object vector of X versus the first object vector of Y.

To determine a fitting complexity (when the components stop being significant) of the PLS model, cross-validation (CV) is often used (Ericsson, 1995). In a model with a good fit the explanation of the variability of the X variables (R^2_X) and the Y variables (R^2_Y) do not differ too much from the predicted variation (Q^2) of the descriptor variables (Y) in the model. R^2_i and Q^2_i are explained below in Equation 4 and 5 (Miljöstatistik, n.d.).

$$R_Y^2 = 1 - \frac{\sum F^2}{\sum Y^2} \tag{4}$$

$$Q_Y^2 = 1 - \frac{\sum (error\ in\ prediction)_Y^2}{\sum Y^2} \tag{5}$$

where F is the residual, as explained earlier in equation 3.

R^2_Y should generally not exceed Q^2 by more than 2-3 units (Eriksson, 2006). An R^2 below 0,5 indicates a large amount of noise in the data set, although the model can still be useful but the results should be interpreted with care and the model should if possible be validated with a validation set (MKS Umetrics, 2012).

The plots produced by PLS regression resemble those produced by PCA, with correlation and score plots showing the placement and eventual grouping of the variables and observations. In the correlation plot the variables *w* and *c* are used instead of the principal components. W and c are the loadings of the X-variables and the Y-variables respectively and indicate how much the variables participate in explaining the other matrix (X or Y) (MKS Umetrics, 2012). The loadings are plotted as the w*c for one principal component versus another. Variables close to the origin show a weaker correlation to the Y-variables than those placed further away. Depending on the position of the variables a negative or positive correlation can be displayed. X-variables positioned close to each other are correlated.

In this project, PLS will be used to further study the variables of interest located using PCA. The relationship between the measured variables and the chlorinated compounds will be studied for correlations. The analysis was done in SIMCA and the interpretation of the PLS regression was done graphically with support of the VIP-tables.

2.5 DEGRADATION DYNAMICS

A study of the degradation dynamics throughout the bioremediation process is done to analyse the distribution of different chlorinated compounds and of other relevant parameters throughout the remediation process. The analysis is done on the degradation dynamics of PCE and TCE to VC. The end product of ethene is not analysed, as ethene is difficult to use as an indicator of complete degradation as it is produced and degraded by many natural processes.

It is instead assumed that when degradation until VC seems to occur, it will proceed to complete dechlorination with VC being converted into ethene.

To examine the degradation dynamics of the process a broad analysis is done, which is based partly on a tool showing the dechlorination and distribution of different chlorinated compounds over time, developed by WSP. In this Excel-based tool the levels of the different contaminants present at the site at the different sampling times are summarized and the dechlorination of the mother product (TCE or PCE) on site is described. As this tool requires more input than the statistical analysis methods and does not accept missing values, somewhat less observations will be used than in the statistical analyses. Dechlorination is defined in the tool as the percentage to which a mother product (TCE or PCE) is degraded, which is calculated by dividing the amount of degradation products available with the total amount of products. As TCE is the main contaminant on the site, it is chosen as the mother product in the tool.

The levels of contamination over time in the different groundwater pipes is also analysed in GIS to obtain an overview of the contamination spread in the system.

3. DATA USED IN THE PROJECT

The data necessary for the analysis was provided by WSP. The background of the project and the collection of data are described below.

3.1 BACKGROUND

The data material was collected by WSP from a bioremediation project on a site in Huddinge municipality. The site is undeveloped as of now, but the planned building project for the premise is a kindergarten and a retirement home. Some decades earlier an industry on the site had been producing printed circuit cards. In this production, they reportedly used TCE for degreasing from at least 1975. As children and elderly people will be spending time on the premise, the remediation must result in levels of contaminants below those specified in Naturvårdsverket’s guideline values for sensitive land use (KM). The permeability of the area is shown below in Figure 5.

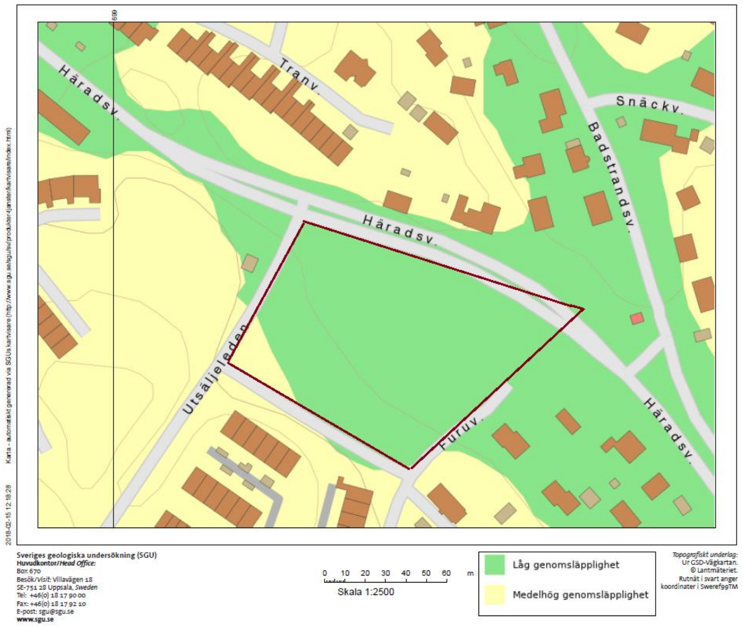


Figure 5. The soil permeability of the investigated site, with green representing low permeability and yellow representing mid-high permeability. The map is based on SGU: s (Sveriges Geologiska Undersökning) map-viewer Permeability, which is based on four levels of permeability: low, mid-high, high, and not classified.

As seen in Figure 5, the studied area can be seen to consist mainly of low permeability except for in the lower left corner where there is an area of mid-high permeability. The soil of the area is shown below in Figure 6.

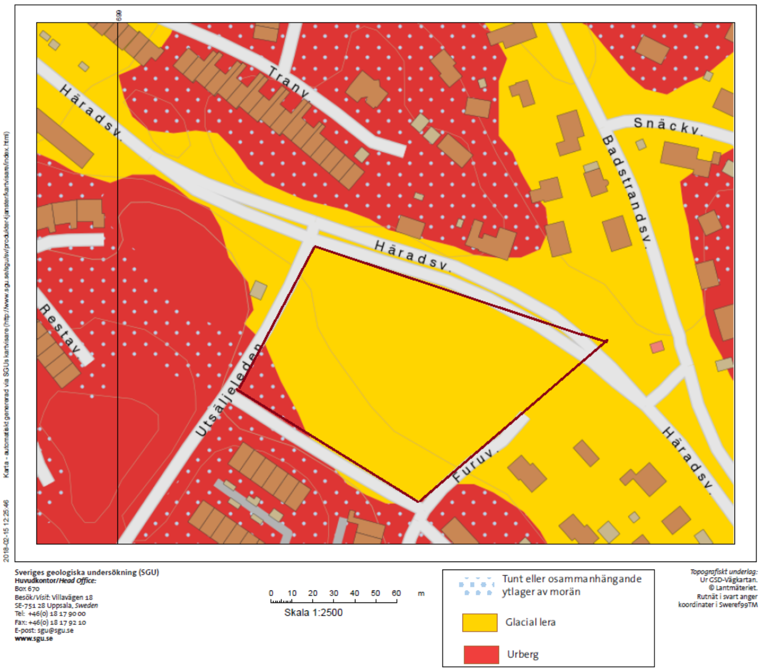


Figure 6. The soil of the investigated site, with yellow representing glacial clay and red representing bedrock. Moraine is represented by light blue dots. The map is based on SGU: s map viewer Soils 1:25 000-1:100 000.

As seen in Figure 6 the studied area consists mainly of glacial clay except for in the lower left corner which consists of bedrock and moraine. Based on sampling done by WSP the top layer seems to be 1-2,5 m of filling, mainly by gravel and sand. Below this layer there is a layer of clay with elements of silt and sand that is around 1-3 m thick. Below this bedrock or layers of sand and silt of varying thickness can be found. It is assumed that the groundwater moves towards the south east due to the position of the bedrock and measurements of the groundwater levels in the groundwater pipes.

The analysis done by WSP before the start of the remediation indicated that the groundwater environment was reductive and that the concentration of electron acceptors (oxygen, nitrate, sulphate etc.) that could compete with the chlorinated ethenes were low. This makes for a good environment for reductive dechlorination and sampling showed the presence of daughter products, indicating that natural dechlorination already was taking place. To speed up the process a stimulus in the form of a carbon source was added. The used carbon source consisted of a three-stage release system from a compound that first releases lactic acids (immediate release), then organic acids (mid-range release) and lastly fatty acids (long-term release).

The carbon source was injected directly into the soil using a steel probe in multiple places within the remediation area. It was also injected along three plume barriers south east of the source area to prevent the spreading of contaminants, as seen in Figure 7 below.

Figure 7. The remediation area (yellow) and plume barriers (orange) to prevent spreading (WSP, 2016b).

Around the 10th of November 2017 drilling was done in the area, to prepare for the planned exploitation of the area. This resulted in air being injected into the soil in several points around the area, which would in part inhibit the dechlorination process.

The aim of the remediation is to achieve acceptable concentrations in the indoor air. To achieve this the mean concentration of TCE in the groundwater is set to be remedied to 50-100 µg/l. The goal is said to be achieved when the following has been observed in three consequent observations with at least two months between the observations: the mean of the levels of TCE are 50-100 µg/l in the contaminated area (in at least 3 groundwater pipes), the levels of DCE are decreasing and ethene and ethane are observed.

3.2 COLLECTION OF DATA

A total of fourteen groundwater pipes were installed, three of which were placed in the area where the highest concentration of TCE in the soil gas was found, and eleven were placed to estimate the area of the plume. Two groundwater pipes were earlier installed on the premise (GR15GW01 and GR14G04U). The placement of the groundwater pipes can be seen in Figure 8. For the monitoring program, post injection, the levels of chlorinated compounds and water chemical parameters were measured in seven groundwater pipes: 15GW01, 15W109, 15W110, 15W111, 15W112, 15W113 and 15W114. These are marked with red ovals in Figure 8.

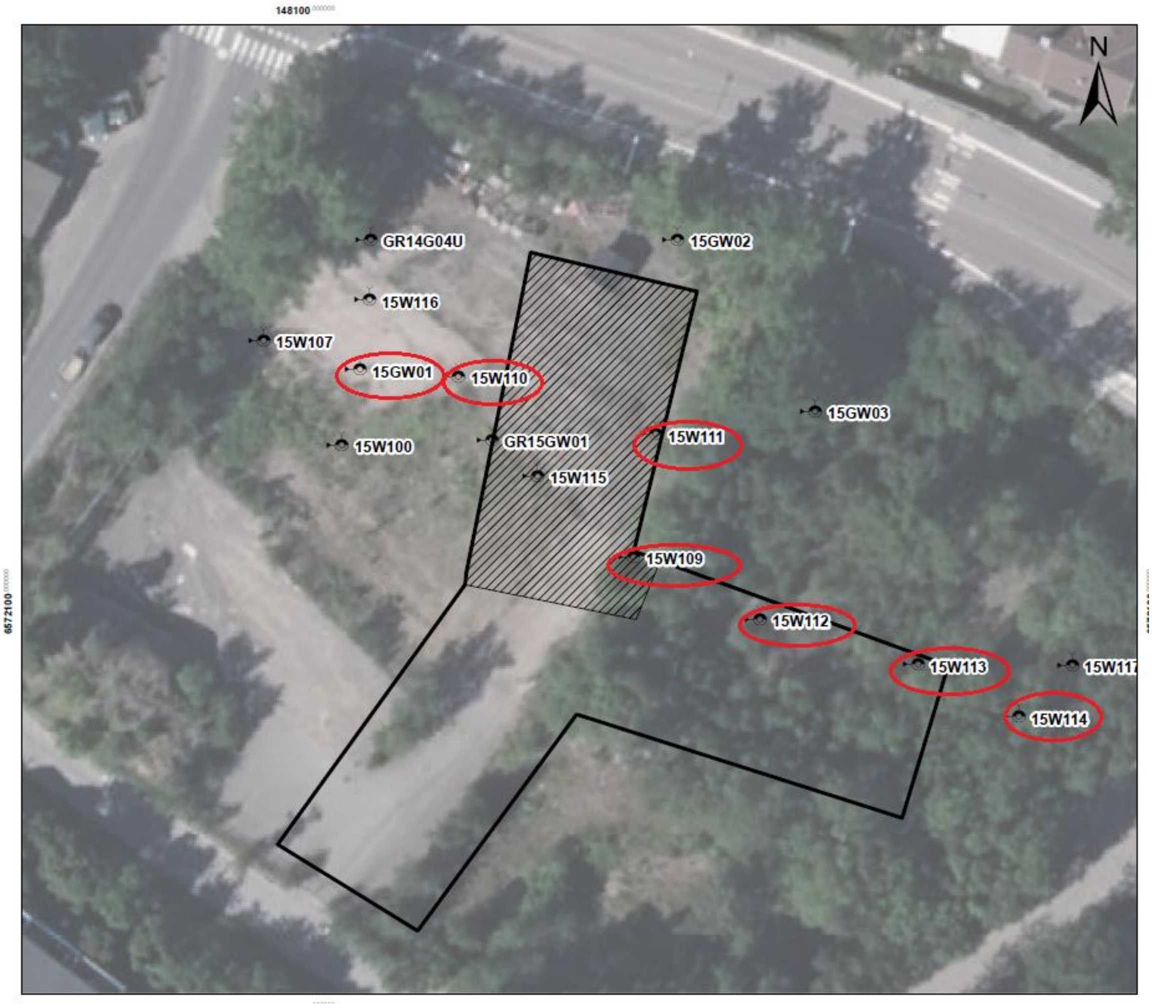


Figure 8. The placement of the groundwater pipes, with the groundwater pipes where the data has been collected marked in red and the contours of the planned building in black (WSP, 2016a).

After groundwater turnover in the pipes using a waterra pump and a tube or bailer, the groundwater was sampled directly into the vials intended for laboratory analysis. During the first year after injection, groundwater sampling was done every six weeks. Field analysis was done on every sample, laboratory analysis was done on every second sample. Year 2 and 3 the sampling was done every third month, and every sample was subjected to both field and laboratory analysis.

During the field analysis the following was measured:

- pH
- concentration of oxygen (DO)
- temperature
- specific conductivity (SPC)
- oxidation reduction potential (ORP)

During the laboratory analysis the following was measured:

- chlorinated ethens and their degradation products (i.e. PCE, TCE, cis-DCE, trans-DCE and VC)
- ethene, ethane and methane

- Chemical parameters in the groundwater: pH, nitrate, sulphate, chloride, Fe^{2+}, Mn^{2+}, alkalinity and dissolved organic carbon (DOC)
-

3.3 HANDLING DATA BELOW LIMIT OF DETECTION (LOD)

In the data set provided from the investigated site, many values were marked as below limit of detection (<LOD), in particular for the pollutants PCE (72%) and tDCE (53,4 %), and also partly for cDCE (26,5%). What the LOD-values states is that the detected concentration is between zero and the LOD, which provides a challenge for data analysis. The exact concentration, or if the contamination is present at all, is unknown and in the data analysis the LOD-data is present as many data points with the same concentration. This can lead to an inaccuracy and a potential large statistical bias, especially when the percentage of LOD-values is above 50 % (EPA, 2009). When choosing to deal with LOD-values by excluding or deleting them, a proportion of the data used to explain a certain situation is lost and can lead to incorrect conclusions (Hesel, 2010). There are several methods that can be used to estimate the concentrations in the LOD-values by for example estimating them from a regression on a probability plot of all the non-LOD-values in the data set. This method could be useful to see how the data may variate, but as the data will be used in correlations analysis in this project, any estimation of the LOD-values might give misleading correlations. The LOD-values will be set to the value of LOD are in the analysis.

4. RESULTS

4.1 RESULTS OF PCA

In the principal component analysis, the data set was checked for outliers. In a PCA outliers can be easily spotted as they are placed outside the 95% confidence interval of the data set. Potential outliers can affect the accuracy of the way the model reflects the process and should therefore be investigated.

The data was log-transformed before the analysis was done, both for PCA and PLS. This is done to make the data set linear, which is a prerequisite for using PCA and PLS. When the data was log-transformed, the variables that where zero or below disappeared. This mainly affected the values of oxidation-reduction potential (ORP), which is why this variable is left out of the analysis. A separate analysis was done with ORP to compensate. The correlations within the data became clearer and a model with a better fit was obtained when the data was log-transformed.

The number of observations available was 75 and for 7 of them data was systematically missing. Data with systematically missing observations is not recommended to be used when performing PCA and PLS in SIMCA. Therefor those points were removed, and the remaining 68 data points were used when performing PCA and PLS regression.

As earlier mentioned, 72% of the observations of PCE in the data set, 26,5% of the observations of cDCE and 53,4% of the observations of tDCE were below the limit of detection (LOD). As the LOD-values are marked at the same value, the lack of variation makes analysing this data with both PCA and PLS difficult and uncertain.

With PCE having such a large number of observations at the limit of detection, the models will not be very certain. Because of this, together with the fact that TCE, not PCE, is the principal contaminant of the site, no analysis done exclusively on PCE will be presented in this study. The number of observations of tDCE at the limit of detection is also large enough to make the resulting models uncertain, and as such a small amount of tDCE is formed in the degradation process, the results of the PCA and PLS regression on tDCE will not be shown either. The results of the PLS regression on PCE and tDCE can be found in Appendix B, but they should be interpreted carefully as the resulting models are uncertain. Both PCE and tDCE are however present on the site and will be kept in the analysis as a measure of how it affects the other contaminants.

4.1.1 PCA for all components

The spread of the observations can be seen in the score plot in Figure 9 below. The observations are colour coded after which groundwater pipe they were sampled from. They are marked with the number of their groundwater pipe and from the first observation to the last, starting at 1. The ellipse in the score plot represents the 95% confidence interval for the observations, and outside it two outliers can be identified. As the confidence interval is at 95%, it can be expected that 5% of the observations are outliers, which with 68 observations corresponds to 3.4. The number of outliers does not exceed this value.

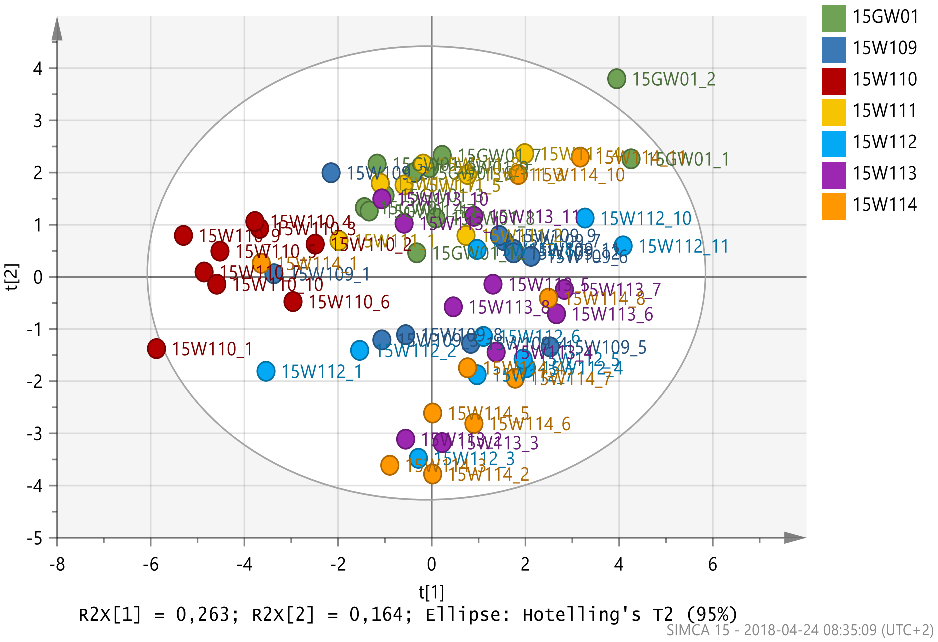


Figure 9. Score plot for the PCA done over all variables.

The outliers observed in Figure 9 are the first observations in groundwater pipe 15W110 and the second observation in groundwater pipe 15GW01, which represent real abnormalities in the data. 15GW01 is located at the source of TCE and as such has higher levels of PCE and TCE for both the first and second observation (15GW01_1 and 15GW01_2) which makes 15GW01_2 an outlier and 15GW01_1 close to being one. Groundwater pipe 15W110 has the lowest initial concentrations out of all the groundwater pipes, which makes 15W110_1 an outlier in the analysis. As the outliers reflect variations in the data, as opposed to misprinted data or typing errors, and are not located far away from the rest of the observations they are not removed as they are seen to hold valuable information.

The correlation between all components were analysed graphically from the correlation plot. It is shown below in Figure 10. See section 2.4 on how to interpret the analysis.

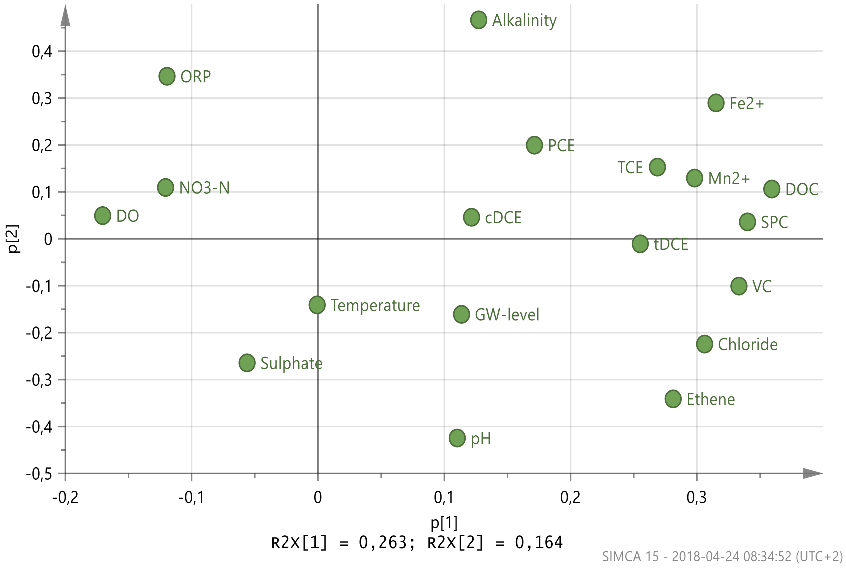


Figure 10. The loadings of the different parameters, with the model explaining 42,6% of the variation within the observations. P_1 and P_2 are the 1rst and 2nd principal components.

When the score plot in Figure 9 is compared with the correlation plot in Figure 10, it can be seen that because the scores of the groundwater pipe 15W110 (red) all keep to the left quadrants, it is indicated that there are higher levels of nitrate, oxygen and oxidation-reduction potential (ORP) present in that groundwater pipe than in the others. The scores of the groundwater pipes 15GW01 (green) and 15W111 (yellow) are mainly located in the upper quadrants, indicating high alkalinity and perhaps higher concentrations of PCE and TCE in those groundwater pipes. The scores of the other groundwater pipes are more scattered and drawing similar conclusions for them is difficult.

Most of the components in the correlation plot are gathered in the two right quadrants. There seems to be a positive correlation between ethene, chloride, VC, tDCE, SPC, DOC, Mn^{2+}, TCE, Fe^{2+} and possibly PCE. Dissolved oxygen (DO) seems to be negatively correlated with VC, tDCE and TCE, and possibly also with cDCE and PCE. The ions Fe^{2+} and Mn^{2+} as well as DOC and chloride also seem to be negatively correlated with oxygen. pH and alkalinity seem be negatively correlated. Other correlations might also be represented in the plot, but as they seem to have a weaker correlation, closer scrutiny is needed to assess them.

4.1.2 PCA of the different chlorinated ethenes

When PCA was done on the chlorinated solvents one by one, without the other chlorinated solvents but together with the water chemical parameters, similar correlations were observed to the results of the PLS regression. The models of the PLS regression had higher degrees of certainty and displayed the correlations clearer, because of this only the results of the PLS regression will be presented.

4.2 RESULTS OF PLS-REGRESSION

Based on the results of the PCA, the observations where analysed with PLS regression. The outliers identified in PCA where not removed as there were not many of them and the few outliers were seen as representing real variation in the data set.

All data sets where investigated both with and without log-transformation in an attempt to obtain the most linear and less skewed relationship between the descriptor variable (X) and the response variable (Y).

A PLS was done on all response variables together, but as no clear correlation could be observed, PLS was performed on each of the response variables separately.

4.2.1 PLS – TCE

When the scores for the descriptive (X) and response (Y) variables with TCE as the response variable in the log-transformed data set were plotted against each other, a linear relationship was obtained, as seen below in Figure 11.

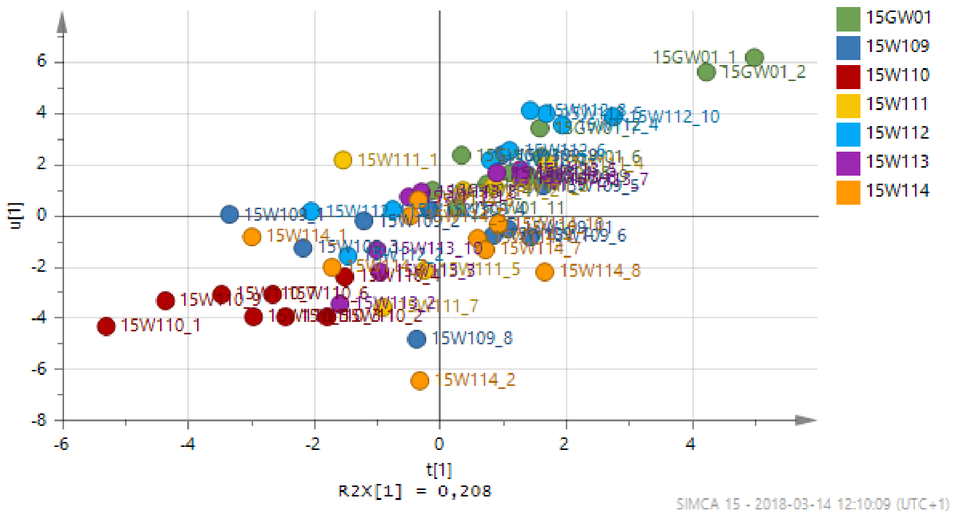


Figure 11. The plot of u1 against t1 (the scores of the Y- and X- matrix) for log-transformed data with TCE as response variable.

As seen in Figure 11, there is a relatively large variation along parts of the regression line, which affects the degree to which the model can be explained using only two principal components which will affect the certainty of the model. As a satisfactory relationship still was obtained, with the data set not showing obvious signs of skewness, the analysis will only be carried out on the log-transformed data.

When the correlations present in the log-transformed data are compared to correlations in the non-transformed data, the correlations remain the same but clearer. In Figure 12 below, the correlation plot of the log-transformed data can be seen, with variables with a VIP-value under 0,5 cleared away to make the correlations clearer.

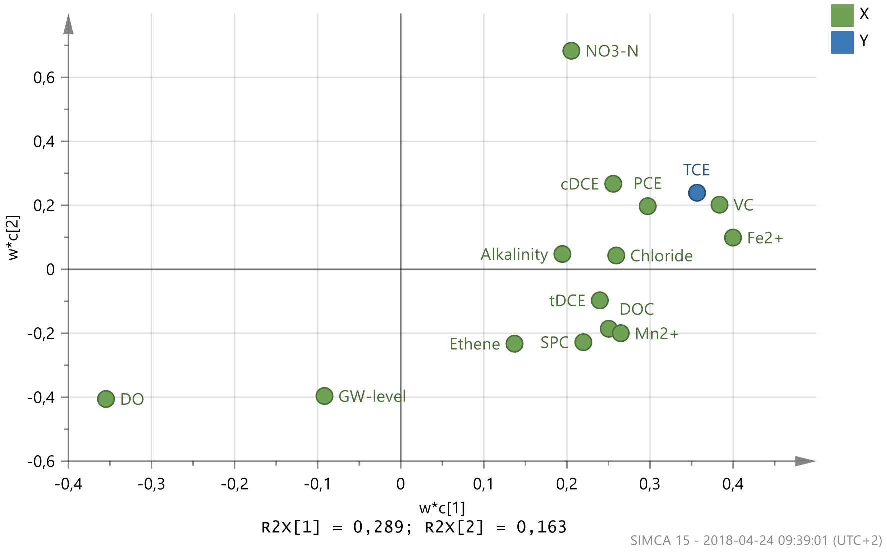


Figure 12. The correlation plot for the log-transformed data with the loadings (weights) of the variables.

The model values can be seen in Table 2 below, where the variation of the descriptor variables (R^2_X) and the variation of the response variables (R^2_Y) together with the fraction of variation of Y predicted by the model (Q^2) and R^2_Y-Q^2 is shown.

Table 2. Showing the values of R2X, R2Y, Q2 and R2Y - Q2.

	R^2_X (%)	R^2_Y (%)	Q^2 (%)	$R^2_Y - Q^2$ (%)
Log-transformed	45.2	64.9	56.8	8.1

As more than 50 % of the variation in TCE is explained by the model, and the predictability of the model is more than 50% while still being less than 20-30% below the explained variation, this model can be seen to have a good fit. In the correlation plot in Figure 12, TCE seems to correlate positively with VC, Fe^{2+}, cDCE, and PCE. There is a strong negative correlation with oxygen and perhaps also with the groundwater level. The observed correlations are strengthened by the VIP-plot, which can be seen in Figure 13 below. The VIP-plot only shows the strength of the correlation, not if it is positive or negative.

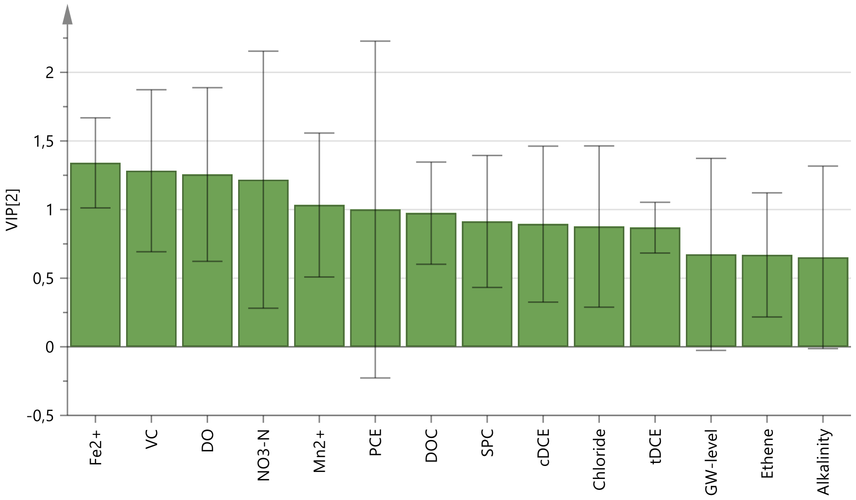


Figure 13. The VIP-plot for the log-transformed observations with TCE as the response variable.

According to the VIP-plot, TCE has a strong positive correlation with Fe^{2+}, VC, nitrate and Mn^2 and a strong negative correlation with oxygen. The observed correlation with PCE has a large confidence interval in the VIP-plot and is therefore uncertain. The other correlations are also more uncertain as VIP-value is below 1, but as the value is above 0,5 they might still be true.

4.2.2 PLS – cDCE

When the scores for the descriptive (X) and response (Y) variables with cDCE as the response variable in the non-transformed data and log-transformed data set were plotted against each other, a skewness in the data could not be avoided, as seen below in Figure 14.

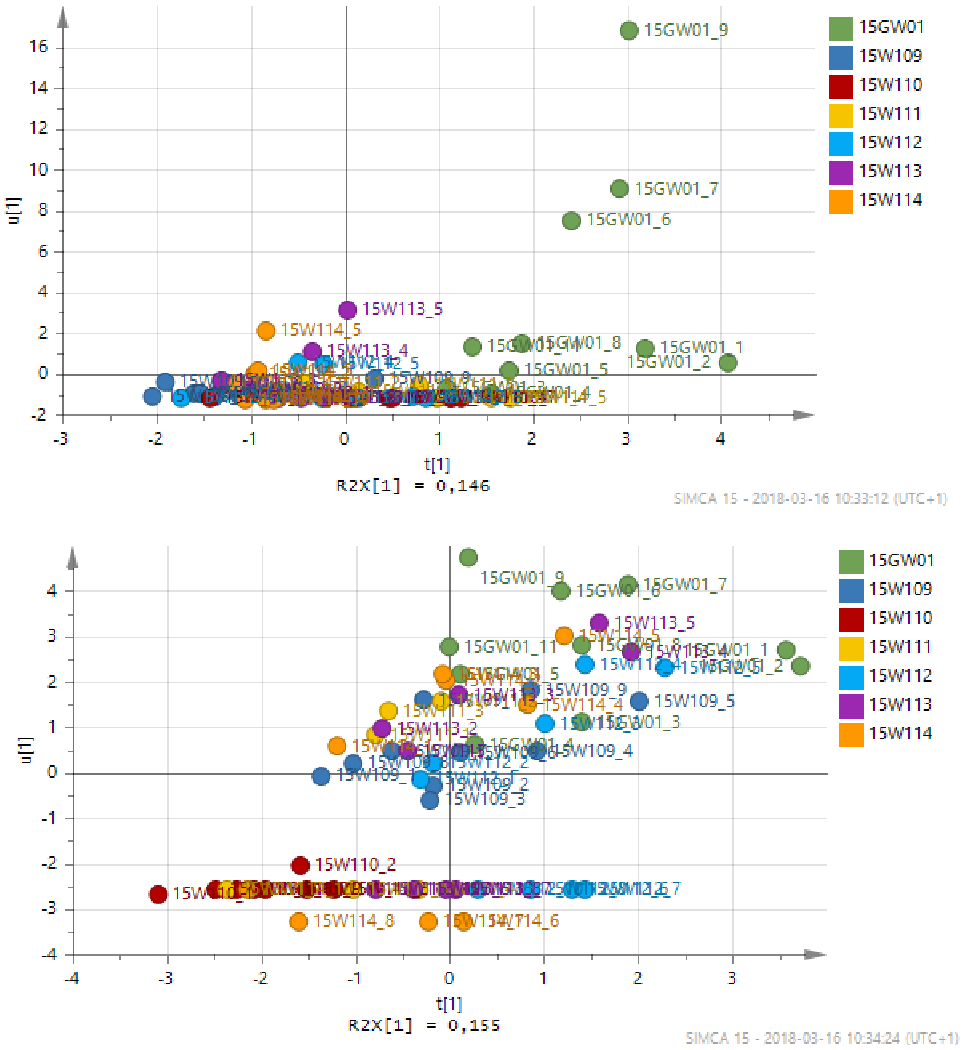


Figure 14. The plot of u1 against t1 with cDCE as response variable, with the non-transformed data (above) and the log-transformed data (below).

The large skewness in the data can be explained by the 26,5 % of LOD-values in the data for cDCE. There is also a large variation along parts of the regression line, which affects the degree to which the model can be explained using only two principal components, making the model more uncertain. The analysis was done on both the log-transformed and non-transformed data to avoid missing possible correlations.

When the correlation plots of the non-transformed and the log-transformed data sets are compared graphically, as seen below in Figure 15, many similarities are found. Strong positive correlations seem to exist between cDCE and VC and TCE in both models. Strong negative correlations seem to exist between cDCE and DOC, oxygen and SPC. The figures have been cleared from all variables with a VIP-value of less than 0,5 to make the correlations graphically clearer.

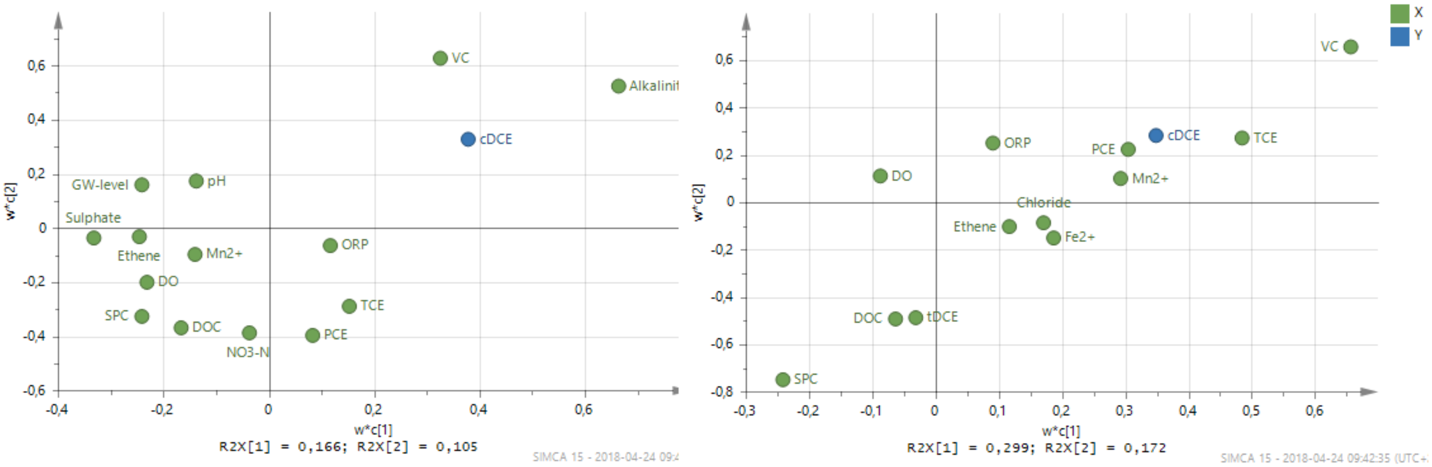


Figure 15. The correlation plot for the non-transformed (left) and log-transformed (right) data with the loadings of the variables.

The model values can be seen in Table 3 below, where the variation of the descriptor variables (R^2_X) and the variation of the response variables (R^2_Y) together with the fraction of variation of Y predicted by the model (Q^2) and R^2_Y-Q^2 is shown.

Table 3. Showing the values of R2X, R2Y, Q2 and R2Y - Q2.

	R^2_X (%)	**R^2_Y (%)**	**Q^2 (%)**	**R^2_Y - Q^2 (%)**
Non-transformed	27.1	37.7	15	22.7
Log-transformed	47.1	41.6	31.4	10.2

None of the models has a difference between R^2_Y and Q^2 larger than 20-30%, which contributes to a good fit. With a higher percentage of the variation in both X and Y explained, as well as with a considerably larger amount of the variance predicted, the log-transformed model has a better fit. However, the predicted variation is below 50%, and as it should preferably be at least 50% for an accurate model, this means that the results must be interpreted with care.

The VIP-plot for the non-transformed and log-transformed data is seen below in Figure 16. Only strong correlations present in both models are seen as significant, which means an VIP-value of above 1.

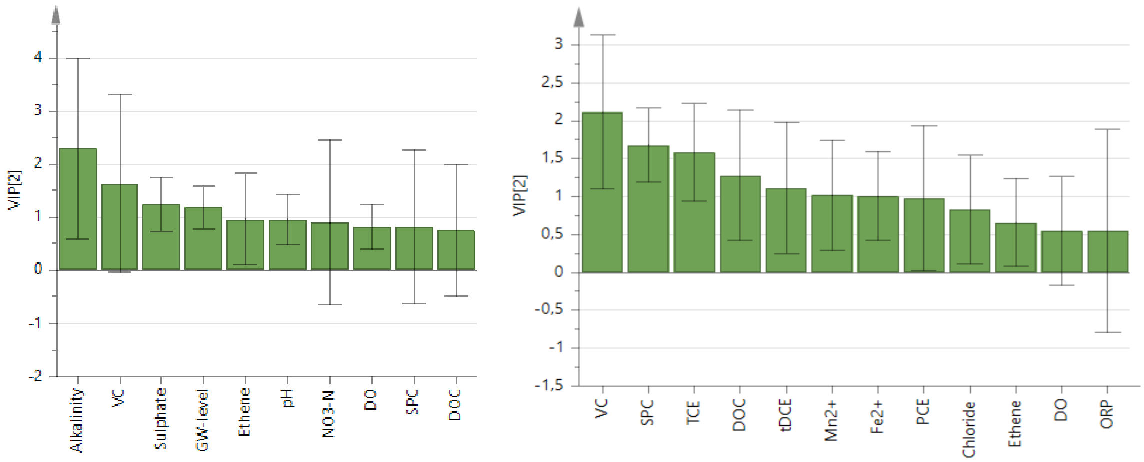


Figure 16. The VIP-plot for the non-transformed (left) and the log-transformed (right) observations with cDCE as the response variable.

The VIP-plots strengthens the strong positive correlations observed for cDCE with VC, as well as the negative correlations with SPC. The negative correlation with dissolved oxygen is slightly uncertain in the model with the log-transformed data as it has a large confidence interval but is more certain in the non-transformed data. The rest of the correlations are deemed uncertain. The model is slightly uncertain, probably due to the large number of data being at the limit of detection, which makes interpretation difficult.

4.2.3 PLS – VC

When the scores for the descriptive (X) and response (Y) variables with VC as the response variable in the log-transformed data set was plotted against each other, a linear relationship was obtained, as seen below in Figure 17.

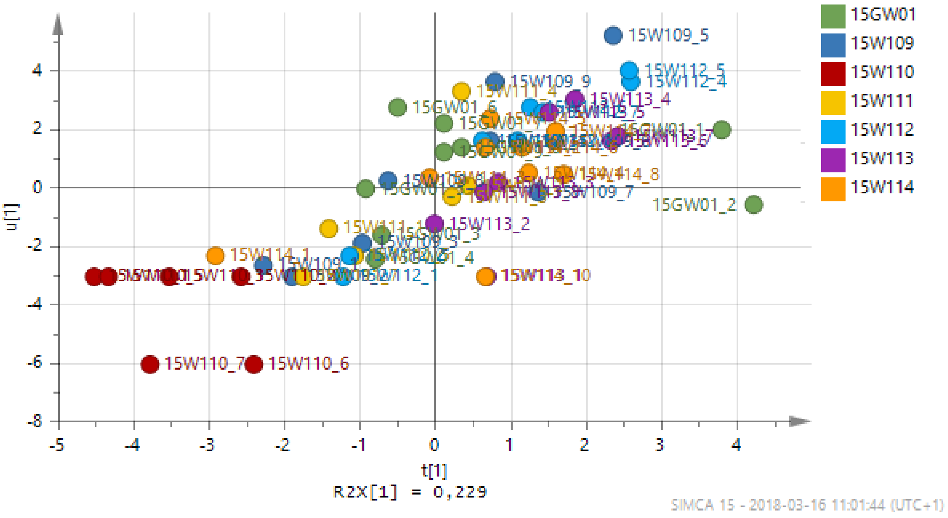


Figure 17. The plot of u1 against t1 for log-transformed data with tDCE as response variable.

As seen in the plot, there is a relatively large variation along parts of the regression line, which affects the degree to which the model can be explained using only two principal components. However, as a satisfactory relation was obtained, the analysis will be carried out on only the log-transformed data.

When the correlations present in the log-transformed data are compared to correlations in the non-transformed data, the correlations remain the same but clearer. In Figure 18 below, the correlation plot of the log-transformed data can be seen, with variables with a VIP-value under 0,5 cleared away to make the correlations clearer.

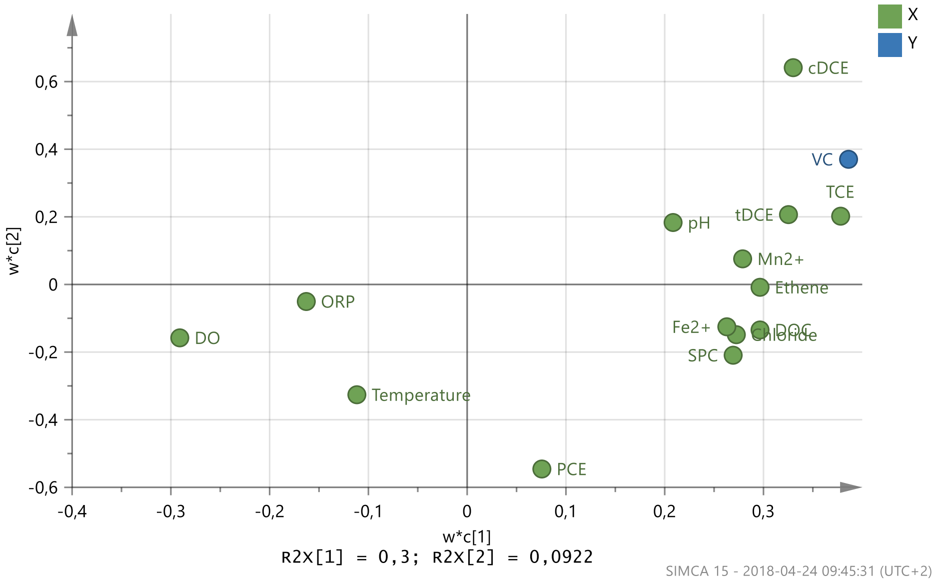


Figure 18. The correlation plot for the log-transformed data with the loadings of the variables.

The model values can be seen in Table 4 below, where the variation of the descriptor variables (R^2_X) and the variation of the response variables (R^2_Y) together with the fraction of variation of Y predicted by the model (Q^2) and R^2_Y-Q^2 is shown.

Table 4. Showing the values of R2X, R2Y, Q2 and R2Y - Q2.

	R^2_X (%)	**R^2_Y (%)**	**Q^2 (%)**	**R^2_Y - Q^2 (%)**
Log-transformed	39.2	72.0	56.2	15.8

A sufficient amount of the variation in the data is explained for the model to have a good fit, and the fraction of predicted variation in Y is over 50%, which also indicates a good fit. The difference between R^2_Y and Q^2 is below 20-30 % as recommended for a model with a good fit. Because of this, the model can be seen giving a good representation of the variation in the original data set.

When interpreting the correlation plot in Figure 18 graphically, VC seems to have strong positive correlations with above all cDCE, TCE and tDCE. A strong negative correlation with oxygen is clear in the correlation plot. The observed correlations are further strengthened by the VIP-plot, shown below in Figure 19.

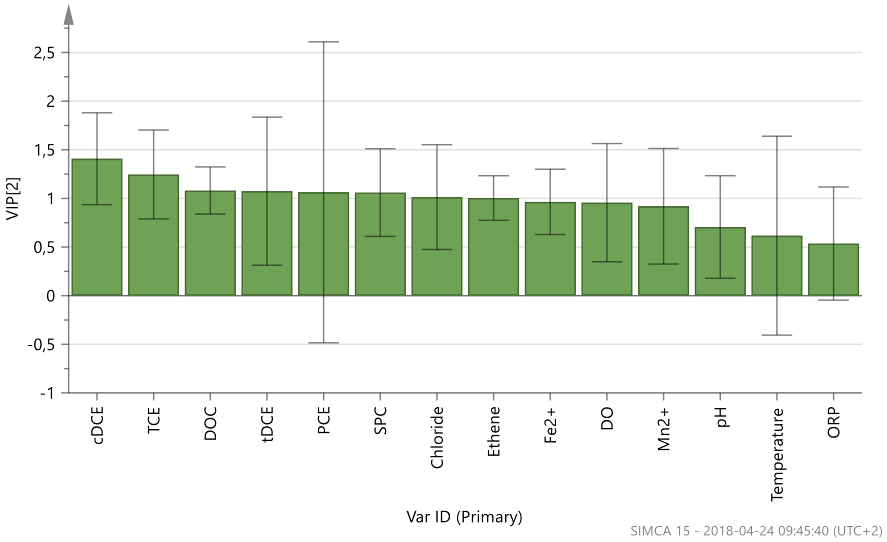


Figure 19. The VIP-plot for the log-transformed observations with VC as the response variable.

All observed correlations mentioned above seem significant. According to the VIP-plot, a positive correlation to DOC may also be present.

4.3 SITE-SPECIFIC PARAMETERS

The site-specific parameters were examined to assess how the conditions on site may influence the success of the bioremediation. As daughter products in the form of mainly *cis*-DCE were present at the start of the remediation, a natural degradation of PCE and TCE already seems to be happening in parts of the site before the start of the bioremediation.

4.3.1 Approximation of the groundwater velocity

The mean of the hydraulic conductivity measured by WSP using slug test in three groundwater pipes was $1,6x10^{-6}$ m/s. These three pipes are all located in the north-west part of the site, around the source area. The conductivity was measured in layers of friction soil above the bedrock.

When the horizontal hydraulic gradient was calculated for each observation from the position of 15GW01 to the position of 15W114 approximately 80 m away, the resulting mean hydraulic gradient was $7,342x10^{-3}$m/m. The hydraulic gradient is calculated from the groundwater surface in the seven groundwater pipes, which was the only data available on groundwater surface. Because of this the calculation of the hydraulic gradient can only be seen as an approximation of the order of magnitude of the gradient.

The porosity of the soil is measured by WSP to 0,375, which when using Darcy’s law gives an estimated groundwater velocity of $3,133x10^{-8}$, which is $2,71x10^{-3}$ m/d. This gives a velocity of around 1 m/year, which again should be seen only as an approximation of the order of magnitude of the groundwater velocity.

4.3.2 Distances between groundwater pipes

The distances between the groundwater pipes measured during the observation period can be seen below in Figure 20. The calculation of the distances was done using a picture from WSP georeferenced with Ortofoto from Lantmäteriet in GIS.

Figure 20. Distances between the different groundwater pipes. Based on a picture by WSP, 2016a.

The distance between the groundwater pipes compared to the calculated groundwater velocity makes it unlikely that the changes in levels of contaminants is due to transport in the groundwater between the groundwater pipes, as the groundwater velocity is too low to cover the distances.

The area is calculated in a rectangle to being approximately 105 m in length and 75 m in width, which gives a total area of around 8000 m^2.

4.3.3 Direction of the groundwater flow

Initially it was assumed that the groundwater moves towards the south east due to the position of the bedrock and measurements of the groundwater levels in the groundwater pipes. As limited data is available on the groundwater flow in the area, the surrounding topography is used to further estimate the direction of the groundwater flow, which is seen in Figure 21.

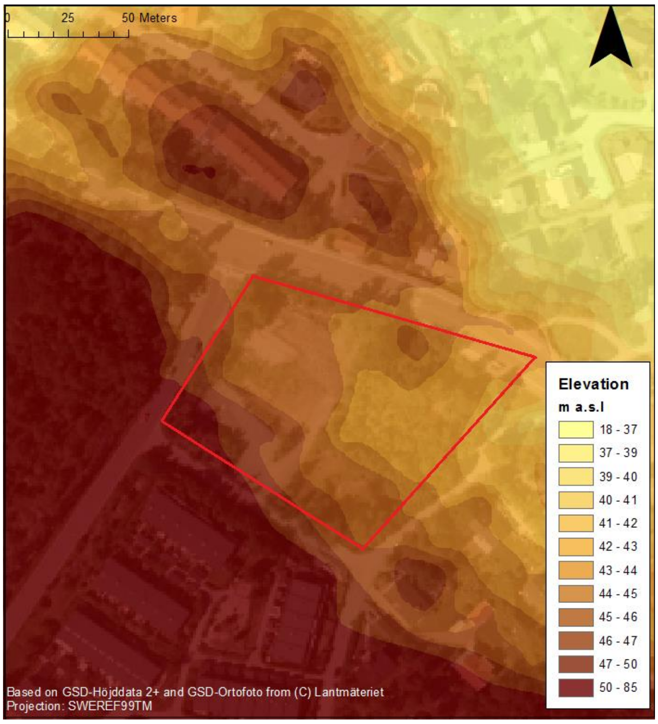


Figure 21. Shows the topography in the surrounding environment of the investigated area (red), based on data from © Lantmäteriets elevationdata and Ortofoto. The contaminated area is marked in red.

As seen in Figure 21, the ground on the contaminated site is highest in the south west part and the lowest in the north east part of the area. This may make the direction of the groundwater flow in the area more north east than south east. As no more accurate estimation of the groundwater flow can be done it is considered possible that the groundwater flow is from the south west to either the north east or south east.

4.3.4 Levels of dissolved oxygen

The variation over time in levels of dissolved oxygen are seen in Figure 22 below.

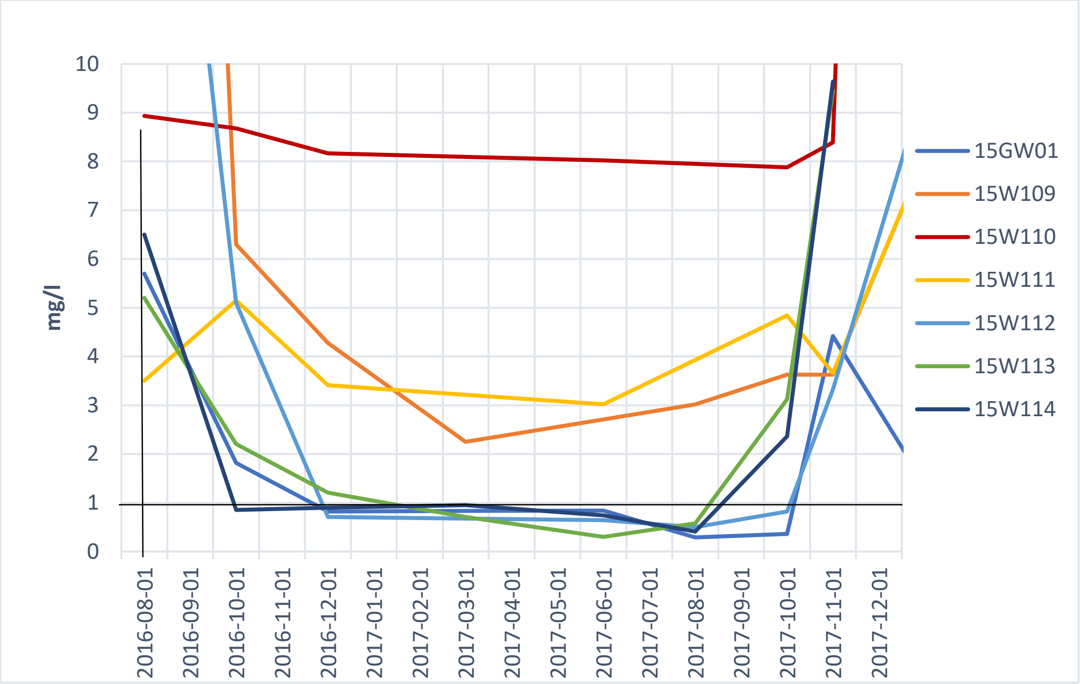


Figure 22. The variation of dissolved oxygen over time for the different groundwater pipes with the time of injection of nutrients marked as a vertical black line. The optimal DO level for reductive dechlorination (USGS, 2006) is marked with a horizontal black line.

As seen in Figure 22 the levels of oxygen drop in all groundwater pipes but 15W111 after September 2016 which corresponds to the injection of the carbon source. After this the levels stay down until a year later in October 2017 after which many of them rise. In October-November 2017 drilling was done in the area, which injected air into the groundwater. All groundwater pipes except 15W109, 15W110 and 15W111 are below the optimal levels of DO during most of the observation time.

4.3.5 Oxidation-reduction potential

The oxidation-reduction potential (ORP) is mostly below the optimal value of -50 mV (USGS, 2006); in the observations ORP is below -50 mV in 67,21% of the observations. The ORP values for all groundwater pipes are shown below in Figure 23.

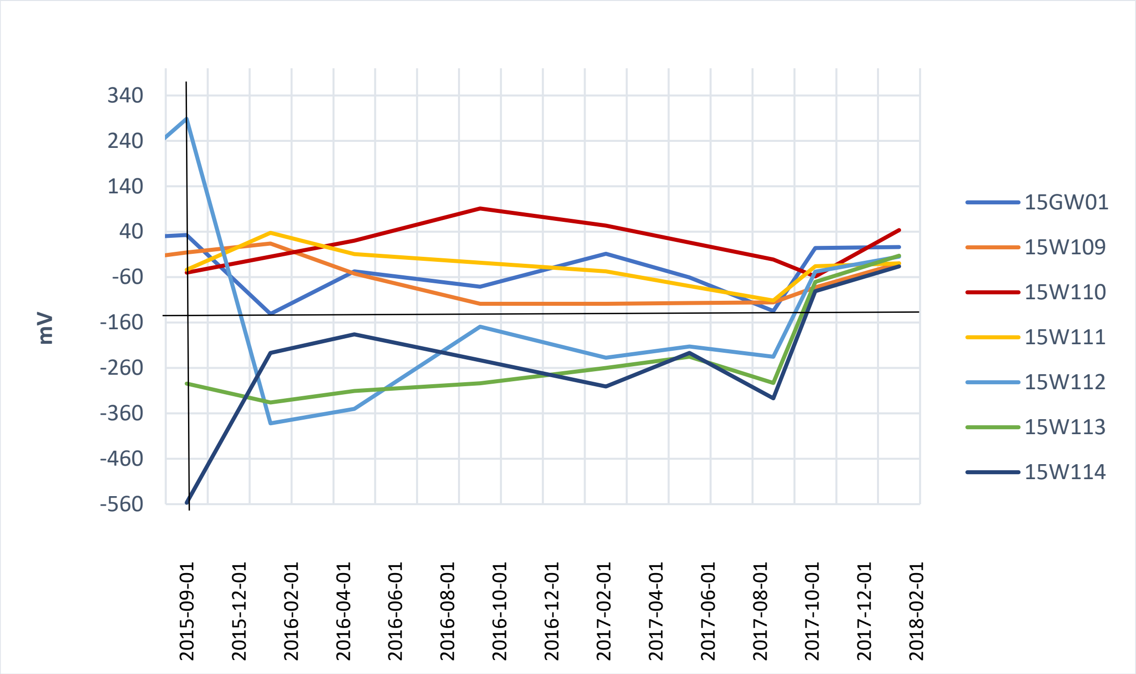


Figure 23. ORP for the different groundwater pipes during the observation period with the time of injection of nutrients marked as a black vertical line and the limit for optimal reductive dechlorination (USGS, 2006) marked with horizontal black lines.

It is seen that the levels of ORP only decreases after the injection of nutrients in groundwater pipes 15GW01, 15W112 and 15W113. The upstream groundwater pipes 15W110 and 15W111 are seldom below -50 mV. The downstream groundwater pipes 15W112, 15W113 and 15W114 have the lowest values of ORP.

4.3.6 pH

The mean of the pH in all observations is within the optimal range of 6,5-7,5 (as observed by USGS, 2006) and the values exceed the optimal interval in 11 observations (18%). This happens mainly in three groundwater pipes (15W112, 15W113, 15W114), with the highest pH observed being 8,81. The variation in pH over the observation period can be seen in Figure 24 below.

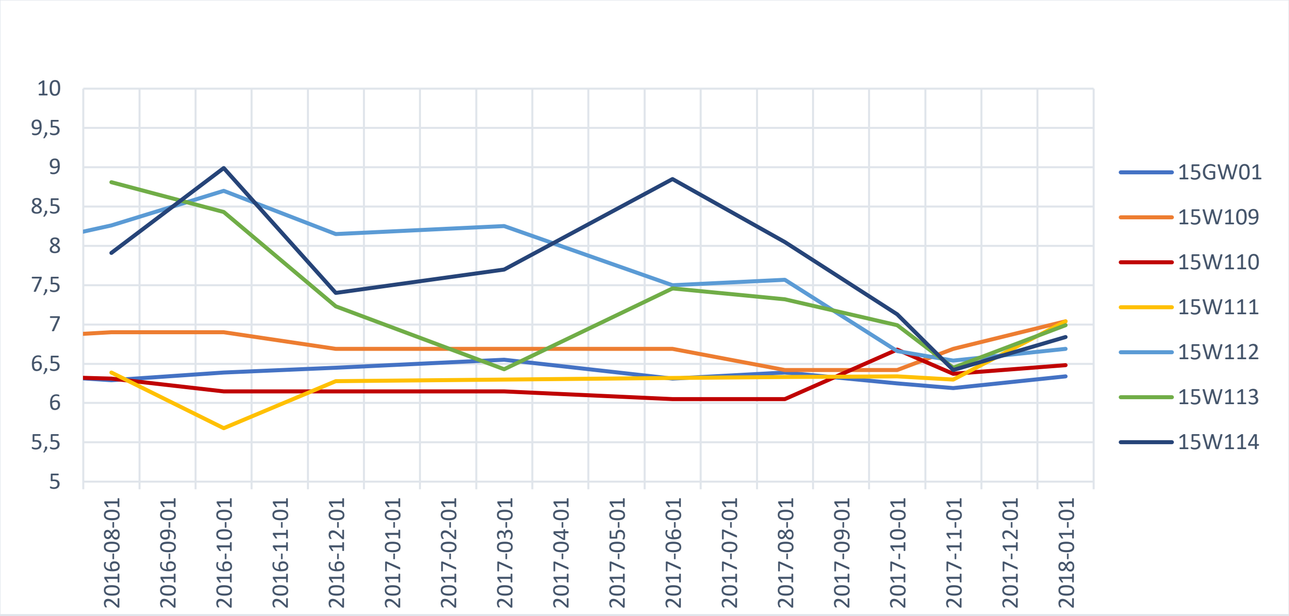


Figure 24. The variation in pH during the observation period.

It can be seen in Figure 24 that the downstream groundwater pipes 15W112, 15W113 and 15W114 generally have a higher pH than the pipes located higher upstream.

4.4 RESULTS OF ANALYSIS OF DEGRADATION DYNAMICS

The levels of all chlorinated ethenes in all groundwater pipes and how they change over time was examined. The separate analysis for each groundwater pipe can be found in Appendix A. A compilation of the changes in the concentration and fractions of chlorinated ethenes was done to closer examine the spread of the contamination.

4.4.1 The variation in the levels of the chlorinated ethenes over time

A compilation of the levels of TCE, cDCE, tDCE and VC over time is shown below in Figure 25. The levels are shown in micromoles per litre water in order to make the comparison visually easier.

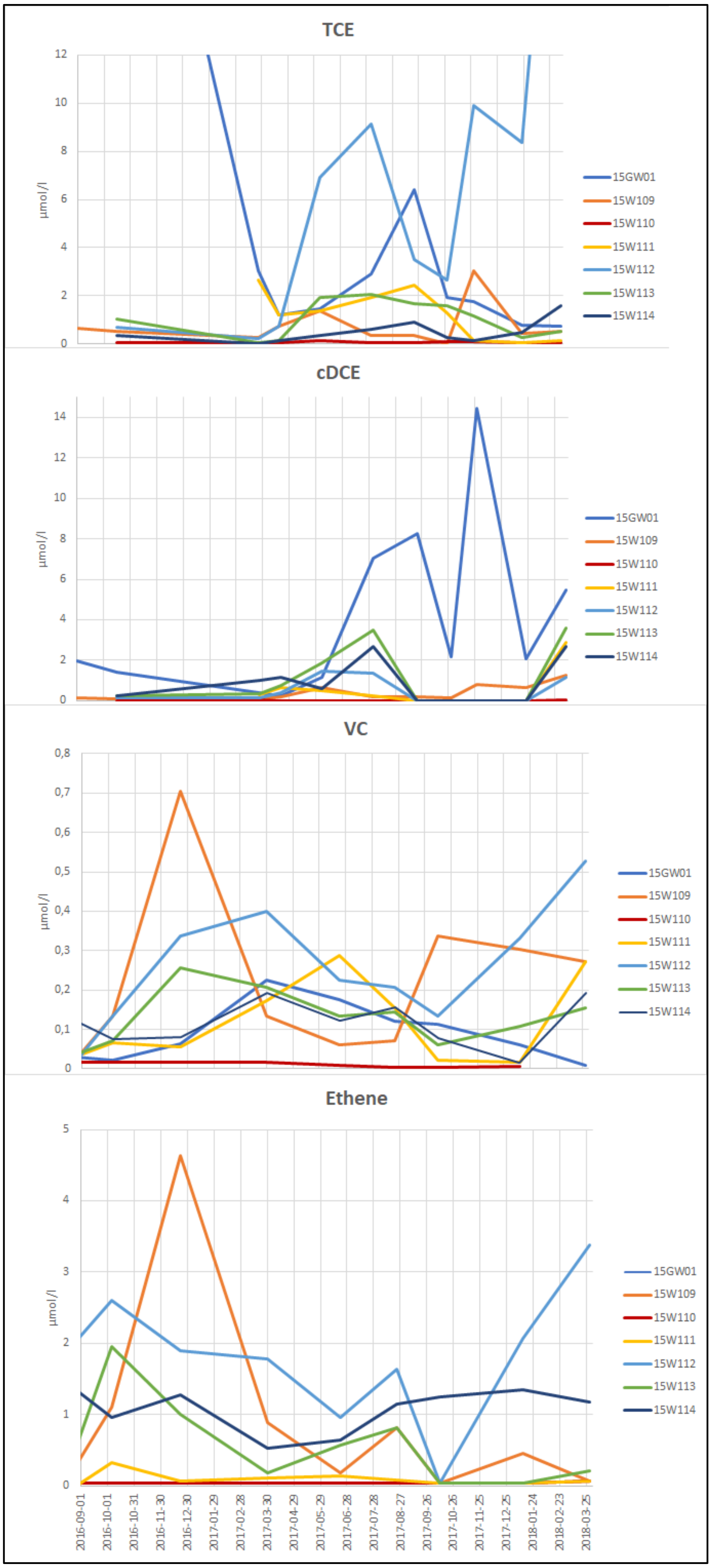


Figure 25. The levels of TCE, cDCE and VC during the observation period. Observe the different scales for the different contaminants.

As the levels of contaminants are very low in pipe 15W110 throughout the observation period, the change in concentration in this pipe will not be commented. The change in the levels of tDCE will neither be commented as they are also very low and are therefore excluded from Figure 25.

As seen in Figure 25 two groundwater pipes have much higher levels of TCE than the rest; these are 15GW01 and 15W112. The levels of TCE decrease initially in groundwater pipes 15GW01, 15W111 and 15W114 and later peak around June 2017. The rest of the groundwater pipes have an initial increase and an earlier peak, situated around March 2017 and have a second peak around September 2017. The largest decrease in TCE happens in groundwater pipe 15GW01 before the time of injection.

The levels of cDCE are initially low in all groundwater pipes but rise with a peak around March 2017 (June 2017 for pipe 15GW01). After this, the levels of cDCE decrease drastically to the limit of detection and stay low in all pipes but 15GW01 and 15W109. The levels stay low until March 2018, after which the concentrations increased in all groundwater pipes. The highest levels of cDCE are found in groundwater pipe 15GW01.

The levels of VC are overall initially low and start increasing after September 2017. The highest levels of VC are found in groundwater pipes 15W109, 15W112 and 15W111. The levels seem to decrease in all groundwater pipes during the summer of 2017 before a final increase in all groundwater pipes before March 2018, which is a similar pattern to the behaviour of cDCE.

The variation in the levels of ethene are similar to the variation of VC, with both VC and ethene being present in the highest concentrations in groundwater pipe 15W109. The levels of ethene are however higher than the levels of VC.

When the initial concentrations are compared to the concentrations observed in March 2018, the levels of TCE had decreased in all groundwater pipes but 15W112 and 15W114, where the increases were 26 and 1.26 µmol/l respectively. The levels of cDCE increased in all pipes, with the largest being an increase of 3.51 µmol/l (15GW01), 2.58 µmol/l (15W111) and 3.39 µmol/l (15W113). The levels of VC increase slightly in all groundwater pipes with the largest increases being of 0.26 µmol/l (15W109) and 0.24 µmol/l (15W111). The levels of ethene fluctuate greatly but the largest change is a decrease of 1.35 µmol/l in 15W112.

To exclude that the observed increases of TCE in the groundwater pipes were due to the decrease in groundwater level, the concentrations of TCE were multiplied with the groundwater level to cancel out the influence of the change in groundwater level, the resulting curves of the TCE levels were identical to the curves of TCE seen in Figure 25. This indicates that the change in groundwater level does not have a large influence on the variation of the levels of TCE.

4.4.3 The variation in the levels of cDCE in certain groundwater pipes

As seen in Figure 26 the concentration of cDCE decreases rapidly in all groundwater pipes but 15GW01 and 15W109 after March 2017 until they increase after January 2018 (the interval is marked with black lines). The variation in the levels of TCE, cDCE and VC in these groundwater pipes is compared to the levels of methane, sulphate and dissolved oxygen and the comparison can be seen in Figures 26 below.

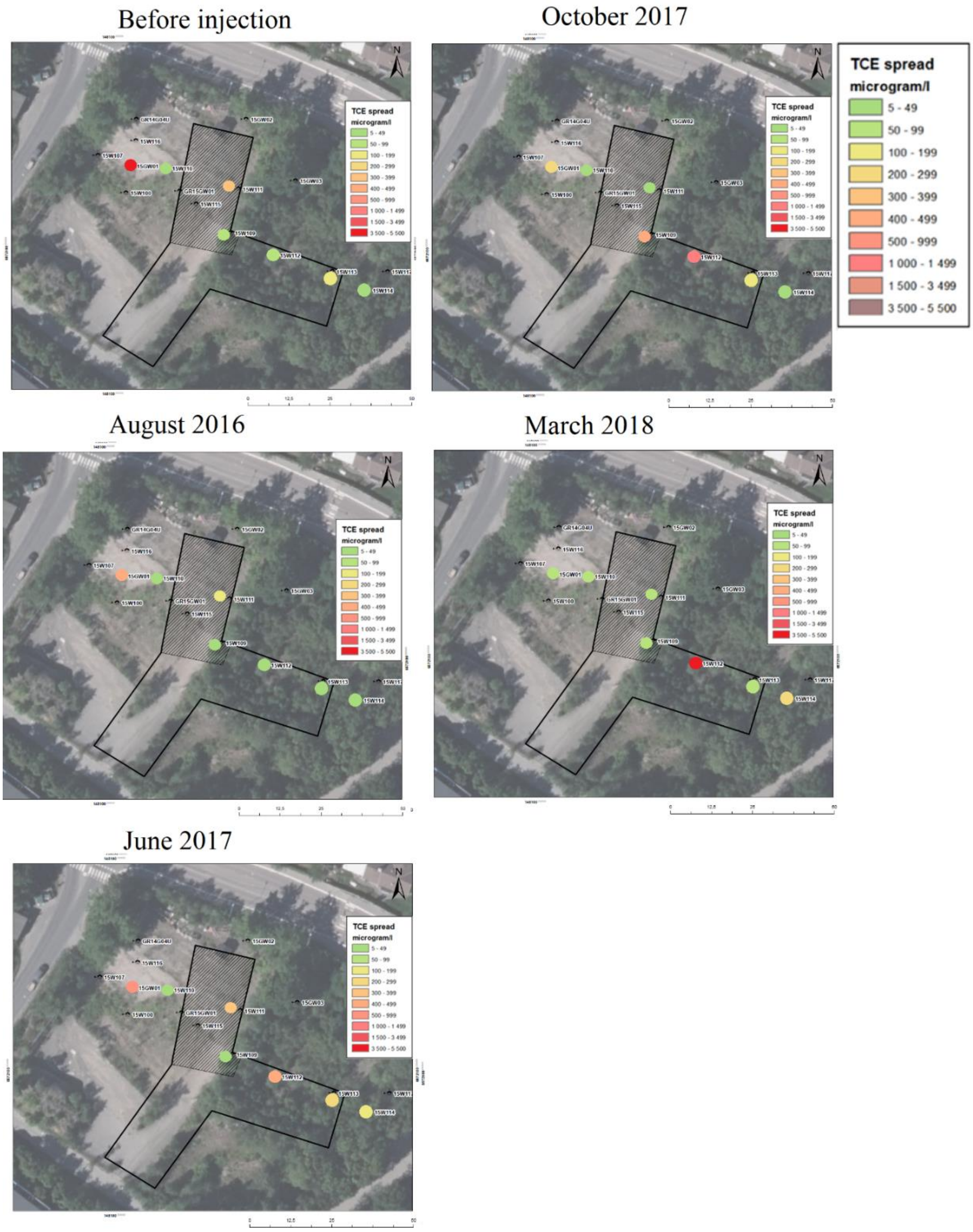
Figure 26. The levels of methane, sulphate and dissolved oxygen compared to the levels of TCE, cDCE and VC in groundwater pipes 15W110, 15W111, 15W112, 15W113 and 15W114.

The levels of cDCE, TCE, VC and sulphate have an overall decrease during the period from March 2017 to January 2018, after which the levels of the chlorinated ethenes all increase. The only exception for sulphate is groundwater pipe 15W111. The levels of methane increase during this same period and decrease after January 2018, except for again in groundwater pipe 15W111. The levels of oxygen are low during most part of March 2017 to January 2018, except for in 15W111 where the levels rise after June 2017 and in 15W110 where they rise after October 2017.

The levels of VC in groundwater pipes 15W110 and 15W112 seem to increase in connection to the decrease of cDCE in the pipes. This can partly be seen in pipe 15W114 as well.

4.4.5 Compilation of the levels of contaminants within the area

In order to observe the movement of TCE though the system, a figure compiling the measured levels of TCE in the different groundwater pipes at different observation times was put together and it is seen in Figure 27 below. The same scale is used at all observation snapshots.



Before injection

October 2017

August 2016

March 2018

June 2017

Figure 27. The change in TCE spread in the groundwater at different times of the observation period.

As seen in Figure 27 the concentration of TCE in the source areas of groundwater pipes 15GW01 and 15W111 slowly decrease over the observation period and the concentration of TCE increases in around groundwater pipe 15W112. The concentration of TCE varies over the observation period which can be seen when comparing the different snapshots. There is a slight increase in the levels of TCE in the source area in June 2017, which later decreases.

Over the observation period the levels of chlorinated ethenes are highest in groundwater pipes 15GW01 and 15W112. The lowest levels are in groundwater pipe 15W110 and in 15W114.

The spread of cDCE and VC at the last observation of this project in March 2018 was modelled and is shown below in Figure 28. Observe that the scale is different for VC as the difference in concentration between the chlorinated ethenes is large. The scale for cDCE is the same as for TCE.

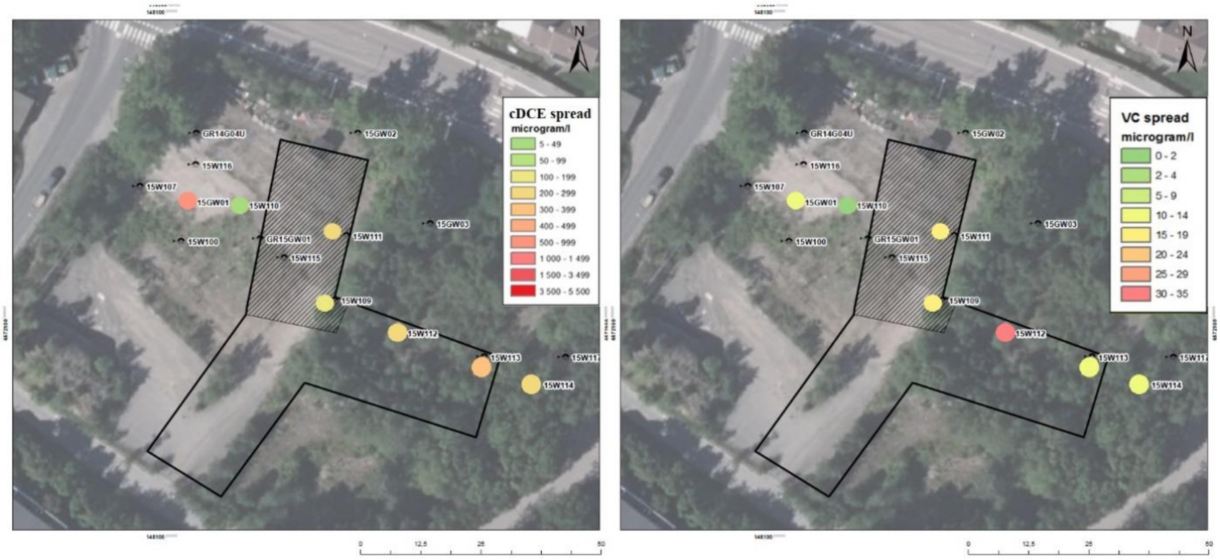


Figure 28. The spread of cDCE (left) and VC (right) on the site in March 2018.

As seen in Figure 28, the spread of cDCE in March 2018 seems to be highest in the groundwaterpipes in the two source areas 15GW01 and 15W111 as well as in groundwater pipe 15W113. The concentrations of VC are much lower and seem to be highest in groundwater pipe 15W112 but also from 15GW01, 15W111, 15W109 and 15W114.

When the molar fractions of the chlorinated ethenes in each groundwater pipe are compared between the initial observation and March 2018, there is a big difference as seen in Figure 29 below.

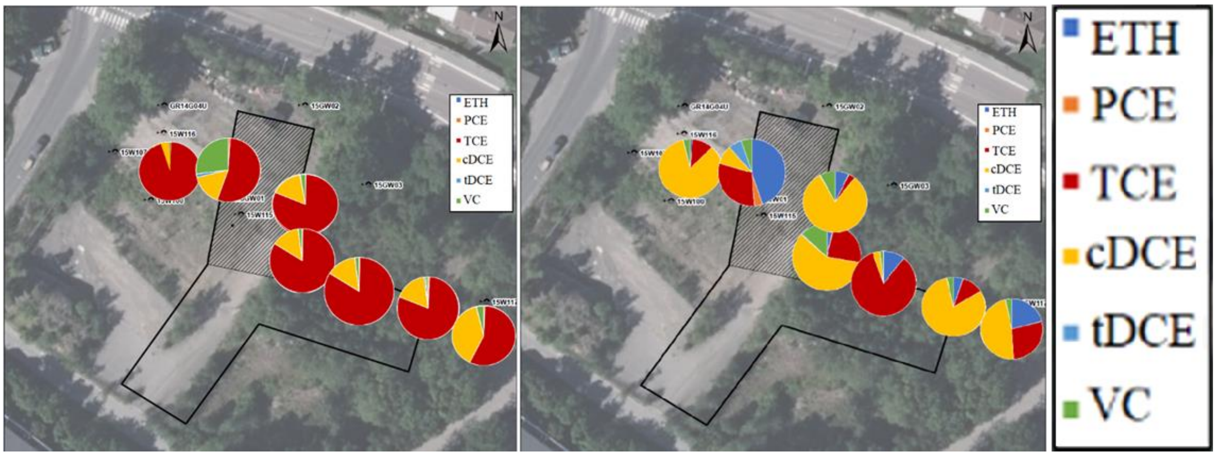


Figure 29. Fraction of chlorinated ethenes before start of remediation (left) and fraction of chlorinated ethenes in March 2018 (right).

In all groundwater pipes but for 15W112 the molar fractions of TCE are larger in the initial observation than in the last observation in March 2018. The molar fractions of cDCE have increased from the first to the last observation in all groundwater pipes but for 15W112 and 15W110.

4.5 MEETING THE REMEDIATION GOALS

To assess the remediation goals, the levels of TCE and cDCE in each groundwater pipe have been complied in Table 5 and Table 6 below.

Table 5. The levels of TCE in all groundwater pipes during the observation period. The levels that are above the remediation goal (below 50-100 µg/l)are marked in red.

Groundwater pipe/Date	15GW01 [µg/l]	15W109 [µg/l]	15W110 [µg/l]	15W111 [µg/l]	15W112 [µg/l]	15W113 [µg/l]	15W114 [µg/l]	**Mean [µg/l]**
2015-09-18	5300	83.7	-	-	-	-	-	**769**
2015-12-01	3710	69.6	4.2	-	90.2	134	45.4	**579**
2016-08-26	400	34	5.4	349	27	7.6	1	**117**
2016-10-06	160	95	5.4	160	95	18	20	**79**
2016-12-22	190	180	16	180	910	250	44	**252**
2017-03-30	380	46	5.4	-	1200	270	79	**282**
2017-06-21	840	47	-	320	460	220	120	**286**
2017-08-23	250	3	10	-	350	210	33	**122**
2017-10-11	230	400	10	19	1300	150	18	**303**
2018-01-12	100	57	8.2	7	1100	32	65	**195**
2018-03-28	94	66	6.4	15	3500	67	210	**565**

The levels of TCE exceed the remediation goal of 50-100 µg/l in many observations and these observations are marked in red. The mean concentration of TCE exceeds the remediation goal in all observation times but one (2016-10-06).

Table 6. The levels of cDCE in all groundwater pipes during the observation period.

Groundwater pipe/Date	15GW01 [µg/l]	15GW109 [µg/l]	15GW110 [µg/l]	15GW111 [µg/l]	15GW112 [µg/l]	15GW113 [µg/l]	15GW114 [µg/l]
2015-09-18	190	12	-	-	-	-	-
2015-12-01	135	9.8	0.9		11.2	21.1	23
2016-08-26	39	7.2	1.7	30.1	16	34	97
2016-10-06	24	21	0.5	61	38	71	110
2016-12-22	110	61	0.5	50	140	180	58
2017-03-30	680	20	0.5	-	130	340	260
2017-06-21	800	21	-	0.5	0.5	0.5	0.5
2017-08-23	210	16	0.5	-	0.5	0.5	0.5
2017-10-11	1400	78	0.5	0.5	0.5	0.5	0.5
2018-01-12	200	64	0.5	0.5	0.5	0.5	0.5
2018-03-28	530	120	1.4	280	110	350	260

The remediation goal was for the levels of cDCE to decrease, but the levels of cDCE have not decreased in any groundwater pipe at the end of the observation period. Many observations are however at the limit of detection until the last observation in March 2018, where the levels increase significantly in all groundwater pipes.

5. DISCUSSION

5.1 THE BEHAVIOUR OF THE CHLORINATED SOLVENTS

Reductive dechlorination seems to be happening all over the contaminated area as the degradation products cDCE, VC and ethene are observed in all groundwater pipes. When the nutrients were injected, the levels of oxygen decreased in all groundwater pipes but 15W111. However, the oxidation reduction potential only decreased in three of the seven groundwater pipes. This contradicts the findings of Eriksson et. al., 2011 which indicated that the injection of nutrients seemed to decrease the oxidation reduction potential. Nevertheless, the reductive dechlorination seems to happen on the site regardless as an increase in the levels of cDCE was seen in all groundwater pipes at the next observation date after the injection of nutrients. This may indicate that low oxygen levels are more important to the degradation process than low oxidation reduction potential.

The PLS regression analysis showed that the strongest correlation trends present for all chlorinated ethenes was a positive correlation to the other chlorinated solvents as well as a negative correlation to the dissolved oxygen in the groundwater.

The correlation of the chlorinated solvents with each other is most likely due to the degradation products being created under the same condition, as well as because when a large amount of mother product is present, large amounts of the daughter products can be created.

Based on the results of this analysis, the level of dissolved oxygen is the most relevant factor to measure to examine the potential of stimulated reductive dechlorination. This relationship will be further discussed.

5.1.1 Relationship between the chlorinated ethenes and oxygen

All chlorinated ethenes correlate negatively with oxygen in the PLS regression analysis, even the mother product TCE. As the degradation products are created under anaerobic conditions, this negative correlation is expected. However, as TCE is not created, only degraded, TCE would be expected to have a positive correlation with oxygen, i.e. if the concentration of oxygen is low, TCE is degraded and the concentration of TCE decreases. The observed relationship might not indicate a direct correlation between oxygen and TCE, it could instead be a result of an event that decreased the levels of oxygen while at the same time increasing the levels of TCE. In five of the groundwater pipes (15W109, 15W110, 15W112,15W113) an example of this can be seen when the nutrients are injected at the beginning of the remediation. When the nutrients are injected, TCE and other compounds bound to the soil can be released in to the groundwater by the physical impact of the injection. Pathways for TCE in free phase migration may also have been created. At the same time the level of oxygen decreases as the oxygen is used by microorganisms degrading the injected nutrients. This could in part explain the observed negative correlation between TCE and oxygen.

The rest of the chlorinated ethenes (cDCE, tDCE and VC) also correlate negatively with oxygen, as seen in the PLS regression analysis. As the anaerobic dechlorinators are most active in the absence of oxygen, these compounds are created mainly in anaerobic conditions and therefore this relationship is expected. The degradation products may also be affected by the physical impacts of the injection of nutrients in the same way as TCE, but not as much as TCE was present in much higher concentrations. This could further contribute to the negative correlation with dissolved oxygen.

5.1.2 The suitability of using PCA and PLS to examine reductive dechlorination

As the system is dynamic with many different factors affecting the remediation, a statistical analysis such as PCA and PLS may not be the most suitable tool to investigate the process of reductive dechlorination. The measured parameters are affected by transport, which further complicates the process, and this is not considered in the statistical analysis. The degradation is dependent on reductive and anaerobic conditions, and therefore the resulting strong negative correlation with oxygen from the analysis is reasonable, but this is not the only factor affecting the remediation.

5.1.3 The activity of TCE

The levels of TCE seem to decrease in all groundwater pipes over the observation period but for the groundwater pipes 15W112 and 15W114. However, the levels fluctuate throughout the observation period which may be due to the impact of processes such as sorption and diffusion, as described by Bjerg (2013), Lu (2011) and Manoli (2012). As the soil is heterogenous TCE may have over time diffused into areas of lower bioavailability such as low permeable clay units, which would provide a challenge and potential delays to the remediation. TCE has been shown to sorbe to soil particles to a higher degree than the lesser chlorinated compounds (Lu et al., 2011), which may also affect the concentration of dissolved TCE in the groundwater.

The area around groundwater pipe 15W112 seems to be affected by an influx of TCE as seen in the increasing concentrations. The reason for this influx should be further investigated in case it is due to a transport of TCE from the source areas, which would mean that much of the loss thought to be due to bioremediation may in fact be due to a transport of contaminants. It may also mean that contaminants could be further transported out of the area submitted to bioremediation. As the soil is heterogenous there is a possibility that there might be a system of units of higher conductivity connecting these two areas, as discussed by Reynolds (2001), Manoli (2012) and Chambon (2010), enabling transport faster than that estimated by the measured hydraulic conductivity. As the levels of TCE are not as high in pipe 15W112 as initially in 15GW01, some degradation may be taking place along the way even if a faster transport exists, although this is uncertain as the levels measured in pipe 15W112 are still rising. Units of increased conductivity could also explain the high decrease of TCE initially in 15GW01, which decreases from 5300 to 400 µg/l (a decrease of 92.5 %) in the year before the remediation has started.

It is also possible that the early decrease of high levels of TCE in 15GW01 and the later increase in 15W112 are not connected, that there instead may be a large sheet of TCE located upstream from 15W112, which after the initial observations on the site moves into the area measured by the pipe resulting in the high levels of TCE. This sheet may have been transported towards 15W112 during the decades in which the site was contaminated or is emitted from an undetected source of TCE located close to groundwater pipe 15W112.

As groundwater pipe 15W112 is observed to have both sufficiently low levels of oxygen and oxidation reduction potential, the conditions are favourable for reductive dechlorination. This may indicate that large amounts of the contamination present can be effectively degraded given enough time and provided that no further transport is present.

5.1.4 The activity of cDCE

The levels of cDCE in all groundwater pipes but 15GW01 and 15W109 plummet to the limit of detection between in June 2017 and keep low till March 2018, regardless of the original concentration of contamination in the pipe. When the levels of TCE, cDCE and VC are compared to the levels of methane, sulphate, and dissolved oxygen in the affected groundwater pipes in Figure 26, it seems likely that the steep decrease in cDCE, sulphate and partly TCE and VC, as well as the increase in methane, indicates very suitable reducing conditions. Methanogens, sulphate reducers and dechlorinators all seem to be thriving and do not seem to be competing as no accumulation of either compound is observed, contrary to the observations of Aulenta et. al. (2007) and Lu et. al. (2001). The amounts of cDCE do not always seem to increase in connection to large decreases in TCE, which might be due to the seemingly high degradation speed of cDCE. Overall cDCE is degraded quickly, even when large amounts of TCE is present and would be expected to in part obstruct the degradation of cDCE. This may also be explained by the favourable reducing conditions.

5.1.5 The activity of VC

The levels of VC are low in all groundwater pipes throughout the observation period, which is not surprising as VC is the molecule with the lowest amounts of chlorine atoms and as such will be degraded only when the larger chlorinated ethenes have been degraded. VC seem to increase in the groundwater pipes closely after degradation of cDCE, indicating that degradation of cDCE is the primary source of VC. VC is the most volatile chloroethene which makes it difficult to quantify correctly.

5.2 REACHING THE REMEDIATION GOAL

Five groundwater pipes do not fulfil the remediation goal with TCE-levels being between 50-100 µg/l in three consequent observations with at least two months apart between the observations, these are groundwater pipes 15GW01, 15W109, 15W112, 15W113 and 15W114. The total mean of the levels of TCE is above the remediation goal in the last three observations and rise in the last observation, as seen in Table 7.

Ethene and ethane is observed in every groundwater pipe, although in very varying concentrations. The remediation goal for ethene and ethane is thus fulfilled. The highest concentrations of ethene can be found in 15W111, 15W112, 15W113 and 15W114.

The levels of cDCE is not declining steadily in any groundwater pipe and because of this the remediation goal for DCE is not achieved. The levels of tDCE are too low in comparison with the levels of cDCE to be considered.

Because of the large variation in the levels of all chlorinated ethenes in all groundwater pipes over the observation period, an approximated time of reaching the remediation goal cannot be estimated. The variation in the levels of contaminates is most likely due to contaminants contained in or sorbed to the soil matrix being released into the groundwater at times by processes such as desorption and diffusion.

As the concentration of TCE has declined significantly in both source area, 15GW01 and 15W111, the principal source of contamination seems to have been remedied, assuming that no other sources of TCE exist. If the cause of the decline of TCE is believed to be partly because of a transport of contaminants, the fraction of remedied contaminants may become smaller, but nonetheless reductive dechlorination is occurring in the area as degradation products are found.

The increase of TCE in groundwater pipe 15W112 needs to be further investigated as it may be due to contaminants being moved more quickly than previously thought in the groundwater. This may lead to further spreading and preventive actions might need to be taken.

5.3 UNCERTAINTIES IN THE STUDY

As the study was limited to 75 observations in seven groundwater pipes in an area of approximately 8000 m^2, the insight into the processes going on at the site is limited. With only a few observation points, important factors might be missed, and results may be interpreted incorrectly. The position of the groundwater pipes has however been chosen after sampling of the area in order to obtain a satisfactory overview of the contamination spread in the area. They have been strategically placed to achieve the observations most relevant to the remediation process, which is in the source area and in the plume. If the placement is correct, the most relevant data may have been collected.

Not all observations could be used as data was missing from some of them, which was solved by interpolation from the data points nearest in time if the program was unable to deal with missing data. This might lead to incorrect results. However, most of the data was present and this contributes to the credibility of the results.

Access to more information regarding the groundwater flow in the area could have given a greater understanding of the processes in the area and would have given a better interpretation of the results. Closer measurements of the levels of chlorinated compounds would have given a better overview of how the contaminants variate during the observation period.

CONCLUSIONS

The main factors affecting the concentration of the chlorinated ethenes seems to be the concentration of dissolved oxygen as well as the release of contaminants into the groundwater by physical impact and site-specific processes such as desorption and diffusion. As such oxygen is the most relevant parameter to measure when investigating the reductive dechlorination, but as the system is dynamic and transport affects the processes attention should be paid to the other factors as well. It is possible that certain areas of higher conductivity are present on the site, affecting the transport of contaminants, which needs to be further investigated. A more thorough investigation of the groundwater flow in the area is recommended to better interpret the results and gain an understanding of the movement of contaminants through the system.

The remediation goal of the mean concentration of TCE being between 50-100 µg/l has not yet been fulfilled, neither has the goal for declining levels of DCE. The concentrations of TCE have however decreased in the two source areas, which might be a sign that the overall concentrations on the site will start to decrease as the remediation continues. However, the concentration of TCE does increase greatly at a groundwater pipe downstream from the source area during the observation period and the cause of this increase is recommended to be investigated. The presence of degradation products in the affected groundwater pipe indicates an ongoing reductive dechlorination, but to speed up the process an additional injection of nutrients in this groundwater pipe may be favourable to the remediation. If the cause of rising levels of contaminants in the downstream groundwater pipe is judged to be because of increased transport of contaminants in units of higher conductivity, measures such as a barrier or pump and treat may be needed to stop the plume from spreading further.

The timespan needed to fulfil the remediation goals is not possible to calculate as the levels of all contaminants in the groundwater pipes vary greatly during the observation period. If more measurements had been done in more observation points it might have been possible to form a more complete picture of the contamination situation and spread. The presence of daughter products in all groundwater pipes indicates reductive dechlorination being performed in the contaminated area which will as time passes decrease the overall concentration of the chlorinated ethenes.

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APPENDIX

APPENDIX A.

A.1 THE SEPARATE ANALYSIS OF DEGRADATION DYNAMICS FOR EACH GROUNDWATER PIPE

A.1.1 Groundwater pipe 15GW01

Groundwater pipe 15GW01 is the assumed source of contamination, its position is shown in Figure 30 below.

Figure 30. The groundwater pipe 15GW01 is marked in red, and the groundwater pipes not part of the observations are crossed over. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvents in 15GW01 over time are shown below in Figure 31, together with the degree of dechlorination over time.

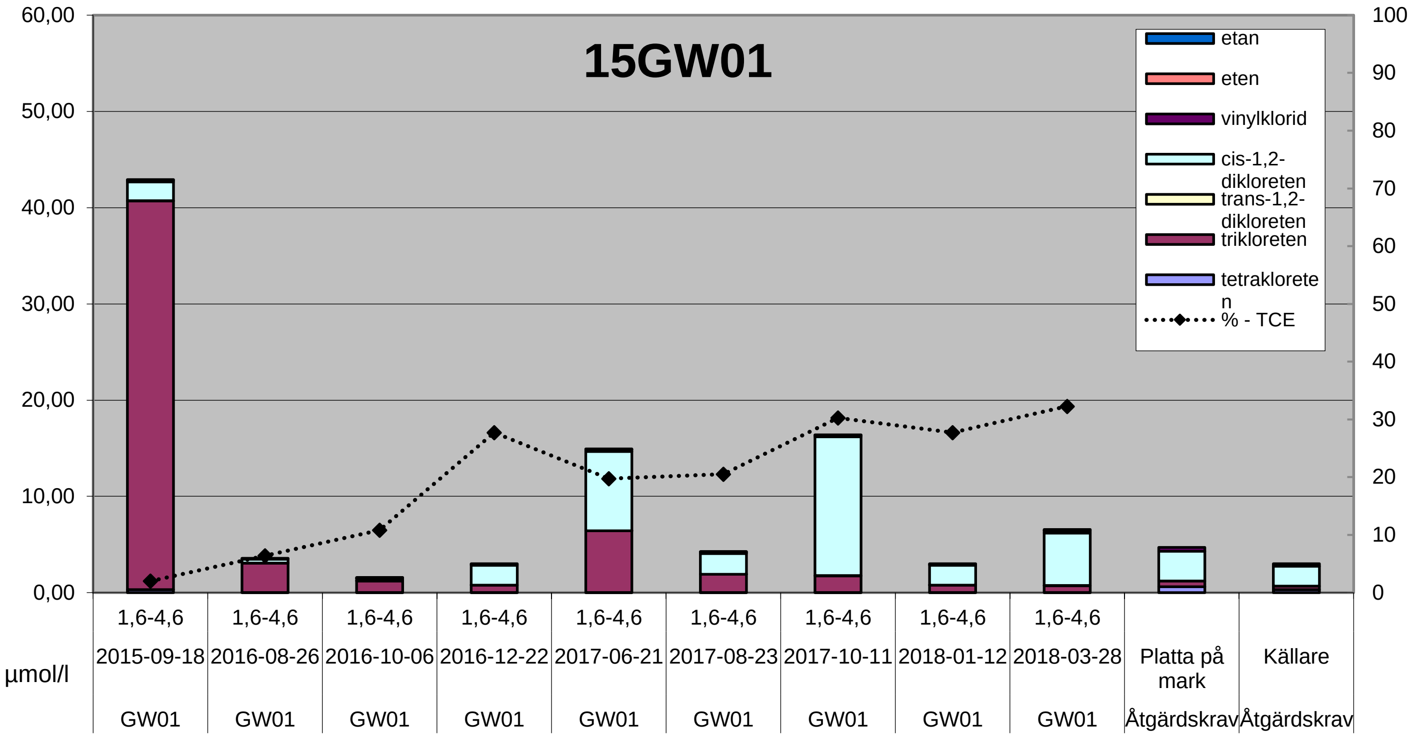

Figure 31. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) are shown from September 2015 to March 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The levels of TCE are very high initially, cDCE is also present at this time. The observed levels of TCE and cDCE drop significantly in the first 11 months between the first and second observation. A decline in the levels of contaminants can be seen from the second to third observation. At the third observation, cDCE start to form in larger amounts, with levels increasing from the fourth to the fifth observation. TCE also increases during this time. From the sixth observation forwards the levels of TCE drop. The levels of cDCE vary and are at its highest during the seventh observation and decline after that, although they increase in the last observation.

A.1.2 Groundwater pipe 15W110

Groundwater pipe 15W110 is the groundwater pipe located closest to the suspected source of contamination in 15GW01. Its position is shown in Figure 32 below.

Figure 32. The groundwater pipe 15W110 is marked in red, and the groundwater pipes not part of the observations are crossed over. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvent in 15W110 over time are shown below in Figure 33, together with the degree of dechlorination over time.

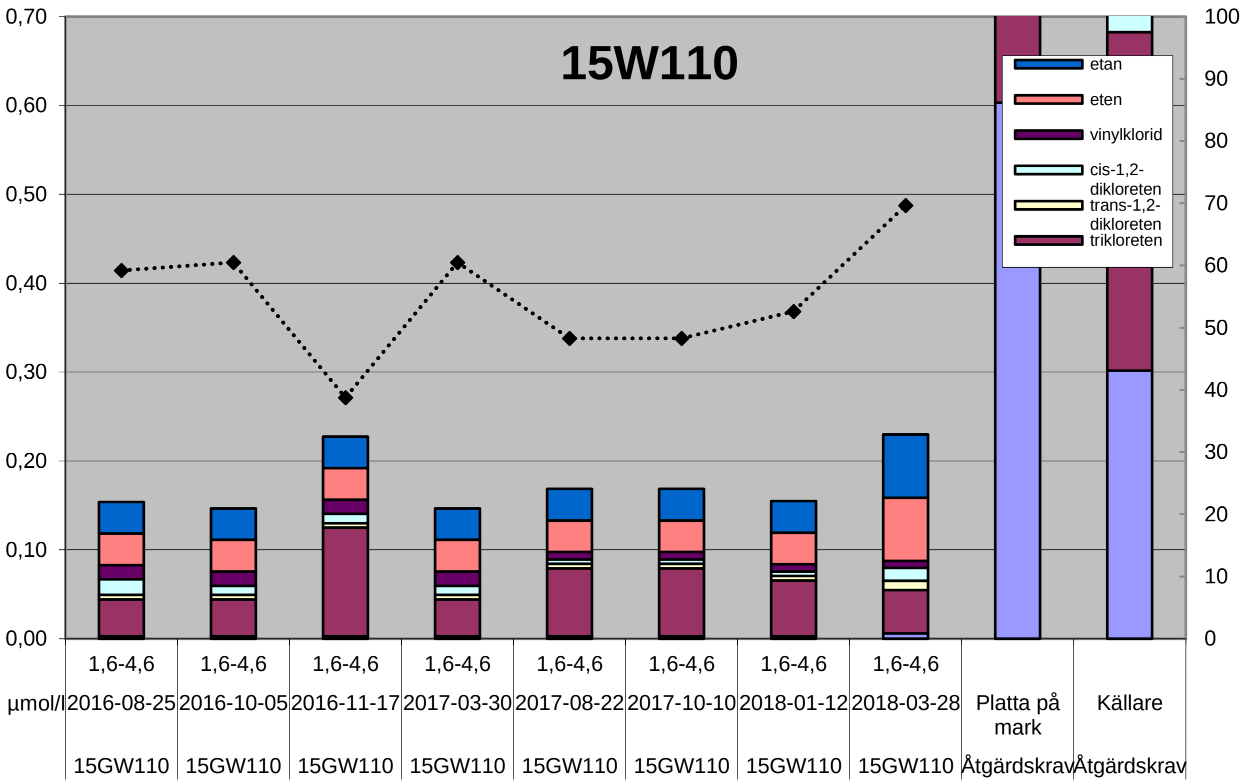

Figure 33. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) are shown from August 2016 to March 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The levels of chlorinated ethenes are the lowest in 15W110 out of all the groundwater pipe, as seen on the scale in Figure 31. The largest amount of the different contaminants is TCE, which seems to be at a steady level during the first two observations, to increase slightly at the third as well as the fifth observation. There is ethane and ethene present in the groundwater pipes, as well as some cDCE and PCE.

A.1.3 Groundwater pipe 15W111

Groundwater pipe 15W111 might possibly be another source of TCE, because of the high initial concentrations. Its position is shown in Figure 34 below.

Figure 34. The groundwater pipe 15W111 is marked in red, and the groundwater pipes not part of the observations are crossed over. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvent in 15W111 over time are shown below in Figure 35, together with the degree of dechlorination over time.

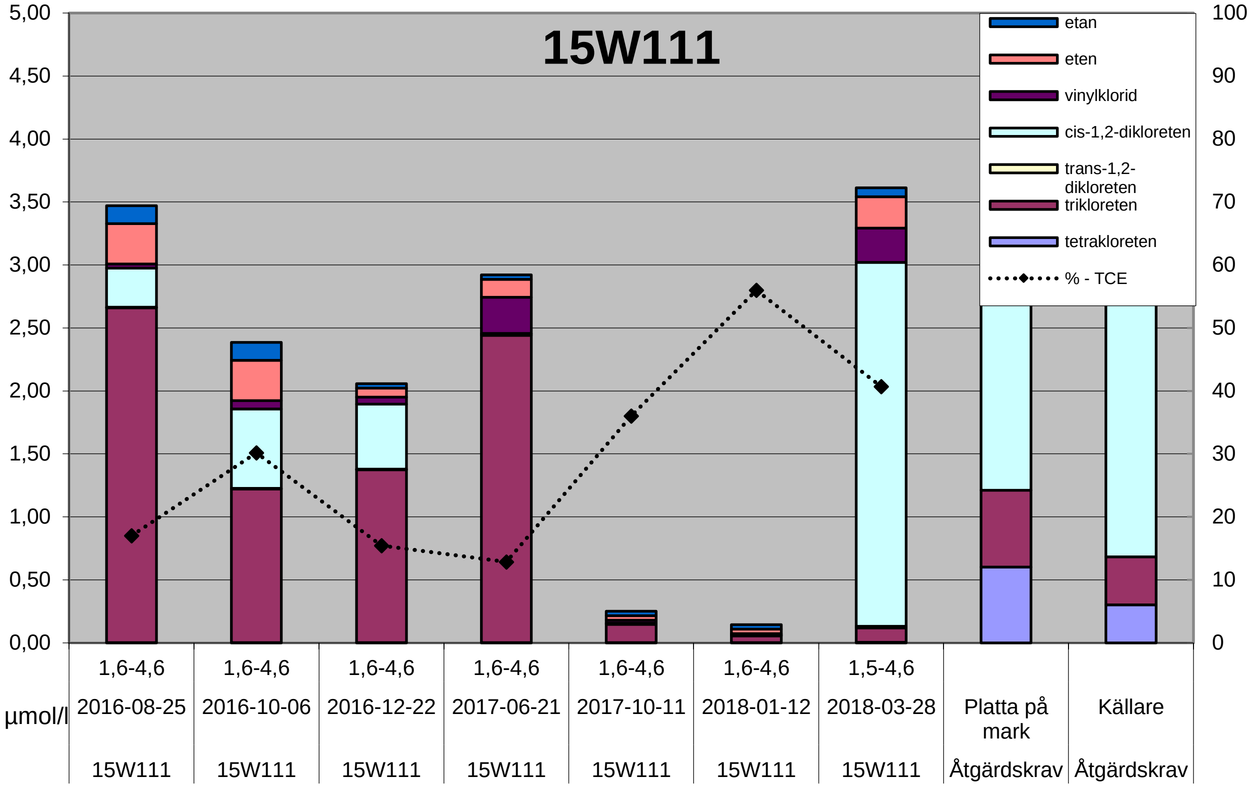

Figure 35. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) are shown from August 2016 to March 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The level of TCE in 15W111 decreases, and cDCE increases, between the first and second observation. Between the third and fourth observation the levels of TCE increases. A significant amount of VC is also observed. cDCE does not seem to be produced from December 2016 to March 2018 even though the levels of TCE decrease. Between the fourth and fifth observation the levels of all chlorinated ethenes decrease. In the last observation the levels of cDCE increase significantly.

A.1.4 Groundwater pipe 15W109

The position of groundwater pipe 15W109 is shown in Figure 36 below.

Figure 36. The groundwater pipe 15W109 is marked in red, and the groundwater pipes not part of the observations are marked with a cross. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvent in 15W109 over time are shown below in Figure 37, together with the degree of dechlorination over time.

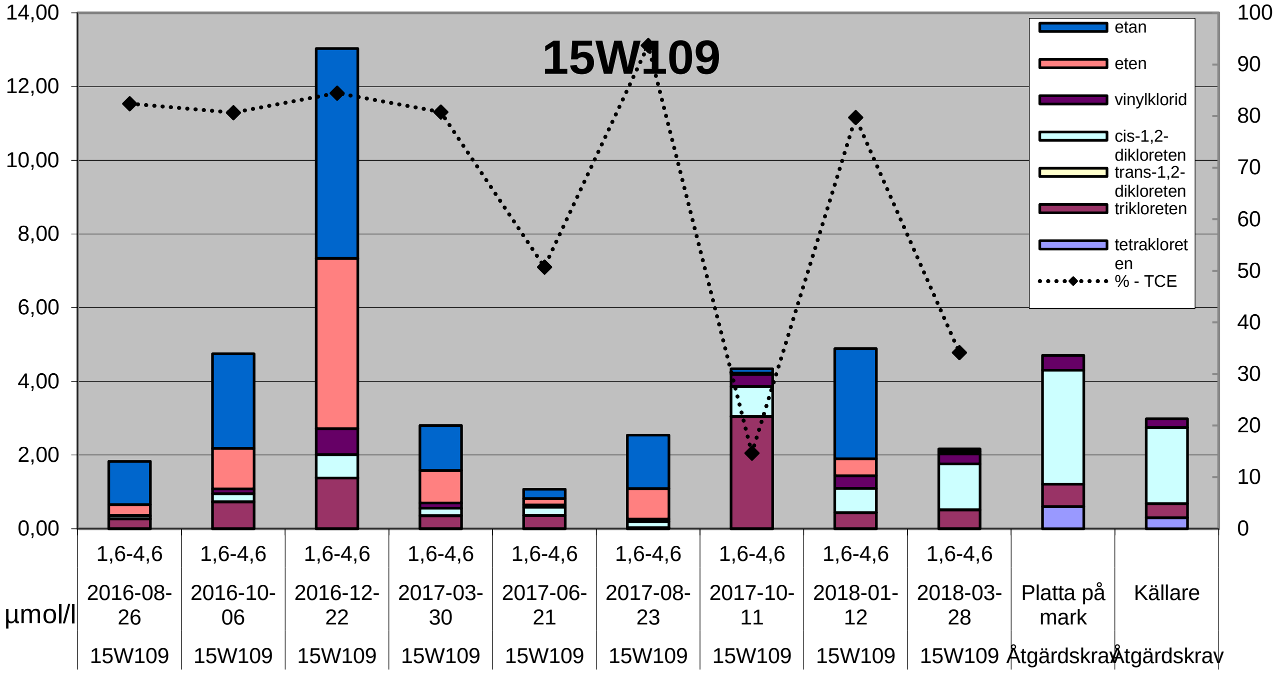

Figure 37. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) are shown from August 2016 to January 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The levels of TCE, cDCE and VC increase from the first to the third observation, but from the third to the fourth observation levels drop. At the seventh observation there is a significant increase in levels of TCE, cDCE and VC, which decrease to the eighth observation. Ethane and ethene are present in high levels.

A.1.5 Groundwater pipe 15W112

The position of the groundwater pipe 15W112 is shown in Figure 38 below.

Figure 38. The groundwater pipe 15W112 is marked in red, and the groundwater pipes not part of the observations are marked with a cross. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvent in 15W112 over time are shown below in Figure 39, together with the degree of dechlorination over time.

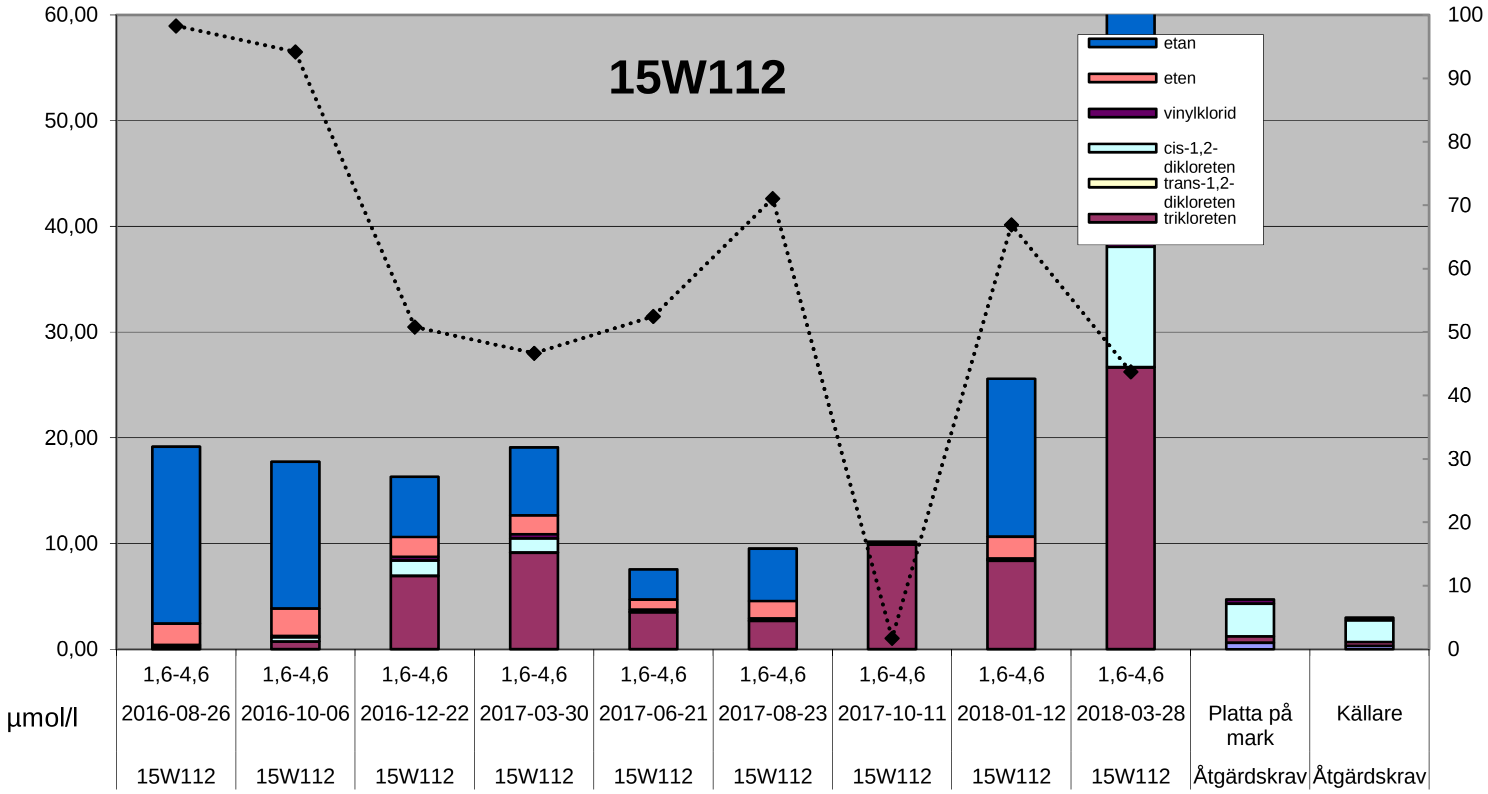

Figure 39. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) in 15W112 are shown from August 2016 to January 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The levels of TCE and cDCE increase from the second to the fourth observation, then decrease. TCE starts to increase during the fifth and sixth observation and is at its highest during the last observation. cDCE is not produced in large quantities until the last observation, and no cDCE seems to be produced from March 2017 to March 2018. Ethane and ethane are present in unusually high levels in the groundwater pipe.

A.1.6 Groundwater pipe 15W113

The position of the groundwater pipe 15W113 is shown in Figure 40 below.

Figure 40. The groundwater pipe 15W113 is marked in red, and the groundwater pipes not part of the observations are marked with a cross. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvent in 15W113 over time are shown below in Figure 41, together with the degree of dechlorination over time.

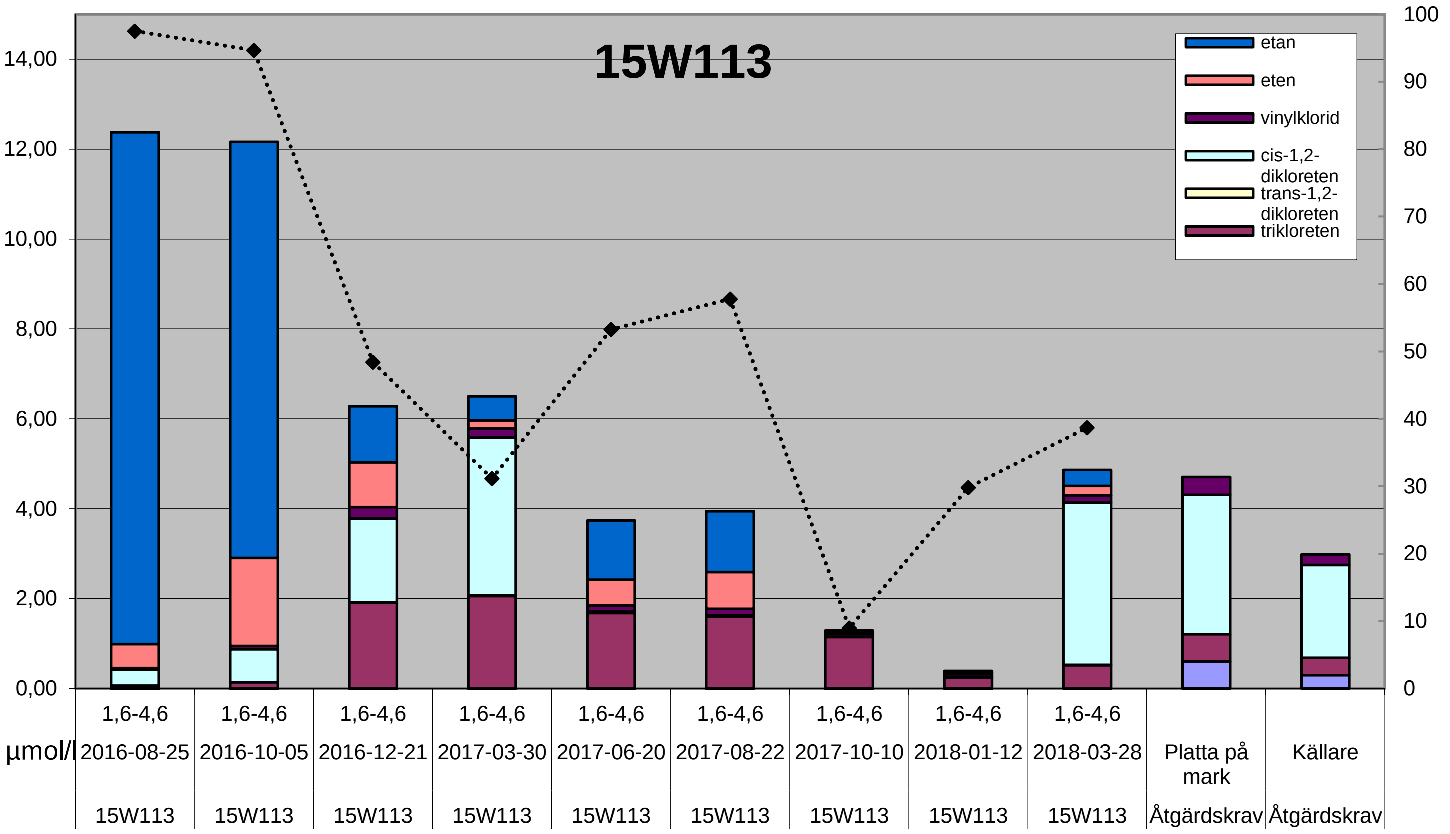

Figure 41. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) in 15W113 are shown from August 2016 to January 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The levels of TCE are low initially, but increase until the fourth observation, when they start to decrease steadily. The levels of cDCE, as well as levels of VC, increase from the first to the fourth observation, after which the production of cDCE seems to stop until March 2018. Levels of VC are present and seem constant, though all observations.

A.1.7 Groundwater pipe 15W114

The position of the groundwater pipe 15W114 is shown in Figure 42 below.

Figure 42. The groundwater pipe 15W114 is marked in red, and the groundwater pipes not part of the observations are marked with a cross. The figure is based on WSP:s figure of the area.

The levels of the different chlorinated solvent in 15W114 over time are shown below in Figure 43, together with the degree of dechlorination over time.

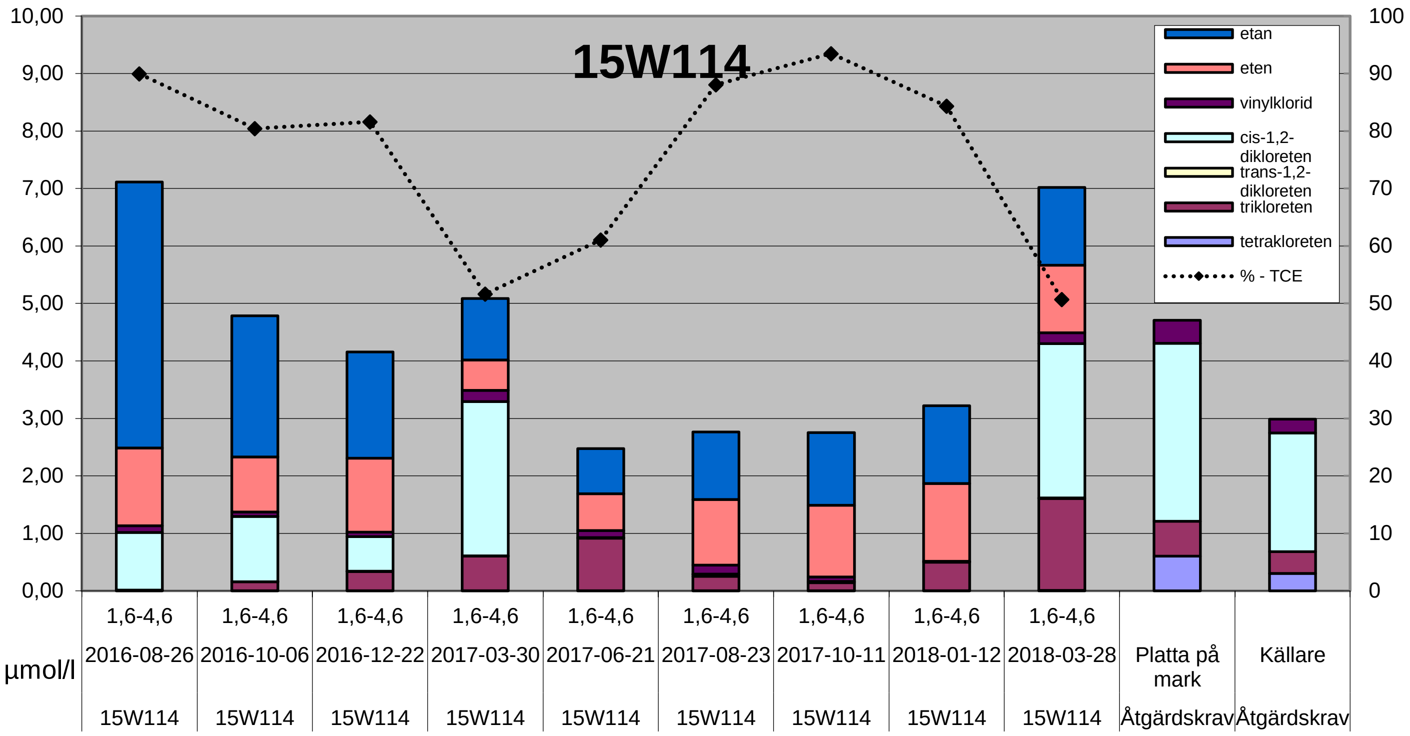

Figure 43. The levels of the chlorinated ethenes and the degree of dechlorination of TCE (0-100%) in 15W114 are shown from August 2016 to January 2018. The two piles to the right represent two different limits of remediation, for building a foundation on the contaminated soil and for building a cellar in the contaminated soil. The levels are shown in moles.

The levels of TCE are low initially, but increase until the fifth observation, when they start to decrease. They increase again from the seventh to the last observation. The levels of cDCE, as well as levels of VC, increase from the first to the fourth observation. After this, there seems to be no cDCE until March 2018, but levels of VC are present and seem more or less constant. High levels of ethene and ethane are present in this groundwater pipe.

A.2 Concentration of methane, ferrous iron and sulphate

The levels of methane are always under 1 mg/l in all groundwater pipes. The lowed observed value is 1 µg/l and the highest is 960µg/l.

The mean of the levels of ferrous iron is above 1 mg/l, but especially in the groundwater pipe 15W110 lower levels of ferrous iron is observed, with the lowest value being 0,05 mg/l and the highest 5 mg/l and a mean of 1,03 mg/l.

The levels of sulphate are all but one above 1 mg/l, with the highest value observed at 440 mg/l in groundwater pipe 15W109. This is the groundwater pipe with the highest observed values of sulphate, with a mean of 325 mg/l. The groundwater pipe with the lowest observed value of sulphate was 15GW01, with a mean of 31 mg/l.

APPENDIX B.

B.1 PLS REGRESSTION WITH PCE

When a linear relationship between the scores of the descriptor (X) and response (Y) variable scores was investigated, it was found that the data was very unevenly distributed, as can be seen in Figure 44. The distribution of the data improved with a log-transform but is still skewed.

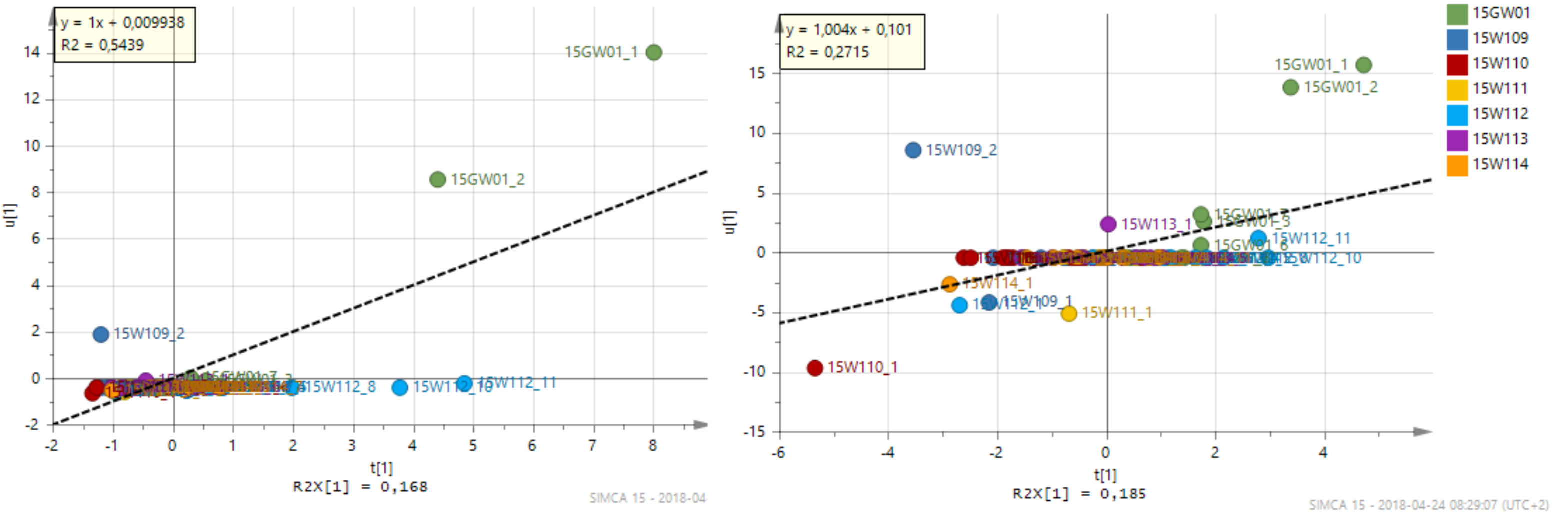

Figure 44. Comparison of the plot of u1 against t1 for the non-transformed data (left) and the log-transformed data (right).

The appearance of the data is most likely due to the fact that 72% of the observations for PCE was marked as below the limit of detection (LOD), as earlier mentioned. Because of this, many values are clustered around the LOD-value of 1 for the non-transformed data (in the left plot) and around 0 ($\log_{10}(1)$) for the log-transformed data (in the right plot). This causes a large skewness in the data set, which makes the model uncertain. The analysis is done on both the log-transformed and the non-transformed data, as none of the data sets show a particularly linear relationship.

The correlation plots resulting from the PLS regression with non-transformed and log-transformed data with PCE as a response variable can be seen below in Figure 45. The figures have been cleared from all variables with a VIP-value of less than 0,5 to make the correlations graphically clearer. Although the loadings of the variables in the different plots have different values in the different plots, the correlations are similar. PCE seems to correlate positively with

TCE, chloride, nitrate, tDCE, Fe^{2+} and cDCE in both plots, and correlate negatively with oxygen, the groundwater level and sulphate as well as possible with DOC and ethene.

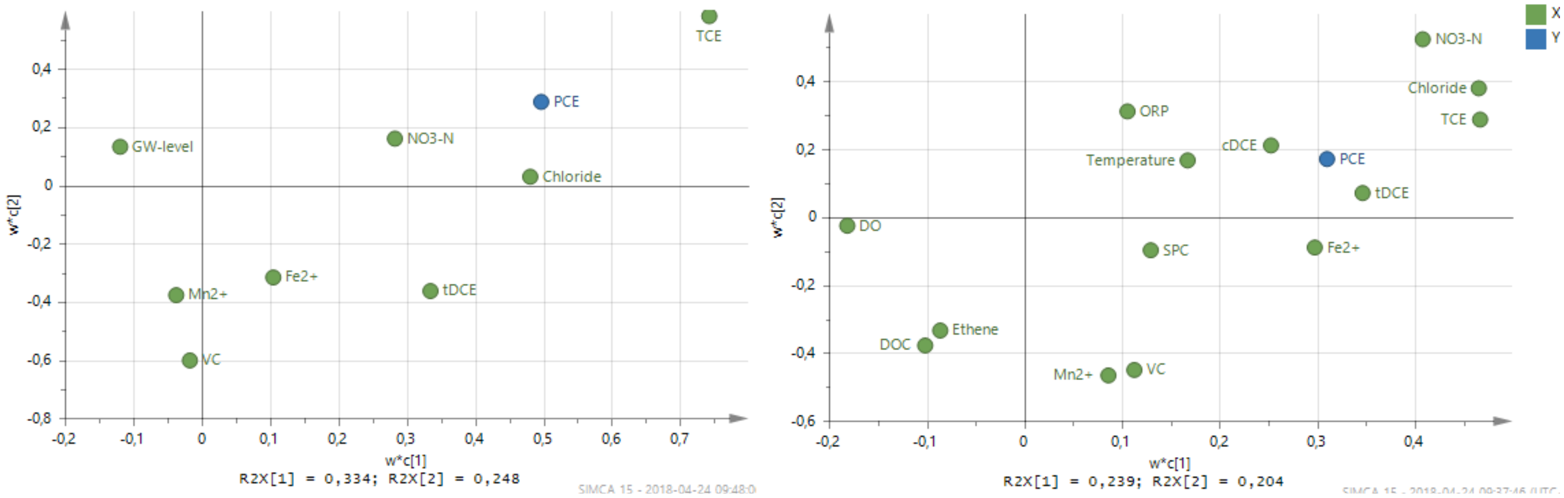

Figure 45. The correlation plot for the non-transformed (above) and log-transformed (below) data with the loadings of the variables, with variables with a VIP-values below 0,5 cleared away.

The model values can be seen in Table 7 below, where the variation of the descriptor variables (R^2_X) and the variation of the response variables (R^2_Y) together with the fraction of variation of Y predicted by the model (Q^2) and R^2_Y-Q^2 is shown.

Table 7. Showing the values of R^2_X, R^2_Y, Q^2 and R^2_Y - Q^2.

	R^2_X (%)	**R^2_Y (%)**	**Q^2 (%)**	**R^2_Y - Q^2 (%)**
Non-transformed	58.2	68.7	42.1	26.6
Log-transformed	44.3	33.8	5.8	27.9

As both R^2_Y and Q^2 should not explain and predict less than 50% of the variation in the model, and the difference between them should not be more than 20-30% for a model with a good fit, the non-transformed data actually generates the better model. Many correlations are the same in the correlations plots of the two models, which is confirmed by the significant correlations in the VIP-plots, seen below in Figure 46.

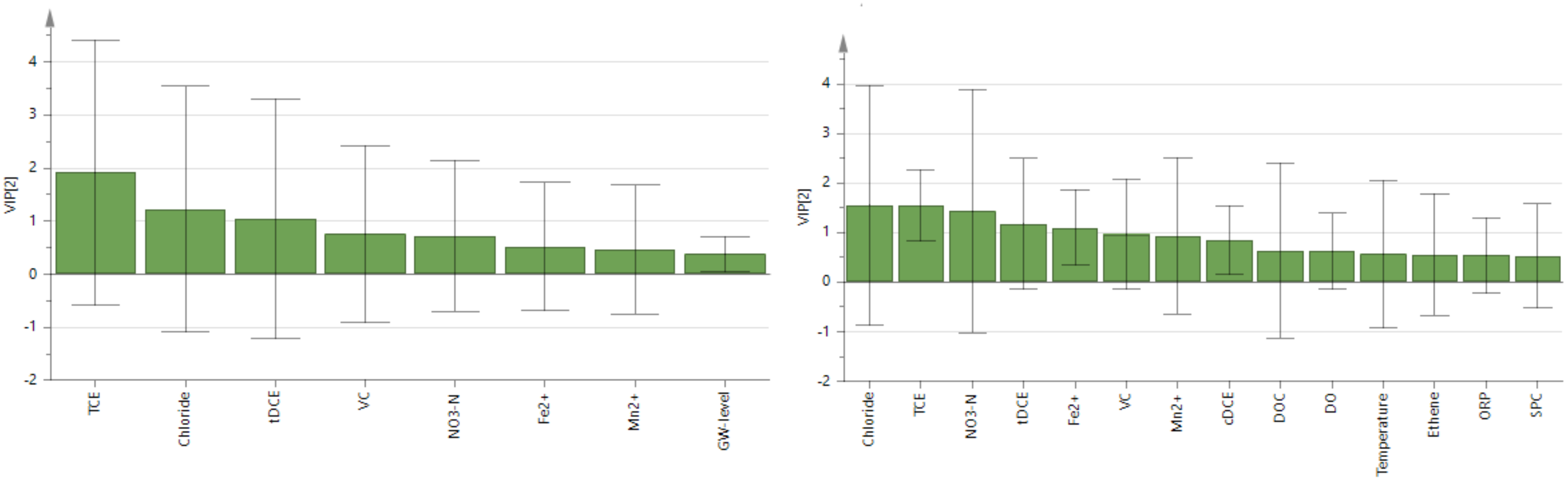

Figure 46. The VIP-plot for the non-transformed observations (left) and the log-transformed observations (right) with PCE as the response variable.

The strong positive correlations with TCE, Fe^{2+}, chloride, nitrate, tDCE and VC are present in both models, as seen in Figure 18. However, all correlations have large confidence intervals in the model of the non-transformed data, which makes the correlations uncertain. For the significant correlations in the model with log-transformed data both chloride and nitrate have large confidence values. The positive correlations that are interpreted as significant are the correlations with TCE and Fe^{2+}. The negative correlations seem uncertain, but PCE might be negatively correlated with VC and oxygen.

B.2 PLS REGRESSION WITH tDCE

When the scores for the descriptive (X) and response (Y) variables with tDCE as the response variable were plotted against each other, it could be seen that many data points had the same value, as seen in Figure 47. As mentioned earlier for tDCE, 53,4 % of the observations were marked as below the limit of detection, which explains the appearance of the data. To obtain less skewness, the data set was log-transformed, resulting in the plot seen to the right below in Figure 47. The skewness remained to the most part, which risks giving an uncertain model. The analysis is done on both the log-transformed and the non-transformed data, as both data sets show a skewed relationship.

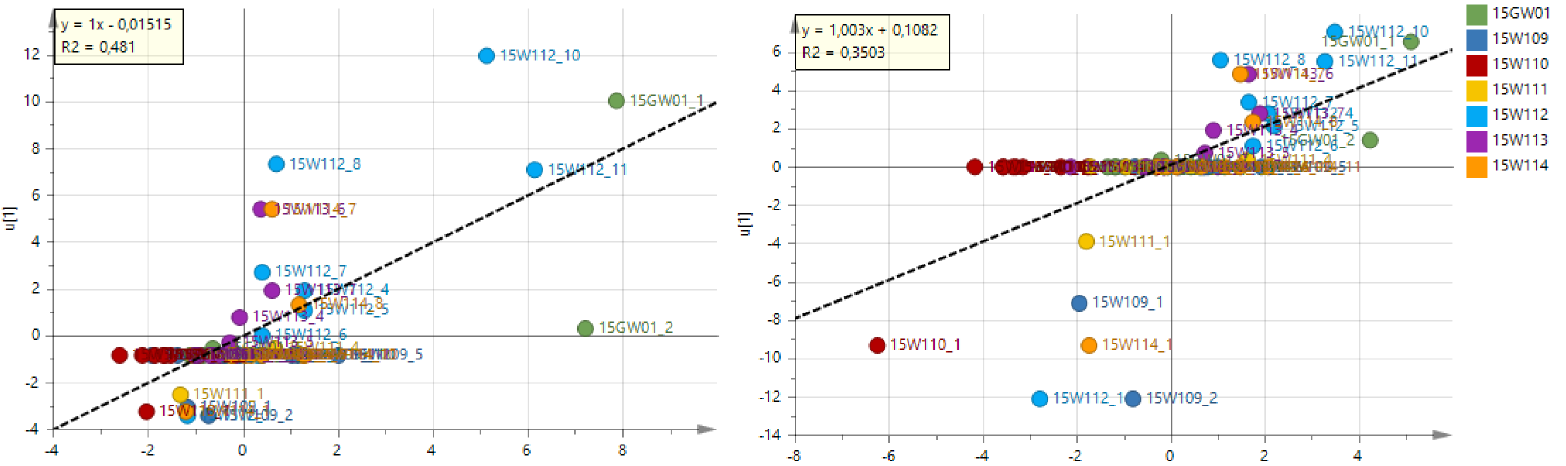

Figure 47. The plot of u1 against t1 for non-transformed (left) and log-transformed (right) data with tDCE as response variable.

When the correlation plots of the non-transformed and the log-transformed data sets are compared graphically, as seen below in Figure 48, strong similarities in the correlations with tDCE are found. The figures have been cleared from all variables with a VIP-value of less than 0,5 to make the correlations graphically clearer.

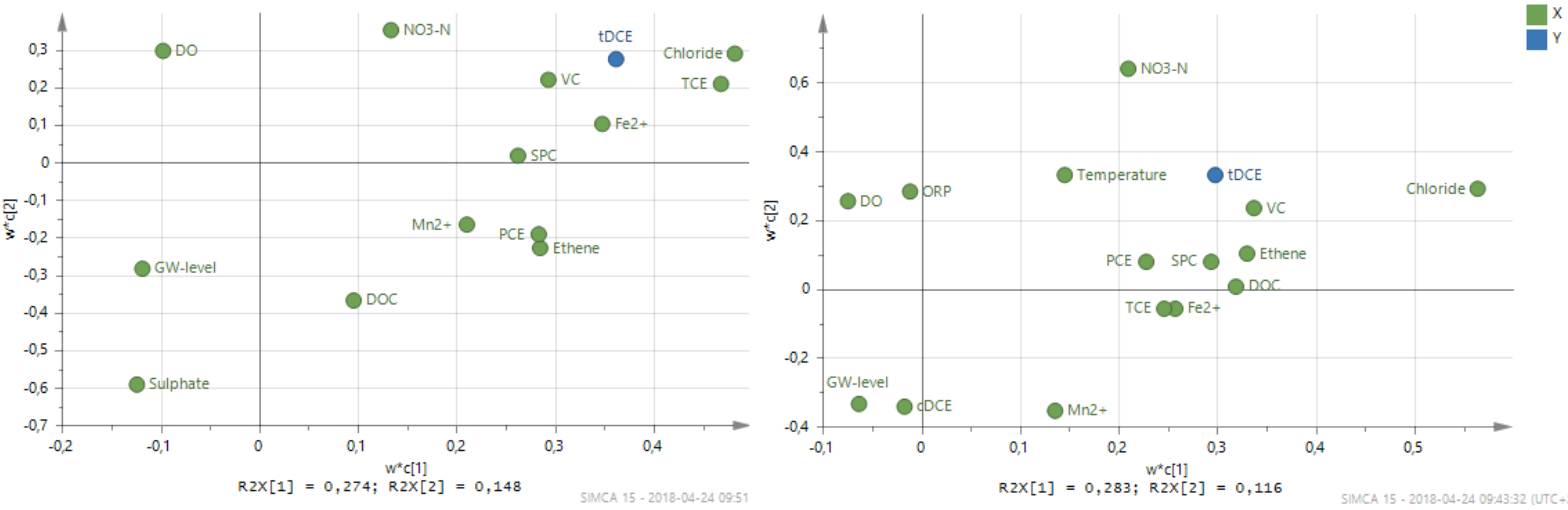

Figure 48. The correlation plot for the non-transformed (above) and log-transformed (below) data with the loadings of the variables.

As seen in Figure 48, tDCE seems to have a positive correlation with chloride, VC, Fe^{2+}, TCE, SPC, PCE, ethene, nitrate and DOC in both plots. cDCE seems to have a negative correlation with oxygen and the groundwater level in both plots.

The model values can be seen in Table 8 below, where the variation of the descriptor variables (R^2_X) and the variation of the response variables (R^2_Y) together with the fraction of variation of Y predicted by the model (Q^2) and R^2_Y-Q^2 is shown.

Table 8. Showing the values of R2X, R2Y, Q2 and R2Y - Q2.

	R^2_X (%)	**R^2_Y (%)**	**Q^2 (%)**	**R^2_Y - Q^2 (%)**
Non-transformed	42.2	57.6	15.3	42.3
Log-transformed	39.9	50.9	26.3	24.6

The model with the non-transformed data explains a lot of the variation in X and Y but does not have a good prediction of the variability. This is not a good model. The model for the log-transformed data explains enough of the variation in the data to be a good fit but does not predicts the variability well enough to give the model a good fit, although it is slightly better than the non-transformed model. However, the results of the model have to be interpreted with care.

The observed correlations, and the similarity between the two models, can be seen their VIP-plots, seen below in Figure 49.

Figure 49. The VIP-plot for the log-transformed observations with tDCE as the response variable.

The strong positive correlations with chloride, VC, DOC and Mn^{2+} can be seen in the VIP-plot. The positive correlation with TCE and Fe^{2+} seem likely although they have a VIP-value below 1. The negative correlation to SPC and DO may also exist but are more uncertain.