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DNAPL characterization in clayey till & chalk by FACT (FLUTe Activated Carbon Technique)

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DNAPL characterization in clayey till & chalk by FACT (FLUTe Activated Carbon Technique)

Master Thesis Report in line with a 30 ECTS thesis at DTU Miljø

Monique Beyer (s101186)

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Contents

Abstract

Chlorinated solvents (PCE, TCE and TCA) were expected to be present as Dense Non Aqueous Phase Liquids (DNAPL) in the clay till subsurface and chalk aquifer at the site Naverland in Albertslund, DK. The behavior of DNAPLs in fractured media, in particular chalk, is poorly understood and characterization is a difficult task. There is a need for a high vertical resolution with respect to contaminant distribution in a difficult medium to access. A new characterization method combining an activated carbon felt and a NAPL FLUTe Liner^{TM} (short FACT) was one of several characterization methods which were tested at the Naverland site and compared in terms of their applicability for DNAPL characterization in a chalk aquifer. The scope of this MSc thesis was to evaluate the applicability of the carbon felt through laboratory testing and application of laboratory results to field sampling and data from the site.

The application of the activated carbon felt as characterization method is developed and described in this study by conducting adsorption and desorption experiments of chlorinated solvents on the carbon felt. The aim was to develop an analytical method, to study the behavior of the FACT (staining and concentration data) exposed to different concentrations of chlorinated solvents and phases (air, water and DNAPL). Subsequently the evaluation of field data was conducted and the site was evaluated based on laboratory results. The common characterization by groundwater sampling (depth discreet) does not allow for differentiation of DNAPL presence and high aqueous concentrations in features such as fractures or in the matrix. The FACT was expected to be a useful tool to differentiate the presence of DNAPL phase and high dissolved concentrations of chlorinated solvent with a high vertical resolution. Hence, it was expected to be of high value in the evaluation of field data.

Results of adsorption experiments showed equilibrium time is reached after 180 h, however due to fast adsorption during the first 12 h, a minimum contact/application time of the FACT liner in the field was set to >24 h. Pentane extraction was found to be the best extraction method for analysis of the carbon felt due to a high recovery. Extraction with water showed very low recovery, however arising the opportunity to store and preserve the samples in water. Thus pentane was added back in the laboratory, not during field work and a minimum extraction time of 48 h is set to reach a state close to equilibrium.

Different types of staining on the FLUTe liner were observed and reproduced leading back to DNAPL presence and high chlorinated solvent content (saturation) in the water phase. Furthermore results of different phase exposures of chlorinated solvents; namely DNAPL, air and water phase, indicated diffusion controlled adsorption demonstrated also by fieldwork samples showing generally higher concentrations of chlorinated solvents in the unsaturated zone than in the saturated zone.

Concentration results of larger and average results of smaller samples are compared in this study showing similar results for different sample discretization. However caution needs to be taken by choosing an appropriate sample location in order not to lose important information such as high peak concentration values. Therefore PID measurement and observation of staining turned out to be useful tools to identify interesting sampling locations with expected high concentrations and therefore the possibility of more discreet sampling.

In general field sample results showed good analogy of concentration evaluation on the carbon felt over depth to obtained data from soil and soil vapour (MIP) sampling (obtained by other researchers during the project). Furthermore the combination of staining and concentration data on the FACT was found to be very useful to trace locations with high chlorinated solvent content or DNAPL presence and to distinguish between probable DNAPL presence (according to the staining) or high aqueous chlorinated solvent concentration (high concentration on carbon felt and light staining). Comparison with first water concentration data showed poor correlation due to water samples represent just the concentration in the bigger, high flow fractures, in contrast to the FACT, which represents also the smaller fractures and pore space of the soil.

It is important to mention that back calculation from carbon felt concentrations on the FACT to water or soil concentration is not possible, due to too high complexity of adsorption processes. However, it was found that adsorption processes of chlorinated solvents to the carbon felt are diffusion controlled, with highest concentrations found in saturated air phase and lower concentrations found during aqueous chlorinated phase exposure. Thus a differentiation and concentrations range of adsorption from different phases (water, air or at direct DNAPL contact) was possible. It was also found that diffusion is dependent on soil properties leading to a different diffusion rate, leading to difficulties of interpreting results from the unsaturated zone, due to variation of water content. Hence the results of the FACT method can be used as a duplicate of the relative amount of contaminant present in the aquifer material, when soil properties are known or are more or less homogenous and with information from soil or water analysis the concentration range can be evaluated.

Overall this method does not provide a direct measure of the concentration per unit weight of pore fluid/soil, but it is a duplicate of the relative amount of contaminant present in the aquifer material. However to estimate real concentrations in the aquifer, the FACT characterization method needs to be accompanied and accomplished by other methods (e.g. water or soil analysis) and the knowledge of water content (saturated/ unsaturated zone) and soil properties (as porosity) is necessary for right interpretation. Furthermore in combination with observation of staining on the FACT and knowledge of the soil properties, the FACT does prove DNAPL presence and furthermore in the saturated zone a differentiation between high aqueous concentration (saturation) and DNAPL presence can be made.

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1. Introduction and scope

This master thesis was supervised by Gry Janniche, Mette Broholm and Poul Bjerg. The work was part of a project taking place from October 2011 till March 2012, where the Naverland site (in Albertslund, DK) served to test several characterization methods and compare their applicability, reliability, advantages and disadvantages in order to provide recommendations on DNAPL site characterization to help the Region to prioritize contaminated sites regarding remediation. The field work involved DTU Environment, the Region of Copenhagen, consultants COWI and Niras and FLUTe participation.

At the Naverland site chlorinated solvents PCE (PerChloroEthylene), TCE (TriChloroEthylene), cis-DCE (cis-DiChloroEthylene) and TCA (TriChloroEthane) are expected to be present in very high concentrations forming Dense Non Aqueous Phase Liquids (DNAPL). The ground water passing through the DNAPL contaminated zone solved part of the chlorinated solvents and a huge contamination plume evolved in the aquifer, shown by former investigations at the site. [Region Hovestaden 2008; Janniche 2011]

Due to their neurotoxic and potential carcinogenic effects, ground water pollution with chlorinated ethenes stand for the greatest hazard to drinking water supply and ecosystem contamination [U.S.EPA, 2004 and 2005; WHO, 2004]. Natural degradation is possible under anaerobic conditions from PCE over TCE and different forms of DCE to VC and Ethene, however hydrogen and a specific type of microorganism are needed. A more detailed description of chlorinated solvents can be found in the report of a literature review done by Beyer (2011).

The behavior of DNAPLs in fractured media, in particular chalk, is poorly understood and characterization is a difficult task. There is a need for a high vertical resolution with respect to contaminant distribution in a difficult media to access. A new characterization method combining an activated carbon felt and a NAPL FLUTe Liner®, as one of the several characterization methods tested at the Naverland site, was studied in terms of its applicability for DNAPL characterization in a chalk aquifer.

Scope

The scope of the MSc thesis was to evaluate the applicability of the carbon felt through laboratory testing and interpretation of field data collected from the site as well as comparison to other field data collected at the Naverland site by other researchers. Part of the master thesis dealt with finding an analytical method to determine chlorinated solvent concentrations on the FACT, precisely the carbon felt. Therefore lab experiments studying desorption in water and extraction in pentane were carried out. Furthermore the handling and application of the FACT in the field needed to be defined, in detail finding the most suitable exposure time of the FACT in the borehole and the possible discretization of sampling. Hence absorption behavior of aqueous chlorinated solvents and discretization of samples were studied in the lab determining absorption curves, equilibrium times and discretization characteristics, respectively. Finally the exposure of chlorinated solvents from different phases, namely air and water phase and as DNAPL, were examined in order to identify sorption kinetics and limit concentrations for interpretation of field samples further on.

Part of the master thesis project involved planning and carrying out sampling of the FACT liner at the Naverland site. 6 FACT liners were installed at the field site, 3 in chalk and 3 in clay till. The analysis of the field samples was conducted and the site was evaluated based on laboratory results. The common characterization by groundwater sampling (depth discreet) does not allow for differentiation of DNAPL presence and high aqueous concentrations in features such as fractures or in the matrix. The FACT liner was expected to be a useful tool to differentiate the presence of DNAPL phase and high dissolved concentrations of chlorinated solvent with a high vertical resolution.

In the following the background is giving an overview including descriptions of: 1st chlorinated solvents, mainly PCE (PerChloroEthylene) and TCE (TriChloroEthylene); 2nd chalk as typical Danish aquifer material; 3rd the most common DNAPL characterization techniques used with the focus on a newly developed technique namely FACT and 4th the site Naverland AB, Albertslund, DK expected to be contaminated with DNAPLs.

Later on the results of laboratory (adsorption and desorption/extraction) experiments are presented; according to these the handling of the field samples is set. Finally the results of the fieldwork are shown and therefore the applicability of the NAPL FACT liner critically is discussed.

2. Background

2.1 DNAPL

DNAPL contamination contributes to 49% of the sites with long term or continuous remediation and effects 22% of the drinking water aquifer wells in greater Copenhagen bearing risk for nature and population. [cont.Sites]

Due to their physico-chemical properties chlorinated solvents can form DNAPLs. In summary Lawrence 1996 and Jørgensen et al. 2010 give an overview of selected physico-chemical properties of PCE, TCE and TCA, given in table 1. At the studied field site the chlorinated solvents PCE and TCE are expected to be present in such high amounts that Dense Non Aqueous Phase Liquid (DNAPL) is still present in the chalk aquifer. Since DNAPLs are (water) immiscible, hydrophobic phase liquids and heavier/denser than water, they form a separate phase and sink in the aquifer [cont.Sites].

Table 1: selected physico-chemical properties of PCE, TCE and TCA

Compound	**Solubility [g/L]**	**K_H [atm.m³/mol]**	**K_{oc} [mg/L]**	**Density [g/ml]**
PCE	0.15 (0.2-0.24)	$2.59*10^{-2}$	364	1.63
TCA	1.5	$1.44*10^{-2}$	152	1.35
TCE	1.1 (1.1-1.4)	$9.1*10^{-3}$	126	1.47

However chlorinated solvents do not automatically from DNAPLs. A certain limit concentration (for single components given by the solubility of the compound in water and for a mix given by the solubility dependent on the molar fraction of the compound) needs to be reached. Since DNAPL has a higher density than water (see table 1), mobile DNAPL continues sinking into the aquifer due to gravity force and soil capillarity causing a spreading of the contamination in the soil and enlargement of the contamination plume in the ground water, until the source is exhausted and all DNAPL is present as residual DNAPL or the mobile DNAPL reaches a layer of low permeability e.g. clay till, thus likely forming pools.

Due to their high density, low viscosity and low interfacial tension, DNAPLs move through fractures and cracks in low permeability layers/aquifer materials. According to the capillary pressures, precisely in case the capillary pressure is higher than the entry pressure of the fractures, DNAPL will enter the fractures and spread in the aquifer. However not all fractures in the local fracture network will be invaded by DNAPL due to too high entry pressures of the fractures. [Kueper & McWhorter, 1991] It was shown DNAPL move also into secondary fractures, meaning that the DNAPL can move much deeper into the aquifer than expected and the before seen as low permeability barrier layers do not act as barrier eventually [Pankow and Cherry, 1996]. Furthermore regarding remediation techniques, penetration into secondary fractures leads to more difficult remediation.

In general a three-phase system is present in the saturated zone (sorbed, dissolved and DNAPL phase) and a four-phase system is present in the unsaturated zone (sorbed, dissolved, gas and DNAPL phase). In depth phase distribution calculations of chlorinated solvents can be found in appendix A.

As shown, chlorinated solvents can be found in different forms. As DNAPL phase, due to its properties, it forms pools and spreads into cracks and fractures of low permeability layers (see fig. 1).

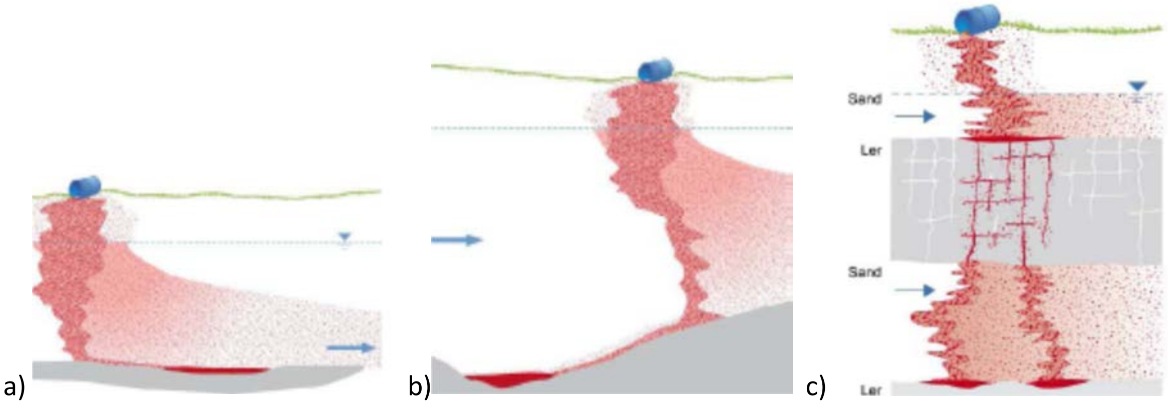

Figure 1: behavior of DNAPL in an aquifer a) sinking and forming of a pool on top of a low permeable layer, b) formation of an upstream pool due to geological parameters, c) diffusion and sorption from cracks and fractures into a layer with low permeability plus pool formation [Jørgensen et al. 2010]

Figure 2 illustrates the processes of contamination over time in fractured media. In fractured media, the DNAPL phase leaking from an underground tank or another source, diffuses first into fractures. With time, the ground water, passing the DNAPL phase, dissolves chlorinated solvents ('oplost stof' in fig. 2) leading to a large contamination plume. Furthermore the chlorinated solvents diffuse and sorb into the surrounding aquifer material. When the source has been removed or terminates, the ground water solves first the chlorinated solvents from the fractures (due to high ground water flow), however the remaining residual DNAPL in smaller fractures or soil pores will take a very long time to be dissolved in the ground water. This also indicates the durability and severity of DNAPL contamination. Thus first priority is to discover and locate DNAPLs, to characterize a side according to its severity of contamination and then remediation action can be taken.

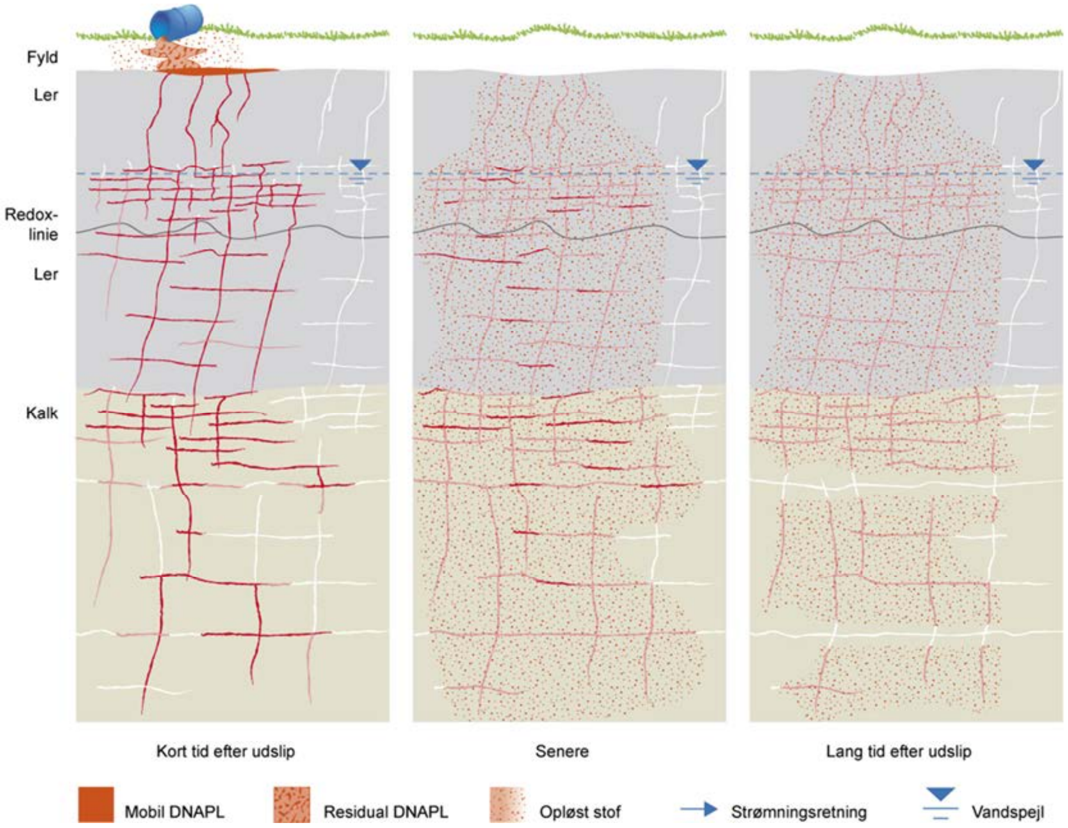

Figure 2: behavior of DNAPL and chlorinated solvents in fractured media over time, left: short time after spillage, middle: later, right: a long time after spillage [Jørgensen et al., 2010]

Impurities of e.g. cis-DCE and TCA in PCE or TCE are quite likely, thus presence of degradation products as cis-DCE found in the aquifer in relatively low concentrations, do not necessarily indicate degradation. Material Safety Data Sheets for dry-cleaning-grade PCE indicate that the purity is ranging from 99% to 99.9% nowadays. Some of the documented impurities of PCE are: TCA, carbon tetrachloride, DCE, TCE, water and other chlorinated solvents [European Communities, 2005]. According to the ICPS commercially available TCE (as chemical reagent) has a higher purity than 99.85% with main relevant impurities as carbon tetrachloride, chloroform, cis-DCE, TCA and PCE. Furthermore they note it is uncommon for an impurity compound to be present at a level exceeding 0.01% or impurities in total exceeding 0.1%. [IPCS, 2012] However it should be noted that impurities in the 1960s have been higher. Furthermore impurities due to transportation can occur.

Further description of chlorinated solvents, their properties and behavior can be found in a literature study done beforehand [Beyer, 2011].

2.2 Danish aquifer

Chalk was deposited during the Cretaceous Period as pelagic sediment and is forming a sedimentary basin in northern Europe. Due to the chalk was fractured and broken up on the surface during the movement of the glaciers, it has typically fractures and cracks in the upper 5 to 10 m and is expected to have a high hydraulic conductivity, a relatively high porosity and low permeability [Janniche, 2011; Region Hovedstaden 2008; Price et al. 1993]. A generally low permeability is observed due to high porosity of 30-50% [Frykman, 2001] leading to high water storing capacity [Downing and Headworth, 1990], but small grain size [Price et al., 1993].

Due to tectonic and glacial history of the material, vertical and horizontal fractures have been formed supporting the formation of an aquifer [Bloomfield, 1996; Rosenbom and Jakobsen, 2005]. The chalk as the Danish bedrock reveals to be an inhomogeneous around 1.5 km thick layer with deposits of calcite and clay. E.g. at the studied field site in Naverland alternating soft and hard zones with sand and gravel layers and flint benches, as well as parallel fractured layers are expected to be present according to a test coring in March 2008 [Vestegnens Vandsamarbejde, 2009]. Additionally chalk can have either a more brittle/pulverulent structure or is very hard material, as mainly occurring in Danish chalk, thus the handling during fieldwork is expected to be difficult [Harris, 2012].

A literature study done beforehand [Beyer, 2011] showed due to its dual-porosity character [Barker 1993] chalk is an interesting, manifold and challenging aquifer material especially in terms of DNAPL contamination and sample handling [e.g. Price et al. 1993; Williams et al., 2006; Bonnensen et al., 2009; Bloomfield, 1996 and Endmunds, 1987]. The Naverland site appeared to be optimal to study and reveal DNAPL characterization techniques in chalk as contaminated material.

2.3 Characterization methods

In general it is very difficult to confirm residual DNAPL presence, due to it often does not flow into a monitoring well since it is caught in the soil pores, thus special characterization methods are necessary [Bedient et al., 1999]. Furthermore the purpose of a characterization method is to get a high resolution over depth, thus some screening tools can be used to identify DNAPL presence, other tools can be applied to verify and quantify DNAPL and concentrations of chlorinated solvents with higher discretization.

First knowledge about the geology of the site is crucial to evaluate the behavior of the DNAPL, since DNAPL transport is dependent among other things on heterogeneities of the subsurface. Moreover some characterization methods are not suitable for all aquifer materials. Furthermore it is very important to obtain data of how much and where free phase DNAPL is present. However, most characterization methods imply, if the DNAPL identification outcome is negative that does not necessarily indicate absence of DNAPL.

There are different approaches to identify DNAPL free phase presence, generally subdivided into direct and indirect method. Direct methods are e.g. measurements via a monitoring well or visual examination of the soil. Monitoring requires useful tools to indicate/prove DNAPL mobile/ free phase presence. However mobile DNAPL phase is difficult to handle, since the monitoring well needs to be installed correctly, not to accumulate too much (in case of passing a DNAPL pool) or in the wrong place (passing 2 DNAPL pools, mobilizing DNAPL). Furthermore visual soil sample examination can be done with the bare eye, either residual blobs are visual or Sudan IV hydrophobic dye or DNAPL spray can be used to visualize free DNAPL. [Cohen and Mercer, 1993]

As indirect methods ground water or soil (pore water, soil air or soil) concentration determination are used. Using a rule of thumb, a chlorinated solvent ground water concentration higher than 1% of the effective solubility concentration indicates free phase DNAPL presence, since the effective solubility is in reality rarely observed due to mixed contamination or false measurement while installing the monitoring well and measuring along a newly created DNAPL “flow” line. [U.S. EPA 1992a; Pankow and Cherry 1996] However, again, a low concentration does not exclude DNAPL presence. Furthermore a concentration limit, as estimated via the phase distribution calculation of chlorinated solvents in subsurface (see appendix 1) of chlorinated solvent in soil is used as a rule of thumb to identify mobile DNAPL presence or the using the partitioning thus estimating the concentration of DNAPL in the pore water and comparison with the effective solubility. [Feenstra et al. 1991] Furthermore geophysical measurements like geo-radar, complex resistivity or electromagnetic induction to model probable DNAPL flow paths are more and more widely used. [U.S. EPA 1992b]

All methods are described in more detail in the literature review [Beyer, 2011]. As an extract, advantages and disadvantages of each method and predicted outcome are given in summary in tab. 2.

Table 2: summary of advantages and disadvantages of the methods for DNAPL characterization [Beyer, 2011]

Method	**Pro**	**Con**
Georadar	On-site, noninvasive, good indication, high horizontal resolution	Background data needed, for monitoring - not detection
Radon	Good indicator, no need for injection or intrusion	in-situ, just indication if close by DNAPL, not tested in DK yet
MIP	qualitative analysis with attached GC, on-site/in-situ, high vertical resolution	Pushed into soil, not applicable for chalk
FLUTe	In-situ, easy handling, fast & direct DNAPL evidence, high vertical resolution	Bore hole needed, not quantitative, not standard in DK
FLUTe & activated carbon felt (FACT)	Potentially for concentration estimation and qualitative analysis, in-situ	Not yet tested, NOM might act as pore blocking, analysis in lab
Sudan IV & DNAPL color spray	fast and easy to handle, direct evidence of DNAPL on-site	not quantitative
water/soil analysis and calculation	More precise data can be obtained about quantity and quality	Ex-situ, more laborious, requires core/soil samples

In conclusion a combination of different methods to get more detailed results is needed since the characterization methods itself lack in one or the other direction. Hence as a combination they complement each other. In addition the placing/installation and application of all characterization methods should be very close to each other to allow a subsequent comparison.

The purpose of this study was to test and evaluate the applicability of a newly developed method namely FACT, as a combination of NAPL FLUTe and activated carbon felt. A more detailed description of the FACT liner is presented in the following.

2.4 NAPL FLUTe and FACT

The NAPL FLUTe liner itself was developed by Keller, C. in 1989 to map NAPLs in cores and boreholes. The tube has a dye striped hydrophobic tubular covering and shows a highly visible straining in case of contact with DNAPL. The liner cover is a urethane coated nylon fabric in tubular form. [Keller, 2011] The cover/FLUTe is put into a borehole (or over a core) filled up with water until the water table obtain optimal contact to the soil or pressed against the borehole walls with pressurized air [FLUTe]. It is afterwards removed by inverting the liner by pulling it out [Keller, 2011]. Figure 3 illustrates the installation and removal procedure of the NAPL FLUTe [Keller, 2011].

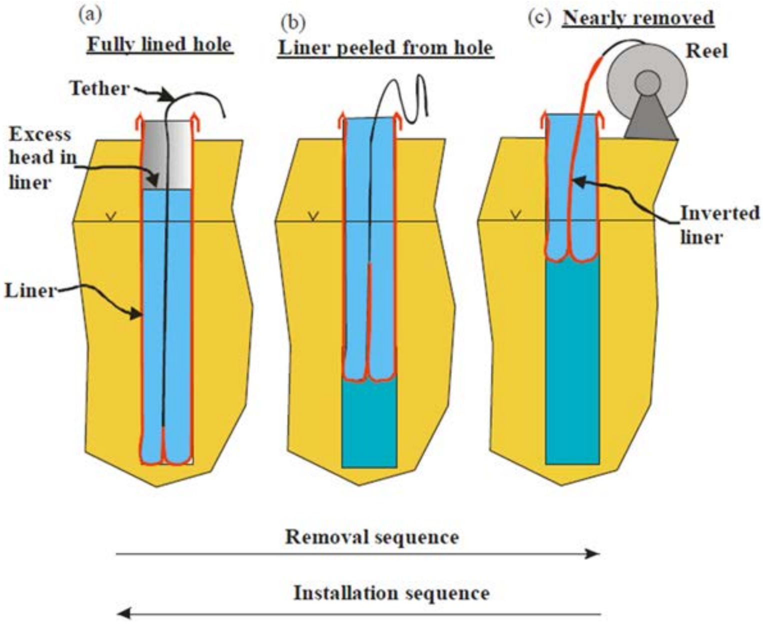

Figure 3: installation and removal procedure of the FACT or NAPL FLUTe liner [Keller, 2011]

The latest development of an activated carbon felt (AC) integrated into a NAPL FLUTe liner by Keller, C. called FACT (United States Patent 7896578) is expected to determine a more precise concentration profile of chlorinated solvents and distinguishing between DNAPL presence and a high aqueous chlorinated solvent concentration. Figure 4 shows the positioning and composition of liner, cover and carbon felt.

Advantages of the FACT are: 1st it represents a direct characterization of the bore hole, 2nd the integrated activated carbon felt allows high vertical resolution. Furthermore a multilevel sampler can be installed subsequently.

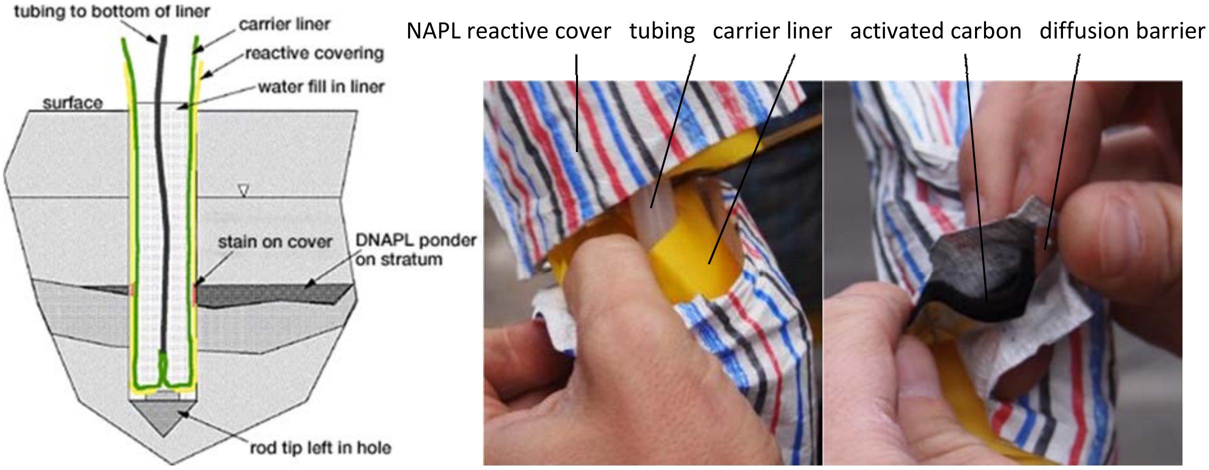

Figure 4: left: positioning of NAPL FLUTe or FACT in borehole [FLUTe]; middle and right: composition of FACT

A Study in Denmark by Keller in April 2010 testing the applicability of the FACT liner in the vadose zone in glacial till showed very good agreement in comparison with the Geoprobe MIP and soil core measurements. Furthermore Keller reports, above the water table they did not find an effect of borehole water contamination on the activated carbon felt. [Keller, 2011] However potentially contaminated borehole water can absorb on the carbon felt during installation in an aquifer leading to high background data of chlorinated solvents and not distinguishable “real”/peak concentration data [Keller, 2011]. Thus during installation the borehole water is pumped out; the liner quickly installed and filled up with clean water just exceeding the water table (see installation figure 4) to obtain optimal contact to the soil. However due to the hydrophobic cover material, the liner is meant to be protected against bore hole water contamination [Keller, 2011].

With the integrated carbon felt, sorption of chlorinated solvents occurs since the activated carbon felt is a hydrophobic, non-polar adsorbent; and subsequent analysis allows a relative quantification of the pollution on site. The advantage of the FACT is to use the staining as first indication of interesting areas, and then discretized fragmentation of the carbon felt allows a discreet characterization over depth. Since there is not much knowledge about analysis of the activated carbon strips (Niras submerged the carbon felt into water and analyzed the resulting concentration in water with a MS with purge and trap; Keller reports about methanol extraction and subsequent GC/MS analysis [Keller, 2011] and Erto et al. (2010b) describes a extraction with acetone and subsequent purge and trap GC FID analysis), thus part of this study focused on determining the best analytical method for the activated carbon felt.

For soil samples for indication a limit concentration, according to phase distribution and saturation calculation (see appendix 1) can be used to justify DNAPL presence. In theory the method of a limit concentration can also be used for the carbon felt to determine DNAPL presence. However, the adsorption and transport processes are in reality very complex due to numerous dependence and interconnection of parameters and processes. Therefore it is useful to test the FACT liner in a “real system” approach (described in chapter 3, lab experiments and 6, Further work), meaning to bring the FACT liner in contact with chlorinated solvents from different phases or “real” aquifer material.

To get a better understanding of the possible sorption pathways, when introducing the FACT into the bore hole and filling it with water for better contact, sorption processes are thought through and shown in figure 5, dependent on unsaturated and saturated zone. [Beyer, 2011]

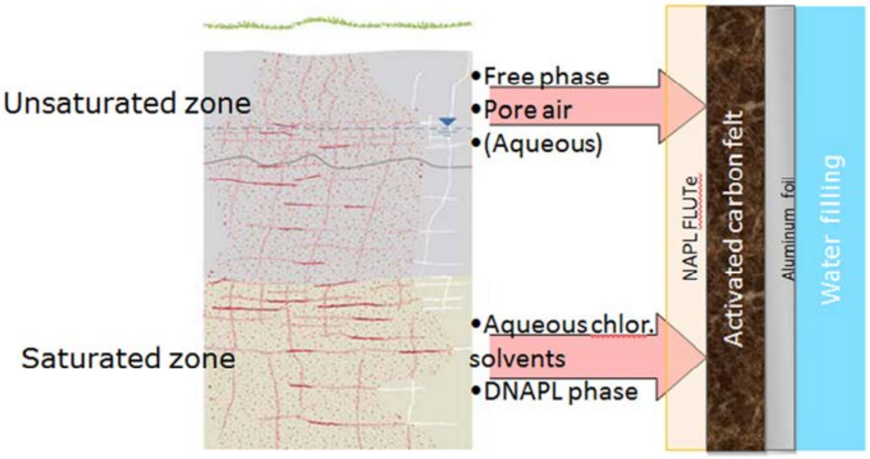

Figure 5: sorption proceses of chlorinated solvents & DNAPL from aquifer material onto activated carbon felt

Figure 5 shows in the saturated zone dissolved chlorinated solvents adsorb on the activated carbon felt, but it is also possible for free phase (if present) to adsorb on the carbon felt – here very high concentrations on the carbon felt are expected. Furthermore in the unsaturated zone chlorinated solvent vapors may adsorb on the carbon felt. Desorption from soil and sorption to the carbon felt is very likely since the activated carbon felt is a better adsorbent compared to soil, due to its higher organic carbon content and very high surface area [Zytner et al. 1989]. A protecting cover of aluminum foil avoids desorption from carbon felt into the water filling in the liner.

For simplification adsorption and desorption to the activated carbon felt are assumed to be linear, reversible and with rapid equilibrium in a homogeneous soil. However studies showed adsorption and desorption follow mainly Langmuir or Freundlich isotherm on granular activated carbon [Zytner et al., 1989; Zytner 1991; Erto et al., 2009 and 2010a; Chuang et al., 2003] and activated carbon [Erto et al., 2010b]. In mixtures, PCE adsorption is independent from the presence of TCE [Erto et al. 2011]. An important fact is that adsorbed TCE is replaced by PCE showing both molecules compete for the same active sites on the activated carbon [Erto et al., 2011; Clausse et al., 1998; O'Connor, 2001].

The adsorption on the carbon felt is expected to be diffusion controlled. Equilibrium times for adsorption vary on granular activated carbon from 15 h for TCE [Arnold et al. 2006], 20 h for PCE [Zytner et al., 1989] to 12 days for a mix of TCE and PCE [Erto et al., 2011]. Hence to get the best adsorption results the application time of the FACT in the bore hole needed to be further evaluated (in adsorption experiments to study equilibrium times of adsorption).

Zytner et al. (1991) studied adsorption and subsequent desorption and found a hysteresis between adsorption and desorption of TCE. The found hysteresis will play an important role when analyzing the carbon felt, due to analysis implies desorption. For analysis non-displace desorption or displace desorption are applicable [To et al. 2008], further described in Beyer, 2011.

Interestingly natural organic matter (NOM), present in groundwater and soil, is likely to adsorb onto the activated carbon felt and block pores and hinder adsorption of organic contaminants as researchers previously showed [Carter et al., 1992; Smith et al., 1987; Kilduff et al., 1998; Pelekani et al., 2001; Li et al., 2003]. These studies are indicating problems that could be faced during the use of the activated carbon felt to determine the correct concentrations of TCE/PCE in case NOM sorbs on the carbon felt. Experience shows NOM is usually low in clayey till and expected to be low in chalk.

However further evaluation is necessary to evaluate if NOM is an issue when facing higher NOM contents in the subsurface.

Since most research regarding adsorption and desorption has been done on GAC, further evaluation on the carbon felt used in this study is necessary. To study adsorption and desorption curves of dissolved PCE/TCE on the carbon felt and to find the most suitable analytical method, lab experiments were conducted.

2.5 Naverland site description

History

At the site Naverland 26AB located west of Copenhagen, Denmark chlorinated solvents PCE and TCE have been handled in large amounts between 1965 and 1983 and a PCE tank was buried in 1966 (filled with sand in 1983) as summarized in Beyer (2011). The contamination is expected to be due to the handling of chlorinated solvents e.g. filling and pumping of PCE out of a tank, storage and distribution of TCE in drums, ect.

Geology

Geology analysis of the site (shown in figure 6) showed the PCE tank is sitting in the back fill (Fyld) underlain by a clay till layer (Moræneler) down to around 7 m b.s. with varying thickness and silt, sand and gravel bars/layers (Grus). Below the clay layer chalk (Kalk) is present with fractured and non-fractured, harder and softer layers. The aquifer is located around 6 to 7m below surface partly covering the clay layer.

First investigations

In summary previous investigation of the groundwater and pore air around the expected contaminated area at the site showed indication of DNAPL contamination in March 2008 [Region Hovestaden, 2008; Janniche, 2011]. A modeling of the contaminant plume on basis of potential measurements to estimate ground water flow in October 2010 was done by Rambøll (fig. 7), showing a huge contamination plume. [Vestegnens Vandsamarbejde, 2007, 2009 and 2011; Region Hovestaden, 2011] Even though a more than 1km long contaminant plume is threatening the surrounding water works, the site has not been scheduled for remediation yet, as it is not located in an area of special drinking water interest [Vestegnens Vandsamarbejde, 2007 and 2011; Janniche, 2011]. Furthermore according to a test coring in March 2008 DNAPL is expected to have reached 25 m b.s. at the site (fig. 6). [Region Hovedstaden 2008; Københavns Amt 2002; Janniche 2011].

So far according to test monitoring at a drinking water collection downstream the contamination plume seems to have mainly a vertical spreading in the top layer of the chalk due to geological parameters. Furthermore cis-DCE a degradation product is found in further distance of the plume indicating natural degradation of TCE and/or PCE takes place. [Rambøll 2011]

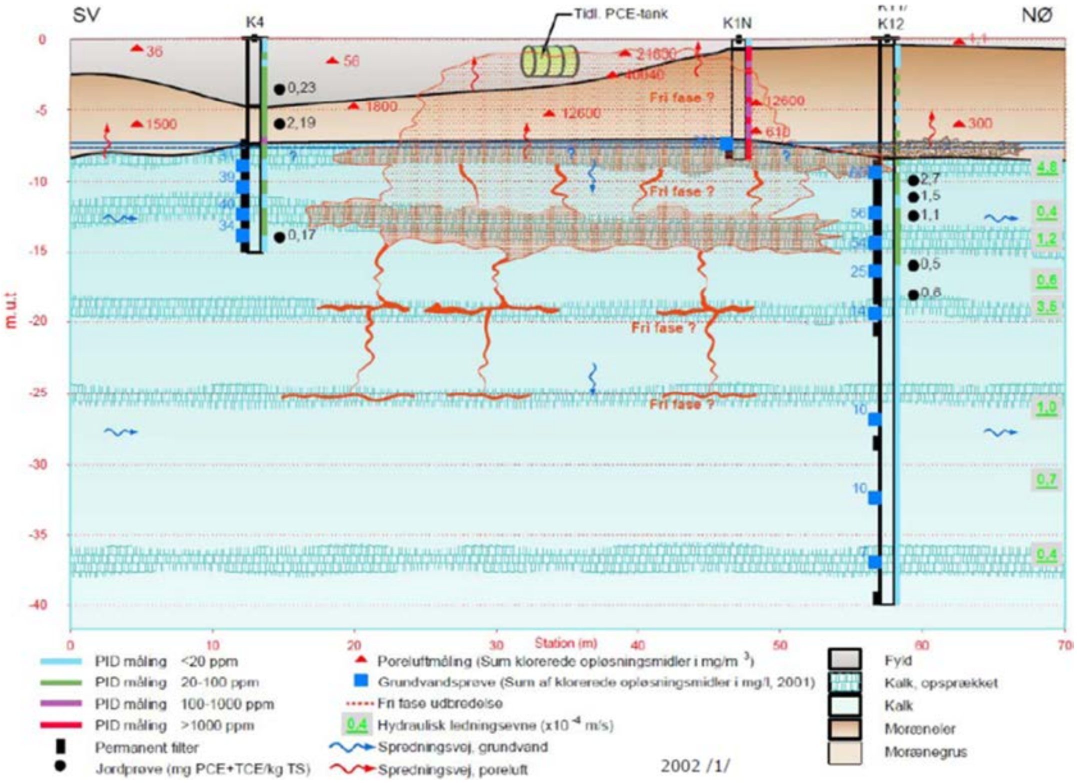

Figure 6: conceptual model of contaminant plume in Naverland according to data obtained in March 2008 with concentration of DNAPL obtained in soil (jord) and groundwater (grundvand), plus values for hydraulic conductivities & geological conditions [Region Hovedstaden 2008; Københavns Amt 2002; Janniche 2011]

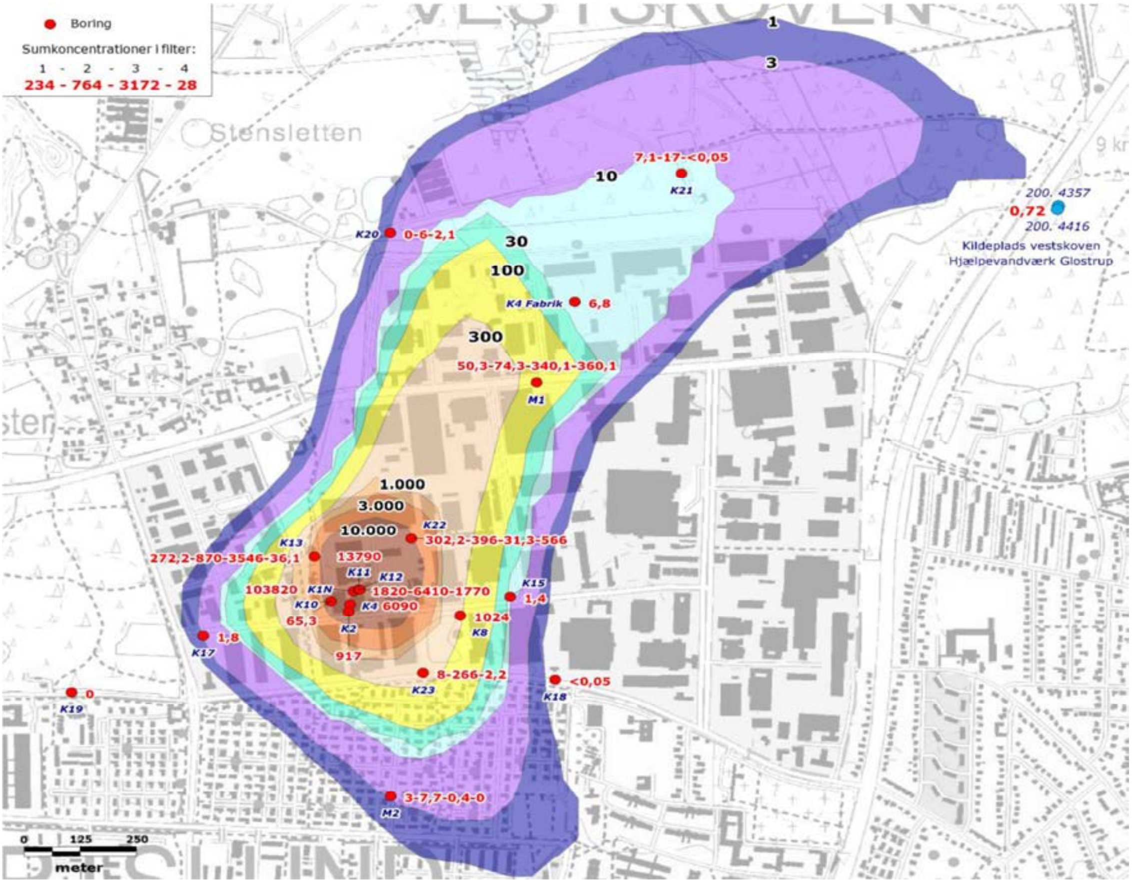

Figure 7: contaminant plume with sum-concentrations of TCE, PCE and TCA with Filter 1 as deepest filter and filter 4 as the uppermost filter close to the top of the chalk [Vestegnens Vandsamarbejde 2011]

Action

Starting in 2002 the capital region (Region Hovedstaden), decided to risk asses and delineate the contamination at Naverland 26 [Københavns Amt 2002; Janniche 2011].

Since 2008 (prospectively till 2015) a test pumping is running (in borehole K11, see fig. 6), pumping out 4-5 m^3/h of contaminated water from the source zone controling the spreading of the plume significantly. Results indicate approximately 700 kg of chlorinated solvents have been removed from the site in 2009 [Region Hovedstaden 2010] . However this has influenced the concentration of chlorinated solvents in the water phase, probably not the residual or mobile DNAPL.

Naverland project

In a cooperation project the Naverland site served to test several characterization methods and compare their applicability, reliability, advantages and disadvantages and helps the Region to prioritize contaminated sites regarding remediation. The project is involving DTU Environment, the Region of Copenhagen, FLUTe^{TM} and consultants GEO, COWI and Niras. In accordance with the Naverland project the below mentioned characterization and analysis methods in clay till – the unsaturated zone and chalk – the saturated zone, are planned to estimate DNAPL free phase and chlorinated solvent concentrations on site:

Characterization methods in clay till:

- Geo-radar (determining surface of the chalk and fractured layers)
- Membrane interface probe (MIP) in clay till
- pore air of soil samples
- Level specific groundwater (sampled with FLUTe liner) analysis with GC/MS
- FACT liner (documentation of DNAPLs and matrix)
- Intact cores (high discretization) analysis with pentane extraction and subsequent GC/MS
- Sudan IV and DNAPL color spray on soil samples and cores

Characterization methods in chalk:

- Level specific groundwater (sampled with FLUTe liner) analysis with GC/MS
- FACT liner
- Intact cores analysis and Sudan IV and DNAPL color spray for first indication

All planned characterization methods have already been tested in former studies (in detail shown in Beyer, 2011; a good summary gives also Kram et al., 2001 and 2002; Lawrence, 1996). However the characterization methods were not documented or tested in chalk. Moreover a newly developed technique using an activated carbon felt attached to the FLUTe liner will be implemented on site. All other methods (except the FACT) showed applicability in different aquifers; however the applicability for the Naverland site in particular the chalk aquifer needs to be evaluated exclusively. Since it is site dependent (due to geological factors etc.), the purpose of the overall project is to clarify and lead the Region, municipalities and other interested parties which methods are useful in case of Naverland and comparable sites with a chalk aquifer.

Master thesis study

This study focuses on the applicability of an activated carbon felt on a NAPL FLUTe® for DNAPL characterization in a chalk aquifer. In the following lab experiments, determining FACT properties, application and interpretation of field work results are described in detail.

3. Lab experiments

3.1 Plan

Table 3 shows the summary of the experiments carried out in the lab studying the FACT in order to use the information gained for sampling, analysis and interpretation of the results during field work. The focus was set on 3 major aims: 1st to find an analytical method to determine chlorinated solvent concentrations on the activated carbon felt, 2nd to gain information regarding the handling of the FACT liner and sampling during the fieldwork and 3rd to interpret and combine the results obtained during fieldwork to characterize the field site. In the following the major aims and the corresponding lab experiments are described and summarized in table 3.

1st Analytical method: Desorption of chlorinated solvents sorbed to the activated carbon felt was carried out in water & pentane to reveal the extraction and analysis method with the best recovery.

2nd Application/handling in the field: Adsorption was studied determining kinetics and equilibrium times to conclude on the most optimal handling on site. Furthermore volatilization was studied in order to find out if volatilization from the activated carbon is an issue and special handling is necessary during fieldwork. Longer samples of activated carbon were tested as well, to test the analogy and applicability to use different sizes of carbon felt samples.

3rd Interpretation of the results: Different concentrations and exposure from different phases were tested on the NAPL FLUTe and carbon felt leading to different staining and different concentrations sorbed to the activated carbon, respectively. The aim was to get an idea about concentration ranges sorbed to the carbon and interpretation of the field samples regarding corresponding concentration and combination of staining and concentration data in the saturated and unsaturated zone.

Table 3: overview of lab experiments and gained information used for field work

aim	**Lab experiment**	**Aim/results obtained**		**Information used for field work**
1.Analyt. method	**Desorption/ extraction**	extraction method(s), equilibrium times	→	Analysis of carbon felt
2.Application & handling in field	**Adsorption**	Equilibrium times	→	Application time in field
	Volatilization	Degree of volatilization		Special handling procedure during field work needed
	Discretization	long and short samples	→	Size of samples and analogy
3.Interpretation of field results	**Staining**	Different staining at different concentrations	→	Interpretation of field work samples
	Sorption from different phases	concentration range on carbon felt and phase differentiation	→	corresponding concentration in matrix

During this project all experiments were kept as close as possible to reality, thus all solutions were prepared with tap water (procedures for preparation of calibration, control and internal standard solutions are given in appendix 0). Furthermore all adsorption experiments were carried out in a 10°C room to keep temperature as close as possible to field /ground water temperature. Furthermore the setups were put onto a slowly moving shaking table to avoid a concentration gradient in the vials. The transfer of samples for analysis was also done in the 10°C room under the use of syringes to keep volatilization at a minimum. Water was weight to use an exact volume. The material of the FACT FLUTe was kindly provided by FLUTe and Niras (illustrations of the FACT FLUTe and carbon felt can be found in chapter 2.4).

For simplification lab experiments were carried out with 1 chlorinated compound, namely PCE. Since determined equilibrium times will be used to reveal the minimum contact time for the FLUTe in the field as well as the minimum time of the subsequent extraction, the compound with the expected highest equilibrium time was used in equilibrium time experiments. Literature showed a lower sorption velocity of PCE compared to TCE [Arnold 2006], thus PCE was preferably used. Furthermore PCE is known to compete with TCE molecules for active sites during adsorption. However in mixtures of PCE and TCE, PCE adsorption appears to be independent from the presence of TCE in contrast to TCE (which is replace by PCE due to competition during adsorption) [Erto et al. 2011]. Thus PCE concentrations was expected to be the most uninfluenced and most meaningful regarding field sample analysis. All experiments were done time and concentration dependent, e.g. at saturated concentration (drop of DNAPL in water phase) and at different dilutions.

3.2 Analytical method

General methodology and materials

In this study non-displaceable desorption was favored using both pure water or water and an organic solvent, pentane, acting as extractant for the studied chlorinated compounds, implying a concentration gradient as driving force.

To study the desorption/extraction of a high PCE concentration sorbed to the activated carbon felt, a PCE solution at saturation was prepared in a bigger volume (> 1L). Moreover saturation was chosen, since it is easiest to keep constant and therefore as close as possible to reality by introducing a drop of PCE, shrinking with time due to compensation of the sorbed amount on the carbon felt, added to the setup (figure 8, right). 12 carbon strips (each around 4 x 2cm) were added by simply hanging the strips onto a thin metal wire. To keep the light felts submerged, glass bodies were added (fig. 8, left).

The first try to prepare a saturated PCE solution showed the PCE forms small drops that sink to the bottom of the glass, but it also stays at the surface of the solution with a film like appearance. When the carbon strips are introduced to the system, they would dip trough the PCE film on top influencing the results of the experiment. Thus the drop of PCE was introduced with a long pipette to the bottom of the flask to avoid film formation and subsequent slow stirring ensured mixing (fig. 8 right).

However for subsequent desorption/extraction, the carbon felt was also adsorbed in different concentrations in 20 ml vials filled with 20 ml of specific PCE solution (headspace was kept as small as possible). A constant concentration during adsorption cannot be realized here; however indication for recovery at different concentrations can be studied. To avoid carryover from adsorption to desorption/extraction, most of the superfluous solution staying on the carbon strips after removal from the adsorption setup, needs to be removed. A soaking experiment showed the carbon felt material gets quite fast (within minutes) soaked with water and water does not run of easily. While squeezing out the water, the material loses carbon fibers or falls apart. In addition there are also carbon fibers in the solution. To remove the superfluous adsorption solution in more gently way, the solution was removed from the carbon felt and drained on a piece of paper cloth (figure 9).

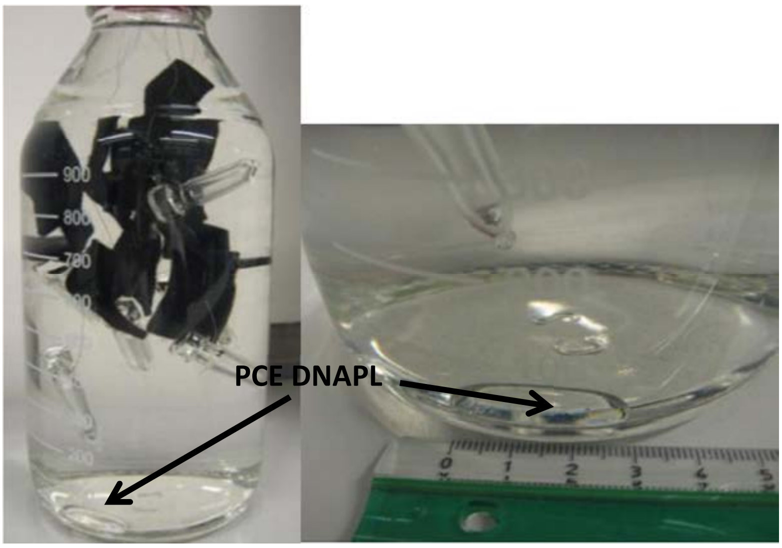

Figure 8: adsorption setup at saturation; left: attachment of carbon felts; right: drop of PCE for saturation

Figure 9: dripping off of carbon felt, which have previously been adsorbed in a certain PCE solution

A gas chromatograph coupled with a mass spectrometer (GC/MS) is used to detect and quantify the concentration changes. With this method the compounds are first separated (in this case PCE, TCE, cis-DCE and TCA and chloroform) in a gas flow column according to their retention time and then the connected MS captures and ionizes the compounds. The ionized molecules or molecule fragments are then accelerated, deflected and detected using the mass to charge ratio (m/z) of the ionized fragment. From every GC peak a mass spectrum is obtained giving the fingerprint for the specific molecule. [Hardy, 2010; Douglas, 2010 and Hites, 1997] The combination of a compounds typical mass spectrum and retention time allows the method to qualify and quantify compound with a very high precision and low limit of detection.

Headspace GC/MS and pentane analysis on a GC/MS were used in this study. Both methods include an internal standard (chloroform), which is used to correct the signal of the sample, so the ratio of compound to chloroform signal can be used to quantify the concentrations. In this study selective ion monitoring (SIM) is used, i.e. a target ion (from MS data) and the retention time (GC output) are used to identify a substance. The ratio of the qualifier and target ion (MS output) is used to qualify the substance. The concentration is then determined using the integration of the peak of the quantification ion (related to the abundance) in comparison of a calibration curve (chromatogram is shown below, fig. 10) and the internal standard (chloroform). Specific qualifying and target ions, ratio and retention time for the compounds used in this study (namely PCE, TCE, cis-DCE and TCA) are given in table 4.

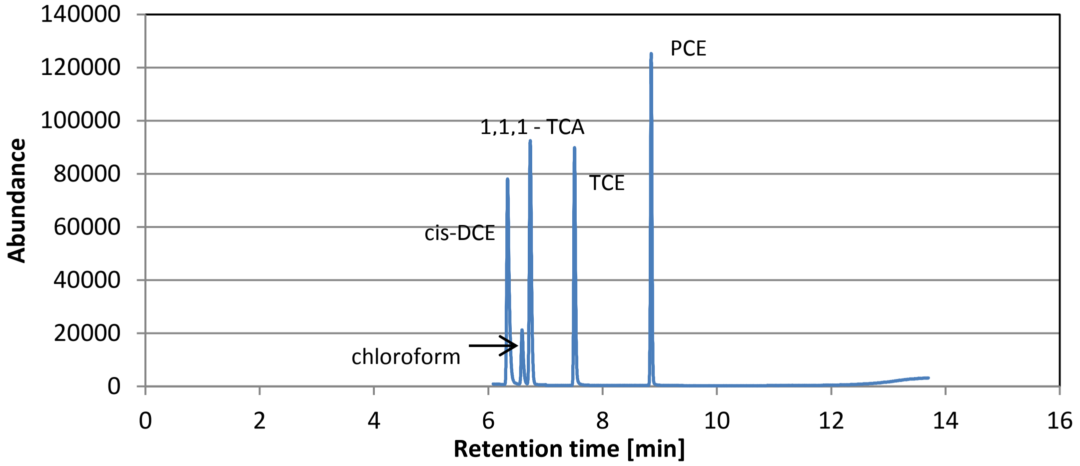

Figure 10: chromatogram of GC/MS

Table 4: Specific qualifying and target ions, ratio and retention time for PCE, TCE, cis-DCE and TCA

	Retention time	Target ion	Qualifier ion	Ratio
Chloroform	8.48	83	47	20
PCE	9.67	166	129	68
TCE	9.06	95	130	100
1,2cis-DCE	8.28	61	96	96
1,1,1-TCA	8.87	97	61	

For aqueous sample analysis headspace the GC/MS was calibrated with a mix of TCE, PCE, TCA, cis-DCE solved in methanol and tap water, the calibration curve and preparation for carried out headspace analysis can be found in appendix A and 0, respectively. However since trends only need to be evaluated in this study, precise concentrations are not crucial. For simplification and economy of time reasons just 1 calibration curve for all runs was made, however with controls (samples with known concentration) after every 40 samples the analysis was tested for correctness. For direct pentane analysis the GC/MS was calibrated with a mix of TCE, PCE, TCA, cis-DCE solved in pentane. More information regarding standard preparation and analytical method can be found in appendix 0. The limit of detection and quantification of the analyzed compounds with headspace and direct pentane analysis with a GC/MS can be found in table 5, calculated by Mikael E. Olsson (DTU Miljø).

Water samples were analyzed with a headspace GC/MS with an Agilent 6890N gas chromatograph type and Agilent 5973mass spectrometer with Perkin Elmer Turbo Matrix 40 headspace auto sampler. The gas chromatograph was equipped with an Agilent PLOT Q column, 30 m x 0.32 mm x 20µm. The headspace analysis is based on equilibrium between headspace (air phase) and sample phase (liquid phase). 1 ml of water samples and 0.5 ml of chloroform were added into 40 ml GC/MS vial. The sample is then heated to 80°C to analyse the headspace and tracing back the compounds and their concentration in the water sample.

Pentane samples were analyzed directly on a GC/MS with Agilent 7890A gas chromatograph, equipped with a ZB-624 column (30 m x 250 µm x 1.4 µm) and a 5975C triple axis mass spectrometry detector. 1 ml pentane samples including internal standard were analyzed after extraction of the carbon felt submerged in water.

Further description of the methods (as column, temperature program or injection) can be found in appendix 0. The calibration curves for both methods were carried out with standards prepared according to appendix 0. Control and internal standard preparation procedure can also be found in the appendix 0. The program MSD ChemStation was used to integrate abundance peaks and receive target responses for calibration and concentration determination.

Table 5: Limit of detection (LOD) & limit of quantification (LOQ) for PCE, TCE, TCA and cis-DCE [by M. Olsson]

Pentane analysis				**Headspace analysis**		
compound	**LOD [µg/L]**	**LOQ [µg/L]**	**precision %**	**LOD [µg/L]**	**LOQ [µg/L]**	**precision %**
PCE	0.49	1.64	9.7	1.2	3.9	10.8
TCE	0.93	3.09	7.5	1.4	2.7	9.3
Cis-DCE	1.02	3.39	8.2	1.0	4.8	7.2
1,1,1 TCA	0.55	1.82	9.7	1.4	2.8	8.5

Desorption in water

As the literature review indicated [Beyer, 2011] extraction with an organic solvent and subsequent analysis was found to be the most effective method to analyze the carbon felt after application in the subsurface. However firstly water, as cheapest, most accessible and practical matter, was used to determine desorption behavior. Therefore 20 ml of tap water were added to the drained off carbon felts in 20ml vials for desorption and subsequent analysis (fig. 11). Over time an increase in PCE concentration in the water phase during desorption is expected and recovery and equilibrium times of desorption are determined.

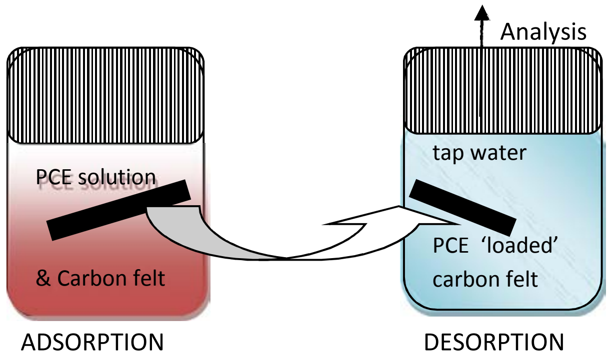

Figure 11: experimental setup to study desorption of dissolved TCE/PCE on the carbon felt; left: adsorption of carbon in certain PCE concentration, right: desorption of carbon in water and subsequent analysis of PCE

Extraction in pentane

Since Lawrence et al. 1990 reported a liquid/liquid extraction method promising good recovery of TCE from soil using pentane; pentane was tested for its extraction efficiency. Pentane is a suitable extracting agent due to its higher K_{oc} value as reported by Lawrence et al. 1990. A K_{oc} of pentane of 1400 L/kg was found by ACD/Labs' ACD/PhysChem Suite and 81 L/kg was found with EPI suite [Chemspider].

For extraction and subsequent analysis the drained off carbon felts (from previous adsorption) were put into 20 ml vials with addition of 10 ml water and 3 ml pentane including internal standard (fig. 10). Subsequent analysis revealed recovery rates for chlorinated solvents from the carbon felt.

Direct headspace analysis

A direct analysis of the carbon felt under addition of 0.5 ml of chloroform was evaluated implying the direct addition of the carbon felt to a headspace GC vial and analysis of the air phase (see figure 12).

Previous extraction/desorption was not necessary, since the compounds are very volatile. A carbon felt sorbed in saturated aqu. PCE and exposed to air for almost 2 weeks and a carbon felt adsorbed in 10mg/L PCE and desorbed in water for 1 week were used to evaluate the applicability of the method.

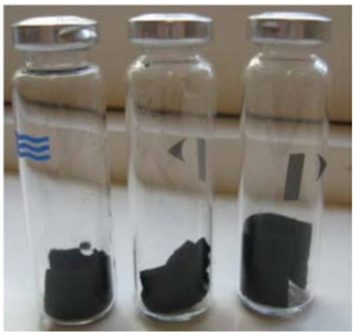

Figure 12: direct analysis of carbon felt in GC headspace vials

3.3 Application and Handling in the field

Adsorption

To study adsorption kinetics, a carbon felt of a known size or mass was put into an air tight vial with a aqueous PCE solution of a given concentration. The subsequent analysis showed a concentration change of PCE over time (analyzed by GC/MS) indicating adsorption shown in figure 13, left. Therefore equilibrium times can be determined, illustrated by the concentration converging to a final value with time. Furthermore adsorption at different concentrations up to DNAPL contact, were tested to determine adsorption kinetics according to Freundlich, Langmuir or linear adsorption. Therefore several carbon felts of known mass were exposed to 20 ml of an aqueous PCE solution with known concentration up to 1 week, to ensure equilibrium is reached. Over time the aqueous solution was analyzed and according to the concentration change, the adsorbed mass determined. To realize DNAPL contact, the carbon felt was put into the lid of a vial and the glass including a drop of PCE was turned around to ensure direct contact of DNAPL and carbon. Blank vials containing the certain PCE concentration are prepared to be used for identifying the loss over volatilization and therefore correcting the concentration change obtained to finally determine the sorbed fraction of PCE to the carbon (by subtracting the "loss" due to volatilization from the total concentration change). The setup for adsorption and blank vials are shown in figures 13 and 14.

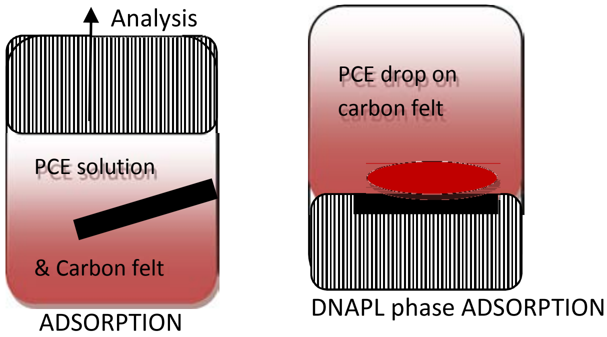

Figure 13: experimental setup to study adsorption of dissolved PCE on carbon felt; left: carbon exposed to a certain PCE concentration and analysis of concentration change; right: DNAPL phase touching the carbon felt

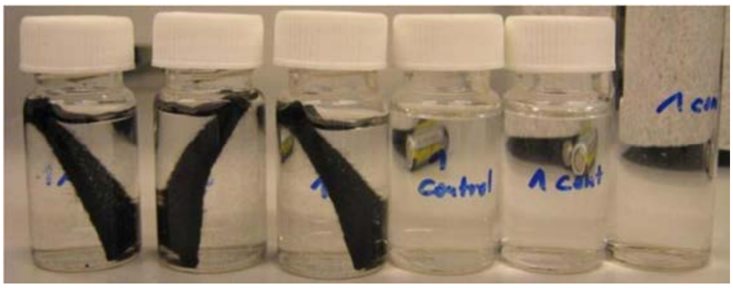

Figure 14: adsorption setup with 3 carbon felts exposed to a certain PCE solution and 3 control vials without carbon felt for determination of the initial concentration and compensation of "losses" due to volatilization

For realization of the adsorption experiments the water/carbon felt ratio needed to be estimated leading to a concentration change of around 30-70% during adsorption, thus the standard deviation of GC/MS analysis did not influence the results too much and the concentration change is actually measurable. A rough distribution calculation can be done using the organic carbon distribution coefficient K_{OC}. A detailed calculation can be found in appendix 2. Results show a carbon felt of a minimum size of 0.75 cm² is needed, when the carbon felt bulk density is assumed to be 1 g/cm³ and a thickness of 2mm. The size appeared to be practically possible and was therefore used in this study.

Volatilization

Evaporation tests to determine volatilization were carried out indicating the necessity of correct handling of the samples. The activated carbon felt was therefore exposed to a high PCE concentration (at aqueous saturation), then left and exposed to air for 0, 3; 5.75 and 22.75 hours in a Petri glass. The Petri glass was covered with aluminum foil to avoid ventilation under the fume hood (fig. 15). Furthermore to let excessive solution run of, the setup was inclined (fig. 15). Afterwards desorption with subsequent headspace analysis revealed the grade of volatilization.

Figure 15: carbon felt left for volatilization in a Petri glass covered with aluminum foil to avoid ventilation

Discretization

From a financial, time and effort point of view, the tendency of taking less but larger samples is favored. However the evaluation of the concentration over depth still needs to be observable. Thus instead of planned 1 to 10 cm field samples, 30 cm samples were tested and evaluated whether longer samples give still an insight into the concentration range and allow a first glance if the sample is interesting and further investigation/discretization is needed. Table 6 gives a summary of the chosen field samples representing samples with high (peak), medium and low concentration. To keep the extraction procedure similar to the extraction used for 1 to 10 cm field samples, the longer, 30 cm samples were put into 40 ml vials with addition of 25 ml of tap water and 5 ml pentane including internal standard (figure 16). After staying around 48 h in the rotating box to extract the chlorinated compounds, direct pentane analysis on the GC/MS followed.

Table 6: 30cm field samples chosen for analysis

Liner No.	**part**	**Concentration range**
CF3	1.20-1.50 m	High peak at 1.45 m
CF3	0.30-0.60 m	Medium concentration around 0.6 m
CF2	6.00-6.30 m	High TCE peak at 6.1-6.15 m
CF2	9.00-9.30 m	Low concentration around 9 m

Figure 16: arrangement of 30cm carbon felt in 40ml vial

3.4 Interpretation of field results

Staining behavior

A drop of PCE as DNAPL was tested on the FACT liner and staining examined. Furthermore the liner was put into PCE saturated air phase and high aqueous concentration (saturation) solution (fig. 17). The aim was to distinguish between DNAPL staining and high aqueous concentration staining.

Figure 17: FLUTe liner material exposed to PCE saturated air & aqu. saturated PCE/TCE to examine staining

Different phase exposure

To test the range of concentrations that can be determined with the FACT and in order to obtain a "limit concentration" indicating DNAPL presence, different phases were tested. The 3 different phases, namely gas, water and DNAPL were applied on carbon felts of a known mass and extracted and analyzed in pentane. Therefore one carbon felt was brought in direct contact with DNAPL in the lid of a bottle (fig. 18 left), another one was exposed to PCE saturated air (fig. 18, middle) and one carbon felt was submerged in aqueous PCE saturation (with drop of DNAPL illustrated in fig 18, right).

Figure 18: adsorption under DNAPL contact with carbon felt in lid (left), adsorption of saturated air (middle) and in saturated aqueous PCE solution with PCE drop

3.5 Results and Discussion

Analytical method

Desorption in water vs. extraction in pentane

Results of desorption in water and extraction in pentane is illustrated in figure 19 showing recovery of initial concentration of PCE due to extraction/desorption over time. Desorption results of carbon felt in water (around 0.14 g each and previously adsorbed in 10mg/L PCE) indicate a very low recovery (fig. 19). A recovery of less than 1% (of concentration in water after desorption compared to initial or sorbed concentration) was reached. Results show a concentration in water reaching max 95 µg/L of the initially 10 mg/L, showing around 9 mg/L are still sorbed to the carbon felt. A very low recovery leads to very low concentration in the water to analyze, leading to a huge uncertainty during analysis. Thus extraction with only water is not the method of choice. However water can be used to preserve/ store the carbon felt samples to avoid volatilization of chlorinated solvents.

A first extraction experiment in pentane was carried out on 3 carbon strips adsorbed in 10 mg/L and desorbed in water until equilibrium (thereby "losing" just ca. 1% of their initial loading). The carbon felts were extracted with pentane for 20 and 26 h. Results indicate a high recovery with pentane extraction, showing 64% and 92% recovery after 20 and 26 h, respectively (fig. 19). Since there is still a slight difference between 20 and 26 h, the equilibrium time is expected to be around 40 or 48 h.

Furthermore 4 carbon felt samples adsorbed in a saturated PCE solution until equilibrium, 2 of them left for volatilization thus reaching a random concentration (the exact concentration is not of interest here) were extracted in pentane (figure 20). Results indicate again a difference between 20 and 26 hours of extraction (around 20%) and good recovery (indicated by high concentrations reached).

During the experiment small carbon fibers were released to the solution, which bears a risk for the subsequent direct analysis of the pentane illustrated in figure 21. However under addition of pentane and water the fibers accumulate mainly at the interface between pentane and water phase indicating the direct analysis of pentane in a further step is possible without interfering with the fibers, since samples can be taken out without carbon fibers.

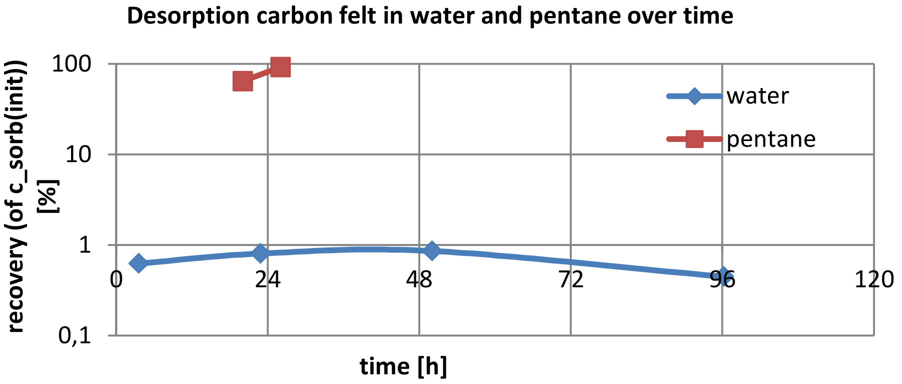

Figure 19: recovery from water & pentane extraction of carbon felt initially adsorbed in 10 mg/L PCE solution

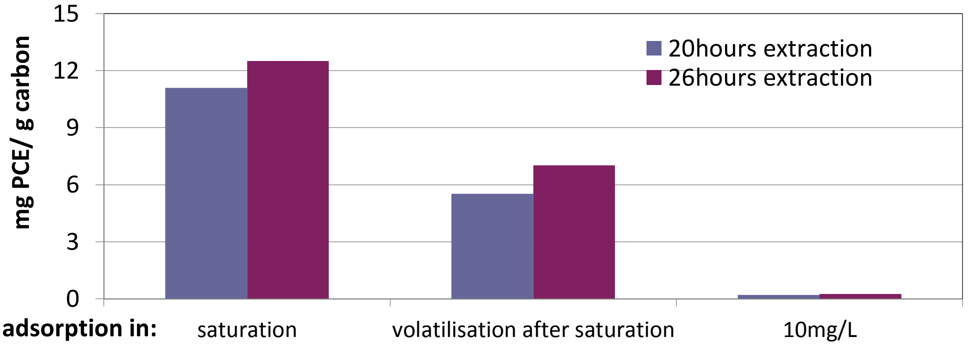

Figure 20: pentane analysis of carbon felts beforehand exposed to different PCE concentrations

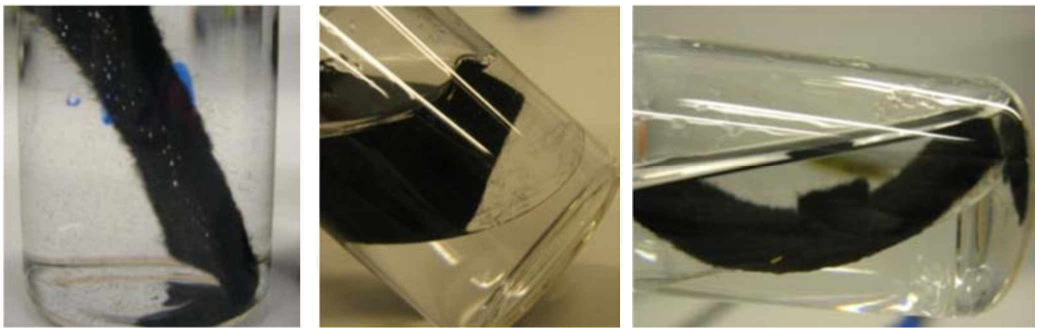

Figure 21: carbon fibers released to aqu. solution (left); carbon felt in pentane plus water (middle & right)

Direct headspace analysis

First results of direct headspace analysis of a carbon sorbed in 10 mg/L PCE showed a GC peak corresponding to a concentration of 4.14 mg/L PCE, thus there is still 59% PCE sorbed on the carbon. This means 41% can be recovered using direct headspace analysis indicating a possibility to analyze smaller concentrations, but it is not suitable for DNAPL or high aqueous concentration analysis.

Comparing the signals of chloroform (as internal standard) from headspace analysis of an aqueous solution and direct carbon analysis, show just 10% of the chloroform is recovered using direct headspace, i.e. 90% of the chloroform is sorbed to the carbon. Thus another volatile compound for use as internal standard, which is unlikely to get adsorbed on carbon, needs to be found. Lenntech Water treatment solutions reports compounds that are unlikely to get sorbed on the carbon (e.g. Acetone, Acetonitrile, Propylene) thus these compounds are more suitable as internal standard.

Application and handling in the field

Adsorption

Results of the adsorption experiment carried out with around 0.14 g carbon felts exposed to a 10 mg/L PCE solution (exact ratio is 3.6 of m(PCE)/m(carbon felt)) are indicated in figure 22. The graph shows the ratio of initial concentration to mass of PCE sorbed (determined as difference between initial and PCE concentration after X hours in water corrected with a blank sample for volatilization losses) in % over time (fig. 22). As expected first adsorption experiments showed around 91% adsorption of the total mass of PCE after 12 and 16 h, 93% after 20h. Equilibrium is reached within 180 h. However adsorption is quite rapid in the first 12 h, over 95% of PCE was absorbed after 50 h.

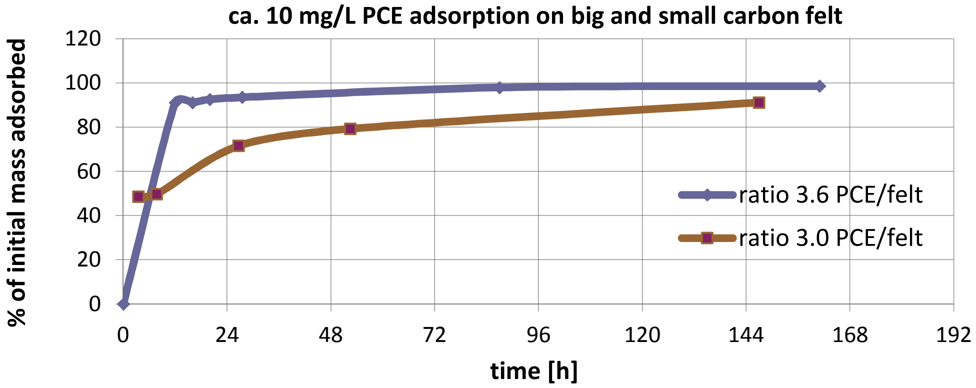

Figure 22: results of adsorption with smaller and bigger sized carbon felt in ca. 10mg/L PCE solution

Also smaller carbon felts (around 0.10 g) were exposed to a 6.5 mg/L PCE solution (exact ratio 3.0 m(PCE)/m(carbon felt)) to see a more moderate adsorption (fig. 22). The results indicate a very high adsorption affinity of PCE towards the activated carbon felt, since an equilibrium concentration close to 95% or higher (as it is the case for the first experiments) is reached after a longer time (>144 h).

The kinetics of the adsorption process was studied. Figure 23 displays the results obtained (PCE concentration in water vs PCE concentration sorbed). It can be seen, adsorption at different concentrations in water showed rather linear distribution (fig. 23). However since the results vary a lot, further examination is needed to draw a clear conclusion. If a linear distribution is assumed a distribution coefficient K_d of 9490 L/kg is reached. Meaning the simple soil approach with K_d as the product of f_{oc} and K_{oc} is not applicable, since with a given K_{oc} of PCE with 364 L/kg, a f_{oc} over 100% is reached. However this can be explained by the very high surface and therefore high amount of active sites of the carbon felt, therefore another approach is needed.

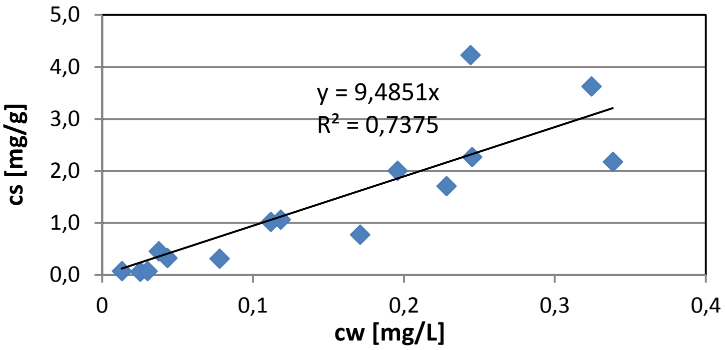

Figure 23: adsorption kinetics of PCE showing a linear regression

Volatilization

Results of pentane extraction of carbon felts exposed to air for 3 to 20 h after adsorption at saturation are shown in figure 20. Results indicate exposing the carbon felt to air, after adsorption in a saturated PCE solution, around 50% of the sorbed concentration is volatized to the air phase (fig. 20, pentane extraction). These results indicate the chlorinated solvents are quite strongly sorbed to the activated carbon felt and volatilization is not as critical as assumed.

Discretization

Table 7 summarizes the average concentration obtained from more discreet samples (2 to 10 cm samples) in comparison with concentration data obtained with 30 cm samples, respectively. It can be seen 30 cm samples showed comparable but not the same concentration data to the average value of more discreet samples. It is shown that results of 30 cm samples vary between 40 and 169% of the average concentration determined with smaller pieces (table 7). However 30cm samples still present the opportunity to analyze longer samples and when high concentrations are obtained further discretization can follow to observe peak values in detail.

Furthermore in section 4.3, figure 42 (results part of chalk field samples) an average value each 30 cm was taken from data obtained by 2 to 10cm discreet samples showing the longer samples still represent the trend obtained by more discreet samples.

Table 7: average concentration obtained from more discreet samples (2 to 10cm) and concentration data obtained with 30cm samples

sample		**average conc. of 2 to 10 cm samples [mg/g]**		**Concentration characteristic**	**Conc. of 30 cm samples [mg/g]**		**% reached of average conc.**	
liner	**cm**	**PCE**	**TCE**		PCE	TCE	PCE	TCE
CF 3	120-150	0.173	0.064	High peak	0.168	0.108	97	169
CF 3	30-60	0.994	0.384	Medium conc.	0.561	0.396	56	103
CF 2	600-630	0.926	1.871	High TCE peak	0.374	1.467	40	78
CF 2	900-930	0.089	0.157	Low conc.	0.075	0.221	84	140

Interpretation of field data

Staining

Five drops of PCE applied on the liner showed instantaneous staining of around 15 to 20 cm diameter (fig. 25 middle and right). The liner kept in the saturated air phase did not show staining (fig. 25 left). However exposure to saturated PCE solution did not result in staining immediately, even after keeping a piece of liner for almost 1 week in the saturated PCE solution (fig. 24). Since TCE has a higher solubility compared to PCE, a drop of TCE was added to the PCE saturated solution. Within 24 h, faint staining occurred on the liner (fig. 26). According to Keller (2012) faint staining might occur in the field at high aqueous concentrations and at long exposure times of the liner in the borehole.

Figure 24: instantaneous staining test with drop of saturated aqueous PCE (left) → effect: no staining (right)

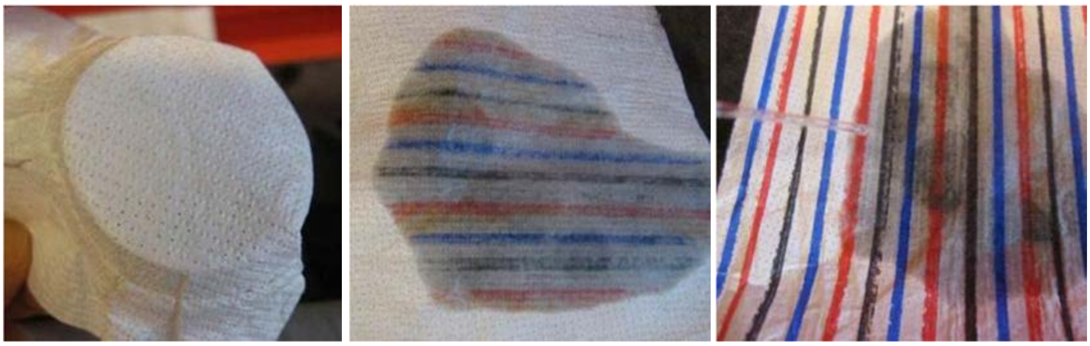

Figure 25: staining test results in PCE saturated air phase (left) and with DNAPL (middle and right)

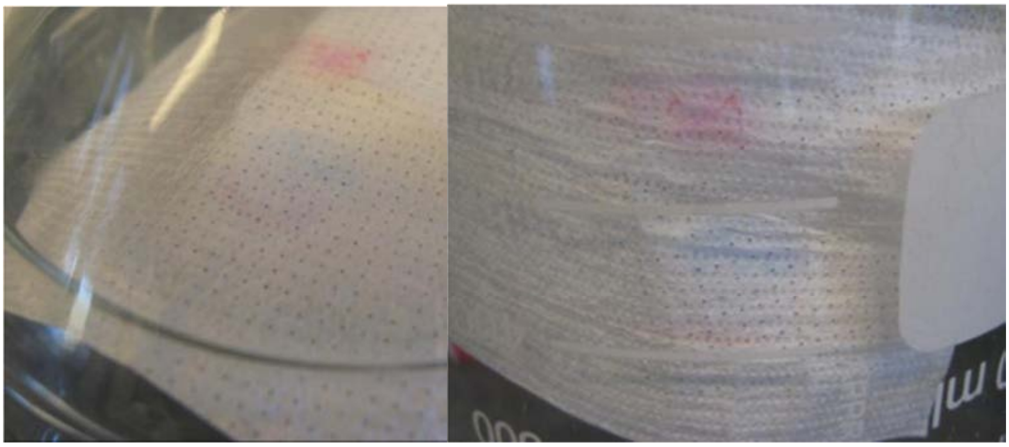

Figure 26: occurrence of faint staining after leaving a piece of FLUTe liner in PCE and TCE saturated solution

Different phase exposure

The carbon felt was exposed to PCE from different phases, namely DNAPL, aqueous and air phase, in order to obtain a range of concentrations indicating DNAPL presence in water, air or direct contact. Results of subsequent pentane analysis are summarized in table 8. The carbon felt exposed to PCE saturated air showed interestingly highest PCE concentration on the carbon (around 45 mg/g) indicating PCE sorption is diffusion controlled and fastest in the air phase. The carbon felt exposed to an aqueous saturated PCE solution, showed around 0.7 mg/g PCE sorbed to the carbon, indicating slower diffusion in the aqueous phase. A drop of DNAPL on the carbon felt showed a slightly higher concentration (around 3 mg/g) compared to the saturated aqueous phase, indicating a similar diffusion mechanism as in aqueous phase, but a higher concentration gradient increasing the diffusion rate.

Table 8: results of carbon felt applied in PCE saturated air, PCE saturated solution and a drop of PCE (DNAPL)

sample	PCE in pentane [mg/L]	PCE on carbon [mg/g]
drop of DNAPL 1	460.71	3.46
drop of DNAPL 2	493.96	2.72
Aqu. saturation 1	172.23	0.49
Aqu. saturation 2	271.74	0.82
saturated air phase	1057.96	45.34

3.6 Sub-conclusion

Analytical method

Lab experiments showed pentane extraction with chloroform as internal standard and subsequent analysis on the GC/MS had the highest recovery. Thus pentane analysis was the most applicable method and is therefore used for analysis of the fieldwork samples. The samples are preferably kept in contact with pentane over 2 nights (> 48 h) to ensure sufficient extraction (close to equilibrium time). The carbon fibers released from the carbon felt should not interfere with the analysis, due to it was shown they accumulate at the interphase between water and pentane. Furthermore desorption experiments in water showed the recovery in water is very low, thus the field samples can be kept in water (preserved) without risking a loss of volatile compounds before analysis. The pentane can therefore be added after submerging the field samples to the water phase in the field and bringing it back to the laboratory.

Application and handling in the field

Volatilization was shown to be not as critical as expected. After 3 or 20 h there was still 50% of the compound sorbed indicating a strong sorption of PCE to the carbon. However the exposure time to air during handling in the field should still be kept at a minimum. In general experiments showed the affinity and therefore sorption of chlorinated solvents to activated carbon is very fast and strong. Adsorption experiments show equilibrium is reached within 180 h, but fast adsorption occurs during the first 12 to 24 hours for high concentrations, thus the optimal time for application of the FACT in the borehole is set to a minimum of 24 h (preferably even 48 h).

Less discreet sample showed not always representative concentrations in average compared to the less discreet samples. This could be explained by the high sensitivity towards DNAPL presence, chlorinated solvent vapors and high aqueous concentrations, leading to sharp peak values and high differences in concentration. Longer samples were not taken at the right same location as the more discreet samples, however very close to. Furthermore in section 4.3 (results of chalk field samples), an average value each 30 cm was taken from data of more discreet (2 to 10 cm) samples showing the longer samples still represent the trend over depth and point out, which parts should be analyzed in more detail. However caution needs to be taken in choosing the location of longer samples. This also shows the importance of a combination with other methods e.g. PID or staining to get a first indication of interesting locations for discreet sampling with high chlorinated solvents concentration or DNAL presence.

Interpretation of field data

Different staining, namely DNAPL and faint staining were reproduced using direct contact of PCE (DNAPL) on the liner and exposure to a PCE and TCE saturated aqueous solution. Furthermore the exposure to different phases indicated the sorption process of chlorinated solvents on activated carbon felt is diffusion controlled. Thus high concentrations of chlorinated solvents are expected to be obtained in the unsaturated zone, and medium or lower concentrations in the saturated zone.

Overall it is shown that a combination of staining and concentration analysis on the carbon plus the knowledge about the phase (saturated or unsaturated zone) is crucial to interpret the results obtained by the FACT liner.

However one should be aware of several possible issues leading to a wrong interpretation of the estimated concentrations of the field samples. E.g. high concentrations on the carbon felt, do not necessarily indicate a high concentration of chlorinated solvents in the soil. It has been shown that adsorption is diffusion controlled, thus high concentrations on the FACT are observed in the air phase, however DNAPL contact showed much lower concentration on the FACT due to aqueous phase like adsorption. This also means concentrations of chlorinated solvents on the FACT in the unsaturated zone are not just dependent on the actual concentration of chlorinated solvents in the subsurface, but also on the water content of the subsurface material. A higher water content is leading to a reduced adsorption and giving the impression of low concentrations present in the subsurface.

Furthermore due to former research showed a competitive behavior during adsorption of a TCE/PCE mix with PCE displacing TCE, the concentration estimation of PCE is expected to be more close to the real concentration in soil/water. In contrast TCE concentrations are expected to be estimated lower than actually present in the aquifer using the FACT. Furthermore in case of pore blocking of the carbon felt due to NOM presence in the aquifer, both TCE and PCE concentrations are expected to be estimated lower.

4. Fieldwork

4.1 Methodology

Fieldwork

A description of the field work preparation can be found in appendix 3. In the following the realization of the fieldwork namely location, installation and sampling procedure of the FACT liners in clay till and chalk are described. A table in the end (table 9) gives a summary of most important information (as FACT properties, installation time and location, ect.)

Three FACT liners were installed and sampled in the unsaturated zone in clay till close to three soil cores sampling locations (see fig. 27). In the following clay till FACTs are referred as CTF1, CTF2 and CTF3. Furthermore three FACT liners were installed and sampled in the chalk aquifer at the same location as soil cores sampling (fig. 27). In the following chalk FACTs are referred as CF1, CF2 and CF3.

All FACT liners were installed with water to be pressed against the borehole wall for best contact. Before installation in chalk borehole water was pumped out to avoid contamination of the FACT with borehole water. Furthermore the FACT liners in chalk were installed up to a depth of 21 m b.s. , with a cased clay part of 8 to 8.7 m, thus the chalk FACT were up to 13 m long; whereas the clay till FACT were up to 8.7 m long. Figure 28 illustrates the installation of the FACT in clay till and figure 29 shows the installation of the FACT in chalk. The liners were removed after 24 h in clay till (figure 30) and after 42 h in chalk. The clay till FACT had a diameter of 7.6 cm with a 0.3 cm thick and 3.8 cm wide carbon felt strip attached on one side. The chalk FACTs had a bigger diameter of 16.5cm with two attached carbon felt strips (on opposite sides) with same properties as in clay till (0.3 cm x 3.8 cm).

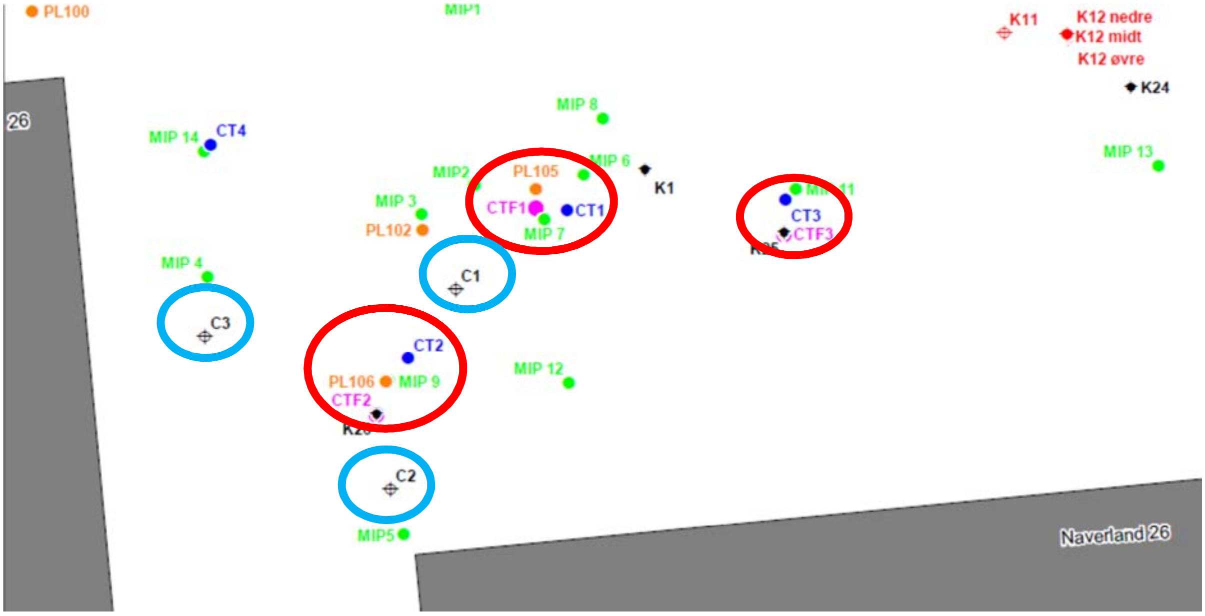

Figure 27: sample locations: soil cores (CT1 to 3), FACT (CTF1 to 3) in clay till – red marked; soil cores & FACT (C1 to 2) in chalk – blue marking

Figure 28: FACT installation; left: FACT material; middle: cutting end of installed FACT, right: installed FACT

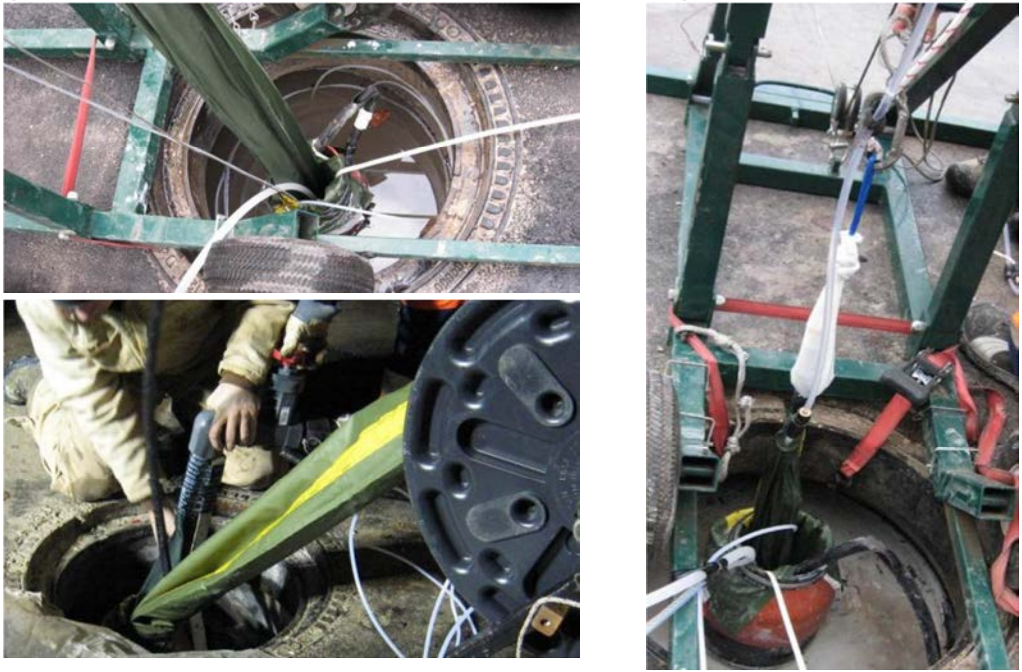

Figure 29: installation of the FACT liner in chalk

Figure 30: removal of FACT; left: pulling the tubing to invert liner & remove water filling; right: final recovery

After recovery of the FACT liner, the sampling procedure starts as shown in figure 31 and 32. For that, first the yellow or green cover liner was cut open and removed to uncover the actual FACT liner. While opening the cover liner and exposing the FACT to air for the first time, a mobile VOC monitor with PID (Photo Ionization Detector) was used to identify interesting locations for subsequent higher sampling discretization (fig. 31 left and middle). Furthermore the FACT was cut and laid open to examine staining (fig. 31, right). Since the FACT needs to be cut and opened to examine the stains, but also the carbon needs to be cut in half to take out the carbon felt samples, the FACT was cut open directly cutting the carbon felt into half (fig. 32 left). Later the discretization of sub sampling was decided according to staining and PID data of the FACT.

The carbon felt was cut into half, so one side is used for sampling, the other side is kept as backup in 30 cm pieces. Samples of 2 to 10 cm length were taken and put into a 20 ml vial filled with 10 ml of tap water (fig. 32, right). After sampling, the vials were weighed to estimate the mass of the carbon felt and 3 ml of pentane including internal standard added. For better contact between pentane and carbon felt, the vials were put into a rotating box at 10°C over 3.5 days to ensure equilibrium is reached. Then 1 ml of sample was taken out for direct analysis on the GC/MS. Another 1 ml pentane sample was taken and kept as backup for eventual dilution.

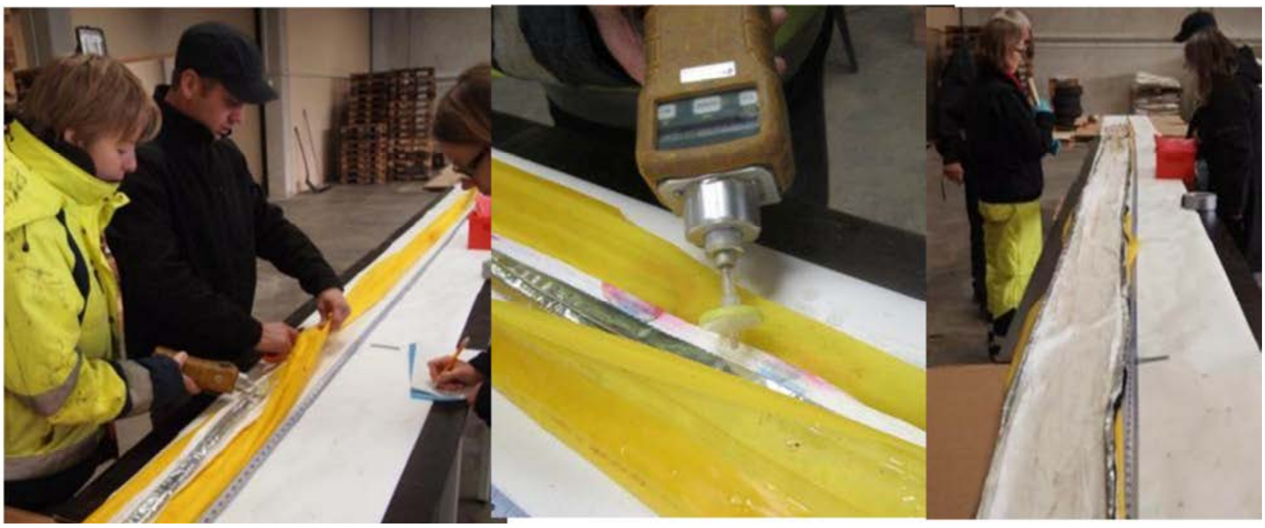

Figure 31: sampling; left and middle: opening of liner and PID measurement, right: examination of staining

Figure 32: subsampling; right: cutting felt into half; middle: sampling of the carbon felt in smaller parts & 30 cm backup, left: vials filled with 10ml water and sample

Table 9: summary of important information about FACT liners installed in clay till and chalk

	CTF1 to 3	**CF1 to 3**
Installed in	Clay till – unsaturated zone	Chalk – saturated zone
Length; diameter (Ø)	Up to 8.7m; Ø of 7.6 cm	Up to 21 m b.s with casing upper 8 m– up to 13 m length; Ø of 16.5cm
Carbon felt	1 carbon strip, 0.3 cm x 3.8 cm	2 carbon felt strips, 0.3 cm x 3.8 cm
Application time	24 h	42 h
Sampling	Entire length, 2 - 10 cm discreet	Not entirely, mainly 5 to 10 cm discreet

Analysis

Since lab experiments showed pentane extraction is the most suitable method, it is chosen for analysis of the carbon felt field samples. Therefore a GC/MS with a GC equipped with a ZB 124 column was used in combination with a triple axis mass spectrometer (details of the method and equipment can be found in appendix 0). The first samples were injected to the GC/MS with 1 µL (data from 25th and 27th of Nov.), then changed to 0.5 µL (data from 29th of Nov. and 5th of Dec.) to avoid overload of the GC/MS due to very high concentrations obtained in the pentane phase. Calibration curves for clay till and chalk FACT samples can be found in appendix B and C, respectively. Standards and controls were made according to appendix 0.

Furthermore staining is observed on the hydrophobic cover (same material as NAPL FLUTe) and PID data are taken with a hand VOC-PID device (type: miniRAE 2000, VOC monitor with PID for detection of VOCs in ppm by volume) calibrated with commercially available gas mixtures of known concentration.

In the following results of clay till and chalk are presented. Due to results of lab experiments done beforehand, high concentrations and staining are expected in case of DNAPL presence and high soil air concentrations. The results from FACT samples (including staining, PID and carbon felt concentrations) will be compared with results obtained by other methods during the Naverland project, namely soil core analysis and Membrane Interface Probe with Flame Ionization Detector (MIP-FID). As an overall result the applicability of the FACT liner and the distribution of chlorinated solvents and DNAPL phase over depth on site will be evaluated.

4.2 Results Clay till – unsaturated zone

Staining and PID

Pictures of staining found on the clay till FACTs are shown below and staining occurrence is summarized together with the found PID data in tables 11, 12 and 13 for CTF1, 2 and CTF3, respectively. The staining can be differentiated according to its strength - very small (< 1 mm), small (around 1 – 5 mm) and obvious staining (> 5 mm) and is graphically illustrated over depth using values 0.25, 0.5 and 1, respectively.

CTF1

The length of CTF1 was 6 m with a hole between 4.8 and 4.95 m due to the liner broke during installation (figure 33). The occurrence of staining and PID data of CTF1 can be found in table 11. Generally the liner showed small, but distinguishable staining (fig. 34). PID values were generally low between 10 and 50 ppm, just 3 location showed higher PID values up to 200ppm (stated in table 10).

Table 10: Flute liner CTF1 PID and staining indication for DNAPL presence

staining		**PID**	
Very small, but well visible staining		mainly low values of around 10 to 50ppm; no smell	
Depth below surface	**occurrence**	**Depth below surface**	**value**
40-56 cm	Small		
around 1 m	Small	at 1 m	100ppm
1.5 m	Small	1.9 m	200ppm
3.36 m	Small	3.4 m	up to 200ppm
5.6 m	small		

Figure 33: CTF 1 hole between 4.8 and 4.95m

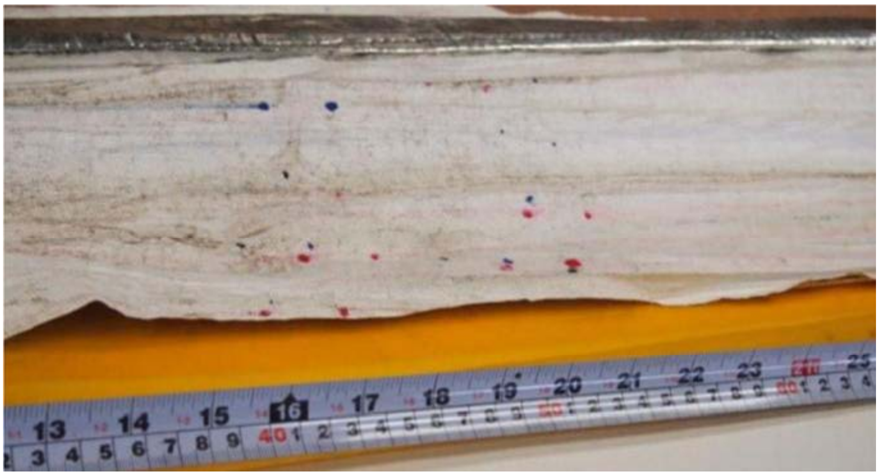

Figure 34: Flute CTF 1 staining at 40-56cm

CTF2

The length of CTF2 was 6.45 m with an overlapping part between 5.3 and 5.4 m due to repair of the liner during installation. Fortunately the carbon felt at the overlapping part was on opposite sides (fig. 35), so samples from both sides corresponding to 2 different sides of the borehole, were taken and compared. Staining and PID data of CTF2 can be found in table 11. Generally the liner showed clear and bigger/obvious staining. PID values were found to be high as well (up to 600ppm). Illustrations of the staining are given in figure 36 and 37.

Table 11: staining and PID indication of DNAPL presence at CTF 2

staining		**PID**	
Obvious staining		higher values than other flutes and intensive smell	
Depth below surface	**occurrence**	**Depth below surface**	**value**
		0-1.5 m; 1.6 m	50ppm; 100ppm
2 m	very small stains	2.07 m; 2.2 m and 2.35 m	500; 100 and 500ppm
from 2.7 to 2.78 m	Obvious staining	2.5 and 2.95 m	400ppm
2.96 and 3.00 m	Obvious staining		
at 3.23 m and 3.38 m	Obvious staining	between 3.1 and 3.5 m	600ppm
at 3.66 m	Obvious staining		
3.74 m & 3.91 - 3.99 m	Obvious staining		
		4.4 m; 4.5 m	300ppm; 250ppm
4.8 m downwards	light/very small	At 5.1 m and 6.4 m	300ppm
		between 5.2 and 6.3 m	around 200ppm

Figure 35: overlapping part of CTF 2

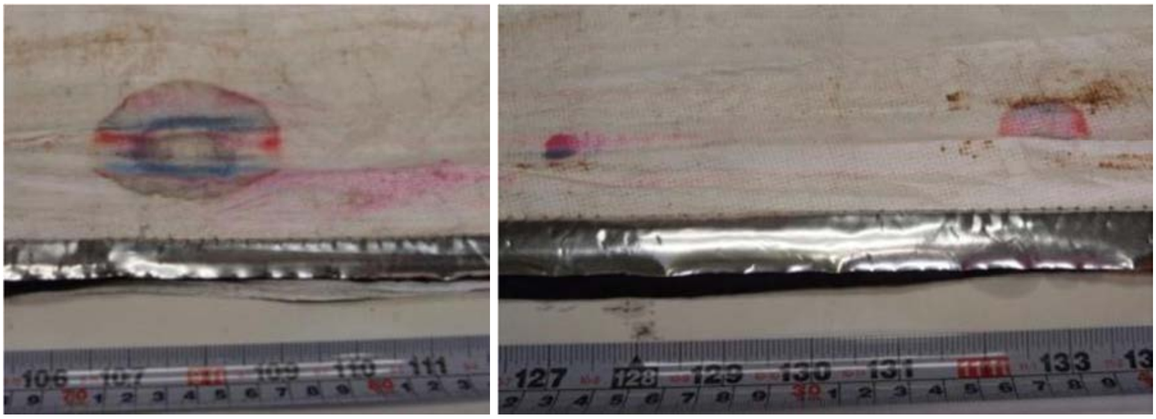

Figure 36: CTF2 staining with 8 cm of diameter at 2.74 m b.s. (left) and at 3.23 m b.s. (Ø 5mm) and at 3.38 m b.s. (Ø 4 cm)

Figure 37: CF2 staining around 3 m b.s.

CTF3

The length of CTF3 was 7.15 m. Staining and PID data of CTF3 can be found in table 12. Generally the liner showed very small, not obvious and mainly red staining (figure 38). However PID data showed values up to 500 ppm at the top part of the liner.

Table 12: staining and PID indication for DNAPL presence at CTF 3

staining		**PID**	
in general very small stains and almost not visible (not clear if it is actually staining)		higher values than CTF1 and smell at the first 1.5m	
Depth below surface	**occurrence**	**Depth below surface**	**value**
from 36 to 59 cm	small stains (mainly red)	around 30 cm	500 ppm
		1.1 m and 1.7 m	400 ppm
		1.5 m	150 ppm
2.44 - 2.53 m & 2.5 -4.4 m	all over small indication of likely staining	2.4 m and 3.45 m	200 ppm
at 4.4 m	staining	4.2 m	250 ppm
		4.8 and 5.55 m	200 ppm
		6.2 m	300 ppm
		down to 7.15 m	around 100 ppm

Figure 38: Flute CTF 3 small, mainly red staining at around 50cm (upper) and very light staining at around 2.5 m (lower)

Concentrations

In the following concentration data obtained from GC/MS are illustrated as a function over depth for each FACT (CTF1, CTF2, CTF3) including staining and PID data for comparison. The "normalized" concentration as mg of compound per g carbon is shown over depth (m b.s). In general cis-DCE and TCA concentrations on the FACT were very low (<< TCE and PCE), thus they are not presented in the following. Trends of TCE and PCE concentration are discussed and compared to the staining, PID data and data obtained during the project by other researchers from soil core samples and MIP-FID.

CTF1

The results of CTF1 are illustrated below (figure 39, left and middle). The FACT concentration data show PCE and TCE reached a maximum concentration around 0.7 m b.s. with 6.1 and 7.0 mg/g on the carbon felt, respectively. PID data are increasing with depth; however data are too few to conclude a trend. Generally the comparison of carbon concentration data with staining at the FACT reveals similar but not the same trends showing: Where staining is observed, not always high concentration in chlorinated compounds was detected (fig. 39, middle and left).

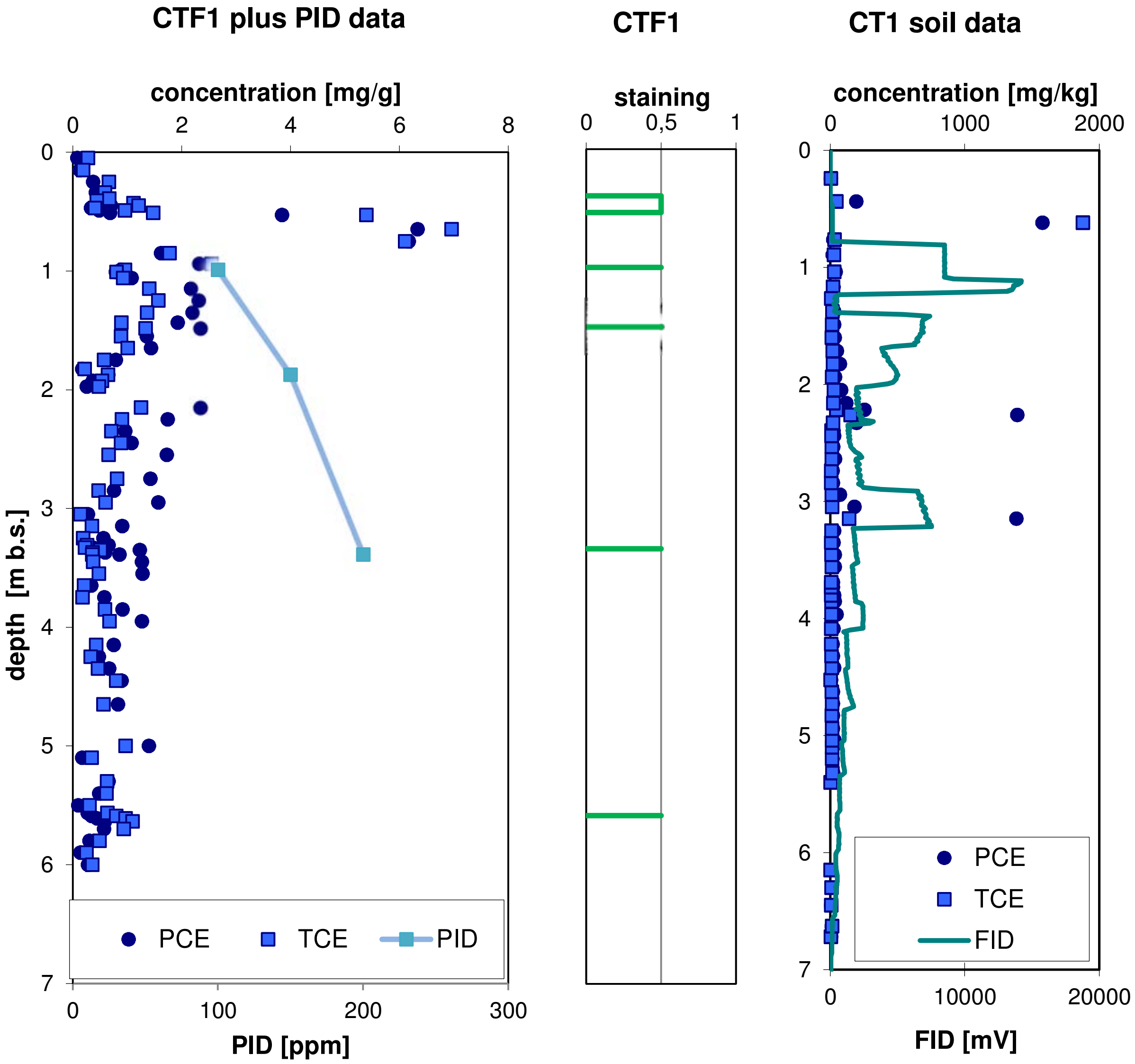

Figure 39: concentration of PCE & TCE on carbon felt with PID data (left) and staining (middle) in function of depth (m b.s.) of CTF1; right: concentration of PCE & TCE in soil with MIP-FID data in function of depth of CT1

Comparison with data obtained in soil and data obtained by MIP-FID show the concentration development over depth (shown in figure 39, right) are very similar to the data obtained by FACT analysis. Soil analysis and FID measurement show the highest PCE and TCE concentration in soil appear at 0.62 m b.s. with 1580 and 1880 mg/kg, respectively, corresponding to high peak values also found on the FACT. Furthermore TCE and PCE in soil show peak values at 2.26 and 3.15 m with 1400 mg/kg for PCE and 140 – 150 mg/kg for TCE. The MIP-FID reaches its maximum at 1.1 m with 14000 mV, close, but not precisely at the place of highest PCE and TCE concentration in soil and FACT. It should be noted that the soil core and FACT sample location had a distance of 1 m.

CTF2

Figure 40 (left and middle) show the results of GC/MS analysis of CTF2 with generally higher PCE than TCE concentrations. However all concentrations are varying over depth. Highest values for PCE on the carbon felt are found around 22 and 25 mg/g at 2.5 m and from 3.8 to 4.1m, respectively. These high PCE concentrations are also reflected by the highest value of PID of 600 ppm between 3 and 3.5 m and observation of clear staining between 3 and 4 m b.s.. TCE is generally quite low reaching highest concentrations of 1.2 mg/g at 5.4 m and 1.3 mg/g at 3.8 m b.s., close to the peak concentration of PCE. The first 2 m of CTF2 show generally low concentrations. Here staining and high concentrations appear at the same locations over depth.

Comparison with concentration data obtained in soil and by MIP-FID show the concentration development over depth (shown in figure 40, right) are very similar to the data obtained by FACT analysis. PCE shows low values for the first 2 m as observed with FACT data and reaches up to 13400 mg/kg at 2.4 m and 12500 at 4.3 m b.s., lying very close to the high concentration peaks of PCE on the FACT at 2.5 and 3.8-4.1 m. The MIP-FID shows quite low values for the first 3 m in soil, and then reaches a maximum at 3.9 to 4.0 m b.s. with 8500 mV. TCE is also low as noticed in the FACT compared to PCE concentrations reaching a maximum of 280 mg/kg at 4.4 m and up to 400 mg/kg at 7.2 m b.s.

Since the FACT was cut and repaired during installation and both overlapping parts from 5.26 to 5.31 m b.s. were analyzed. Results in table 13 shows a change in concentration (increase in this case).

Table 13: GCMS data for overlapping part in CTF2

Average depth [m]	PCE [mg/g]	TCE [mg/g]
5.125	0.43	0.10
5.175	0.60	0.17
5.225	0.84	0.20
5.28	**0.99**	**0.001**
5.285	**4.51**	**1.29**
5.335	4.12	0.91
5.38	2.95	0.75
5.425	4.05	1.13

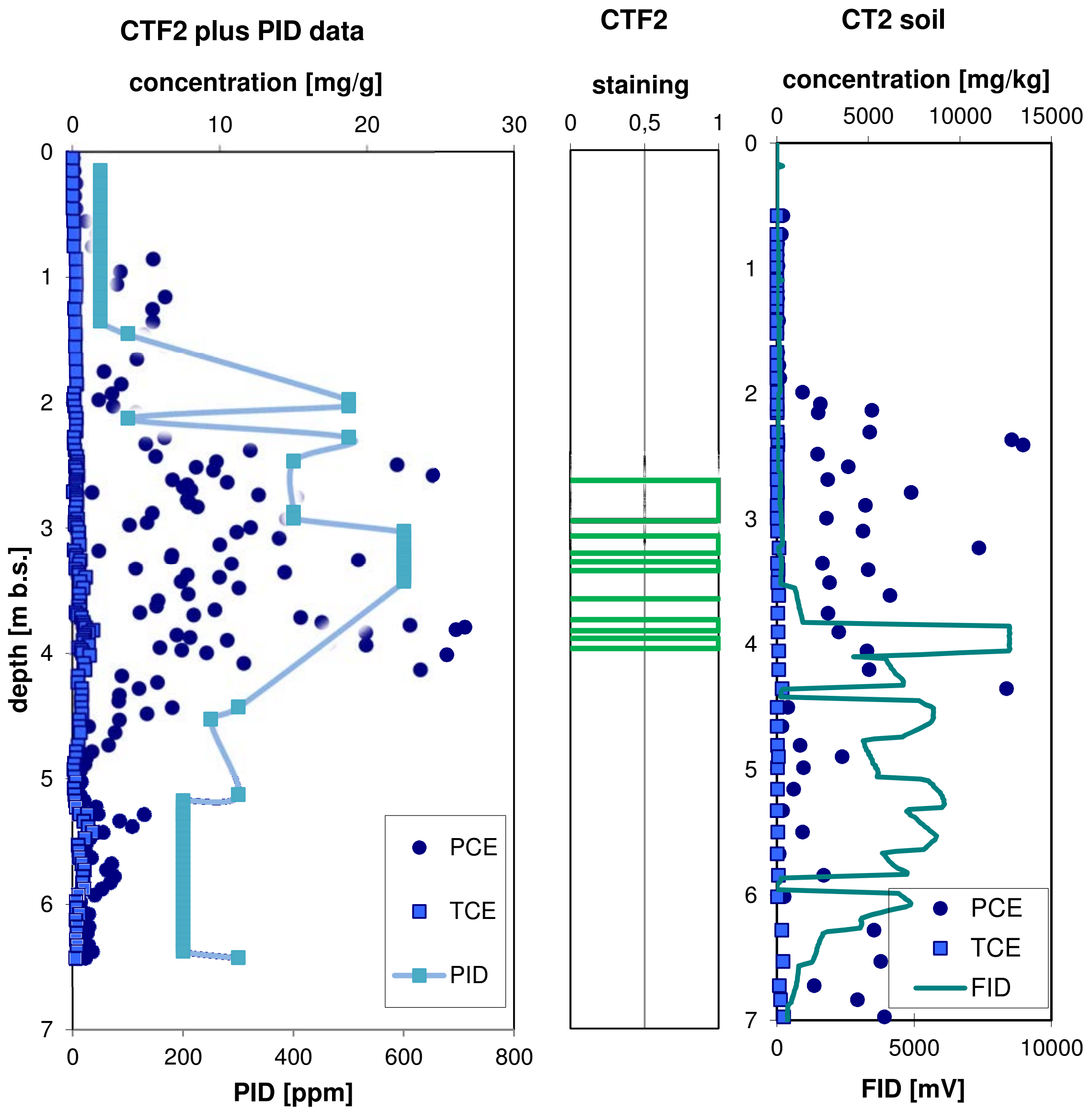

Figure 40: concentration of PCE & TCE on carbon felt with PID data (left) and staining (middle) in function of depth (m b.s.) of CTF2; concentration of PCE & TCE with FID measurement in soil (right) over depth of CT2

CTF3

CTF3 showed generally higher concentrations of PCE and TCE in the upper part from 0.4 to 1 m b.s. Concentrations up to 110 mg/g of PCE are reached on the carbon felt at 45 cm and TCE reaches a maximum of 106 mg/ g at 44 cm. CTF 3 shows the highest concentrations compared to the other FACT liners. However only staining and PID data did not indicate higher concentrations compared to the other FACT liners. The data obtained for CTF3 are presented in figure 41 left and middle.

Comparison with data obtained in soil and MIP-FID data show the concentration trend over depth (fig. 41, right) is very similar to the data obtained by FACT. The highest concentrations in soil are obtained around the same locations as highest concentrations on FACT, e.g. highest concentration of PCE is reached at 36 cm with 1423 mg/kg in soil and 110 mg/g of PCE are reached at 45 cm (fig. 41).

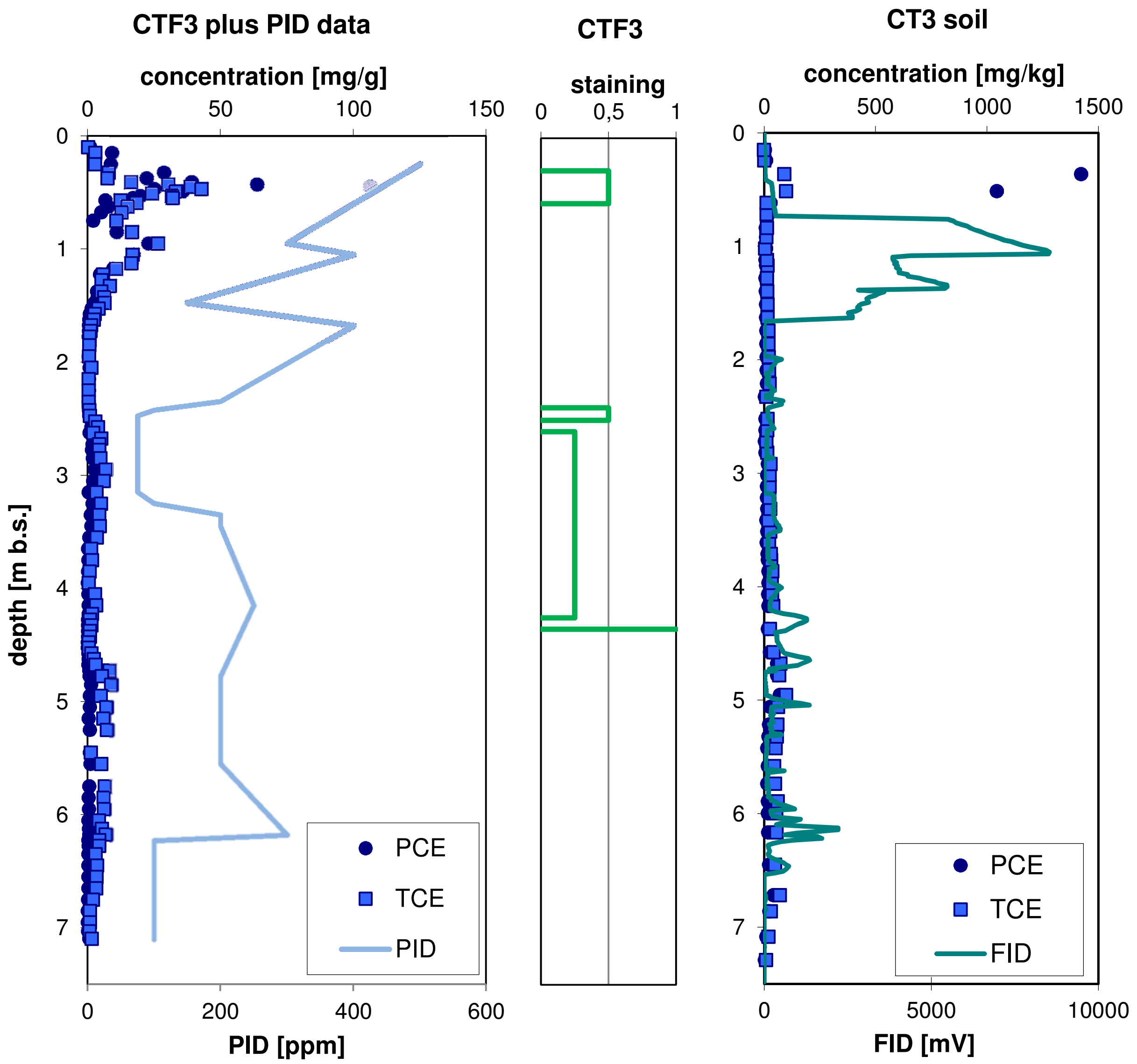

Figure 41: concentration of PCE and TCE on carbon felt with PID data (left) and staining (middle) of CTF3 in function of depth (m b.s.); soil core concentration data of PCE and TCE and MIP-FID data of CT3 over depth

As an example CTF3 was chosen to illustrate concentrations on the FACT that would be obtained with 30 cm discreet samples (by simply taking the average of concentration data of more discreet samples taken in the field). In figure 42 it can be seen the concentration trend over depth is still visible with lower discretization of 30 cm compared to 2 to 10 cm discreet sampling (fig. 41, left) with PID and staining data still same discreet. However just 1/3 of the high PCE concentration on the FACT at 0.45 m is reached with the 30 cm average value (fig. 42) compared to 2- 10 cm sampling data (fig. 41, left).

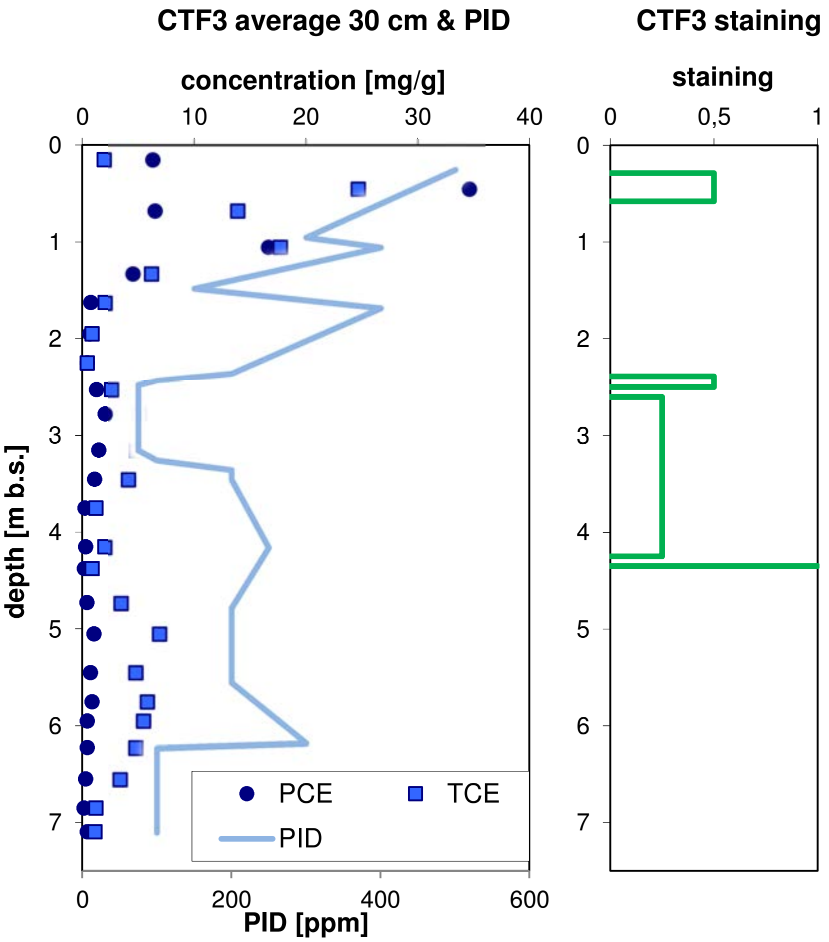

Figure 42: average data of CF3 30cm discreet including PCE & TCE concentrations on the carbon felt and PID (left) and staining data (right)

4.3 Results Chalk – saturated zone

Staining and PID

Pictures of staining found on the chalk FACT liners are shown in the following. Occurrence of staining and PID data are summarized in tables 15, 16 and 17 for CF1, CF2 and CF3, respectively. The staining can be differentiated slightly different to the chalk FACTs, due to staining occurred mainly very faint. For illustration purposes staining can be differentiated according to its strength (very light, light, medium light and (obvious) staining illustrated by values 0.25, 0.5, 0.75 and 1, respectively.

CF1

The length of CTF1 was 9.7 m plus a casing of 8 m of the clay till part, thus CF1 reached 17.7 m b.s. CF1 showed light staining from 8.9 to 9.1 m b.s., at 10.2 and 10.7 m all the way down with a stain at 16.50 m b.s. (fig. 43 and 44). In general the second half of the liner showed higher PID values and more staining. A summary of staining and PID data can be found in table 14.

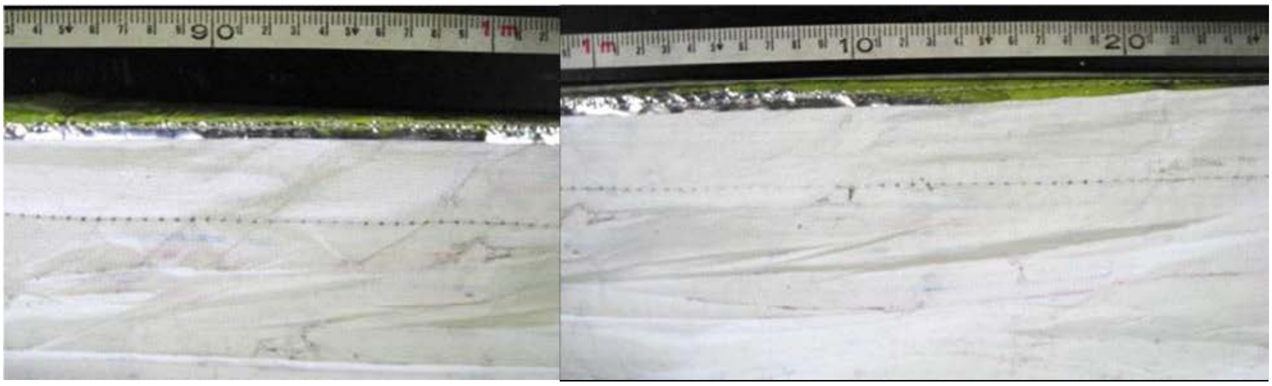

Figure 43: light staining of CF1 from 8.9 to 9.1m

Figure 44: light staining CF1 all the way down to 10.7m

Table 14: summary of staining and PID data of CF1

staining		PID	
in general very small stains and light stains		mainly high values in the end of the liner; smell	
Depth below surface	**occurrence**	**Depth below surface**	**value**
8.9 – 9.1 m	Light staining	9.20 m	80 ppm
		9.9 m	160 ppm
From 10.2 to 10.7 m	Light staining	10.2 m	100 ppm
All way down to 16.5 m	Light staining	12.2 m	250 ppm
		at 11.4 and 12.9 m	200 ppm
		13.3 m	190 ppm
		13.7 m and at 14.3 m	330 and 320 ppm
		14.4 till 15.5 m	200 ppm
		at 15.6 m	100 ppm
		16.4m and 16.5 -17.75 m	370 and 260 ppm

CF2

The casing of CF2 was 8.7 m and the length of the FACT in chalk 11 m, thus CF2 reached 19.7 m b.s. CF2 showed light staining around 16.6 – 16.8 m, 7.80m and from 14.7 to 14.95 m b.s. (fig. 45). PID data showed generally higher values in the end of the liner (14.7 m b.s. downwards), but did not correlate well with the observation of staining (summarized in table 15).

Table 15: summary of staining and PID data of CF2

staining		PID	
in general Very small/faint staining		mainly high values in the end of the liner; smell	
Depth below surface	**occurrence**	**Depth below surface**	**value**
		8.90 m	100 ppm
		9.2 to 13.1 m	Low up to 40 ppm
from 14.7 to 14.95 m	Medium light staining		
16.5m & 16.6-16.8 m	Medium light staining	15.5 m, 15.6 m, 15.9-16.1 m	Around 150 ppm
		17.2 - 17.3 m	120 ppm
		at 18 m	120 ppm

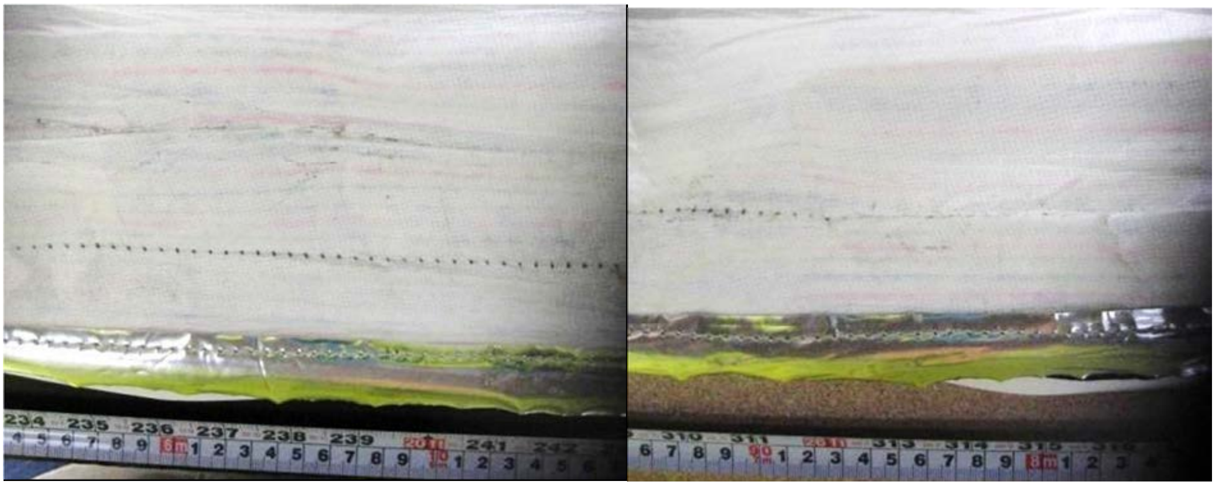

Figure 45: medium light staining CF2 around 16.7 m and 14.8 m

CF3

The length of CF3 was 13 m, sampling was done until a length of 12.2 m, the casing was 8.5 m, thus CF3 reached 20.7 m b.s. PID measurement was not available for CF3.The FACT liner showed medium light staining at the first 75cm on the "eastern" side (facing the contaminant plume) and a small blue stain at 14.5 and 14.55 m b.s. (shown in fig. 46 and 47).

Figure 46: medium staining CT3 from 0 to 75cm

Figure 47: blue staining CT3 at 14.5 m

Concentrations

Concentration results from GC/MS, staining and PID of all FACT liners (CF1 to 3) installed in chalk are shown below including a comparison with soil concentrations determined by other researchers during the Naverland site investigation. Generally all FACT liners in chalk show the same concentration range, but lower concentrations are obtained compared to the FACT liners in clay till.

CF1

Samples of CF1 were taken over the entire length from 0 to 9.75 m, equivalent to 8.00 to 17.75 m b.s., due to a casing of 8 m in the clay part. PCE concentration development over depth does not show the same trend as PID development. PCE concentration on the carbon felt is decreasing over depth (fig.48, left), however TCE concentration and PID values are increasing over depth, also indicated by occurrence of very light to light staining (fig. 48, middle). Generally concentration data vary highly. A high PID measurement and staining was found at 16.5 m, which corresponds to an increased TCE concentration up to 3.6 mg/g between 10.6 and 17.7 m b.s.

In comparison concentration data obtained in soil (figure 48, right) showed a very high outstanding value (could also be a mistake!?) of 183.9 mg/kg of PCE at a depth of 13.3 m b.s. When this high point was ignored and the data are zoomed, the highest concentration obtained for PCE is 45.7 mg/kg at 9.6 m (corresponding to the light staining at the FACT at 9 m) with a decreasing concentration over depth (as also shown for FACT data). TCE concentrations in soil were generally lower then PCE and did not show a clear peak value. The highest concentrations found for TCE are 14 and 13.5 mg/kg at 12.6 and 13.3 m b.s. However the increasing trend of TCE concentration as found on FACT samples and staining at 16.5 m were not indicated by soil concentration data.

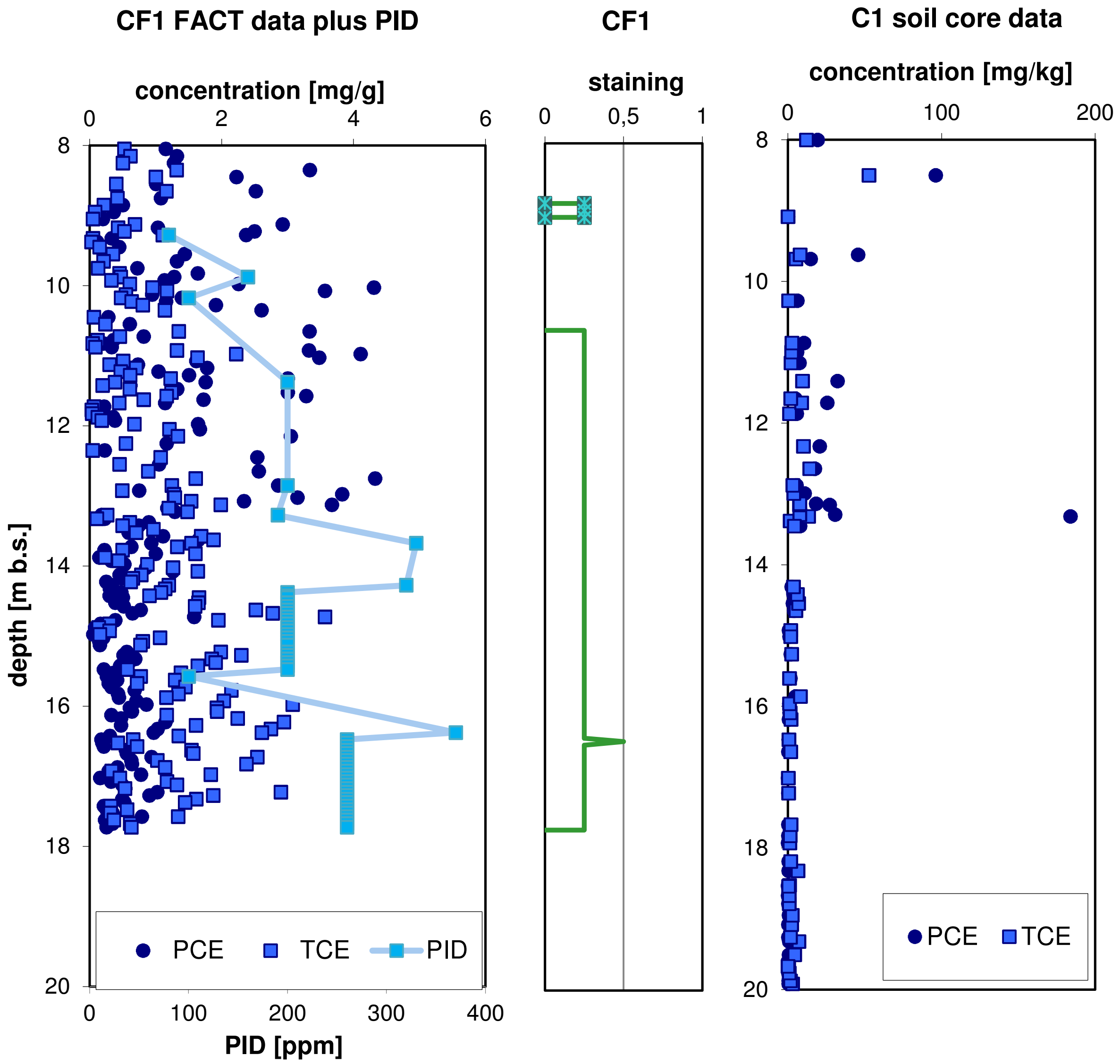

Figure 48: PCE and TCE concentration on carbon felt with PID measurement (left) and staining data (middle) over depth of CF1; PCE and TCE concentration in soil (right) over depth

CF2

The total length of CF2 was 11 m, the clay till casing was located up to 8.7 m, thus the FACT reached 19.7 m b.s. Due to a limited number of samples, the below mentioned samples were taken as given in table 16. Results from GC/MS, PID and staining of CF2 are illustrated in fig. 49 left and middle.

Table 16: sampling location of CF2

Depth [m b.s.]	8.7-9.6	10.8	11.8	12.7-13.3	14.5-19.7

In general CF2 showed lower PCE than TCE concentrations on the carbon felt. Highest concentrations of PCE and TCE are obtained close to 14.8 m b.s. with a concentration of 2.0 and 4.0 mg/g, respectively. Also staining is indicated at this depth and PID data increase up to 150 ppm at 15 m b.s.

In comparison soil data (presented in figure 49, right) show a similar trend as concentration data on the FACT with generally higher TCE concentrations than PCE and highest concentrations around 15 m b.s. with 11.5 mg/kg for TCE and 6.9 mg/kg of PCE in soil.

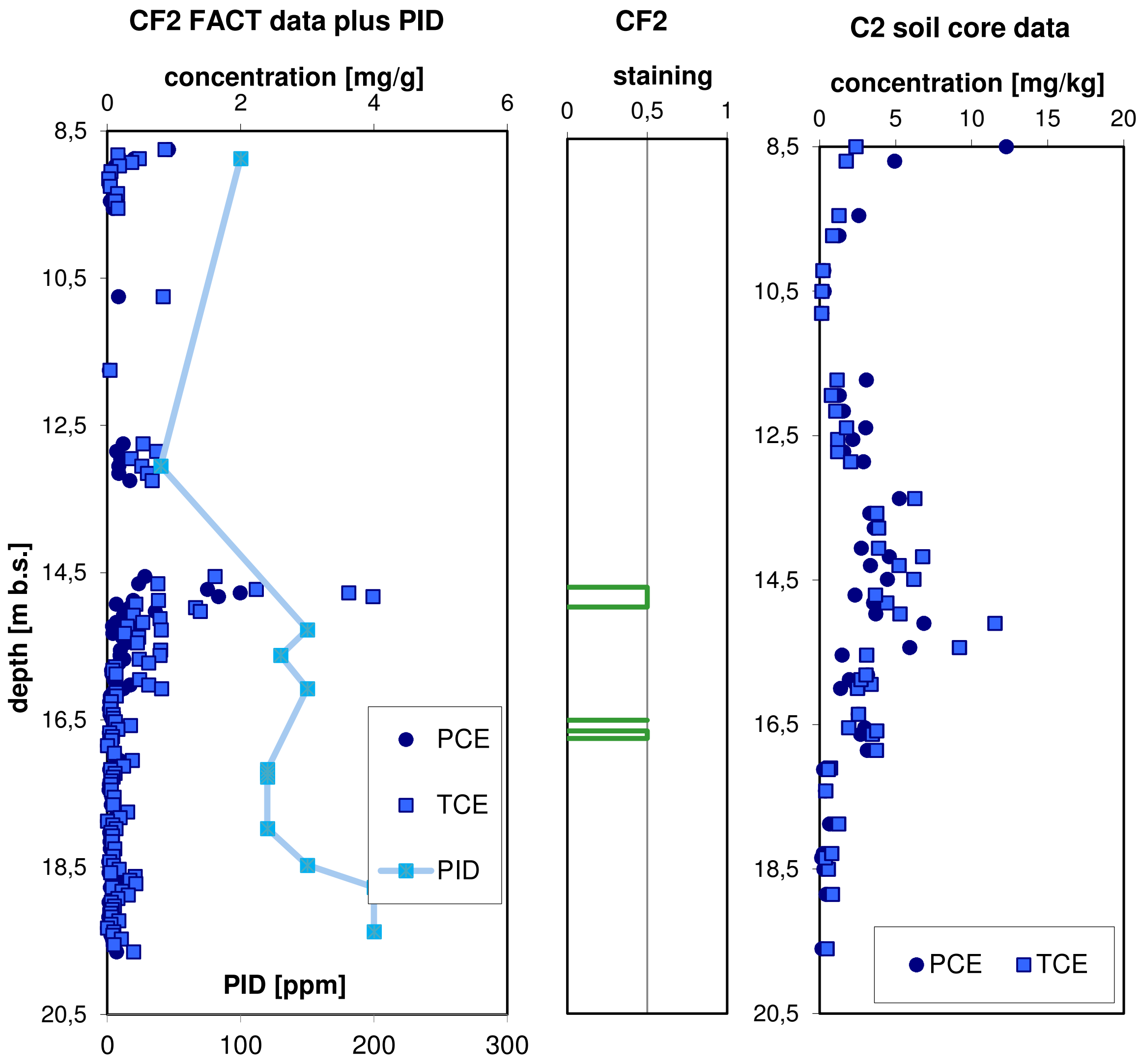

Figure 49: PCE and TCE concentration on carbon felt with PID (left) and staining data (middle) and PCE and TCE concentration in soil core C2 over depth (right)

CF3

The total length of CF3 was 13 m with a clay till casing of 8.5 m; samples were taken as given in table 18. GC/MS data and staining for CF3 can be found in figure 50 left and middle. No PID measurement was available during sampling of CF3. Medium light staining was found for the first 75 cm (corresponding to 8.5 to 9.25 m b.s.) and light staining from 14.75 to 14.85 m b.s corresponding to the higher values of PCE found with around 1.33 mg/g at 14.8 m b.s. Furthermore at around the same height (9 m b.s.) as medium light staining occurs, 2.33 mg/g for PCE as highest concentration on the FACT is found. Overall GC/MS data of the carbon felt of CF3 show a concentration decrease over depth with PCE concentration generally higher than TCE concentrations.

Table 17: sampling location CF3:

Depth [m b.s.]	8.7-9.5	9.7-9.95	10.8-11.4	11.9-14.2	14.7-15.1	15.9-16.3	17.2-17.4	18.0-19.1	19.6-19.8	21.0-21.3

In comparison data obtained with chalk core samples show generally higher TCE concentrations compared to PCE, in contrast to FACT data (fig. 50, right). Highest concentration of TCE occurs at 13.5 m b.s. with 21.18 mg/kg and PCE with 13.23 mg/kg at 12.9 m b.s. However these data cannot be compared with FACT data, since no samples were taken at this particular depth.

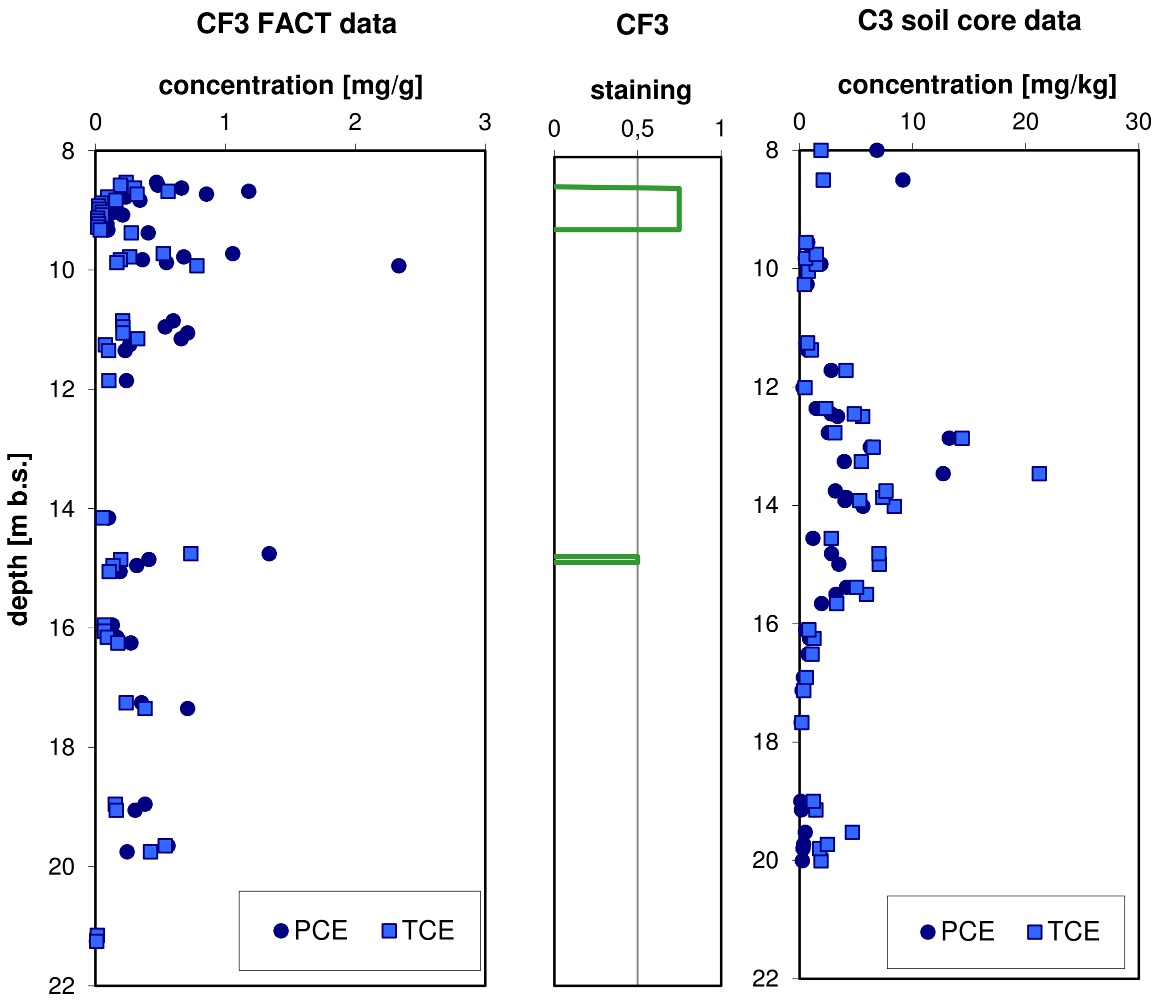

Figure 50: PCE and TCE concentration on carbon felt (left) and staining (middle) over depth of CF3 and PCE and TCE concentration (right) over depth measured in soil

In the following water concentration data of the upper part of the chalk aquifer provided by Krüger A/S analyzed with purge & trap GC/MS are compared with average values obtained on the carbon felt at a respective depth (upper 20 cm of chalk chosen) summarized in table 18. It can be seen both TCE and PCE are higher in location 3 (CW3 and CF3) than in location 2 (CW 2 and CF2), however data do not indicate correlation regarding the concentration ratio of both locations (tab. 18). Furthermore the ratio of PCE to TCE was tested determining similar concentrations for PCE and TCE on FACT samples CF2 and CF3, however PCE concentrations in water samples are shown to be higher for CTW2 and lower for CTW3 than TCE concentrations.

Table 18: Water data of upper part of the chalk (right at the intersection between clay till and chalk) provided by Krüger A/S in comparison with upper 20 cm FACT data (marked as average data Ø)

Sample ID	medium	TCE	PCE	Ratio PCE/TCE
CTW 2	Water	1400 µg/l	2300 µg/l	1.6
CTW 3	Water	54000 µg/l	30000 µg/l	0.5
Ratio CTW3/CTW2		~ 40	> 10	
CF 2 upper 20 cm	FACT	Ø 0.23 mg/g	Ø 0.20 mg/g	0.9
CF 3 upper 20 cm	FACT	Ø 0.50 mg/g	Ø 0.49 mg/g	1.0
Ratio CF3/CF2		2.2	2.5	

4.4 Discussion and summary

Interpretation of results

In the following, a small site description and expectations are given, summarizing the locations where DNAPL or high aqueous concentrations were found.

In the upper clay till part concentrations were expected to be high (especially close to the location of the former PCE tank) and DNAPL presence was expected. According to a test coring in March 2008 the DNAPL phase was suspected to have migrated as deep as 25 m b.s. moving through fractures ect. [Region Hovedstaden 2008; Københavns Amt 2002; Janniche 2011], (see also fig. 6, chapter 2.5). Furthermore geology analysis showed fractures around 25 m b.s., between 18 and 20 m b.s., between 12 and 14m b.s., where DNAPL presence or at least high aqueous concentrations were expected. Results in this study indicate a verification of some expectations. Different concentrations on the carbon felt and staining were expected and determined during field work in the saturated and unsaturated zone.

Unsaturated zone: In this study DNAPL was found in the clay till part mainly in CTF2 with a clear evidence of big stains starting at 2.7 m b.s. down to 3.9 m b.s. CTF2 was expected to show less DNAPL presence since it is located in a farer distance from the buried PCE tank. However another, yet unknown spilling might have taken place in the past or favorable pathways/transport. Also high aqueous concentrations indicated by faint staining were found on CTF3 between 2.5 and 4.4 m and at CTF2 at 4.8 m downwards. Furthermore carbon felt analysis in saturated PCE air (showing no staining) and in touch with DNAPL PCE (indication of staining) justified high carbon felt concentrations (mainly in CTF3) sorbed from the vapor phase in clay till leaving no staining. However in contrast to CTF3 the other FACTs, namely CTF1 and CTF2, showed lower concentrations on the carbon felt, even though DNAPL staining was found on CTF2. This can be explained by the installation of the FACTs in clay till with water instead of air as originally planned. Normally the (yellow) cover liner of the FACT is meant to be water tight, however CTF1 and CTF2 broke during installation, thus leading to water in the soil matrix and reduced sorption of chlorinated solvents to the carbon felt.

Saturated zone: Generally concentrations found in chalk were lower compared to concentrations found in clay till and staining was mainly faint. This is in accordance with the findings during lab experiments in this study, showing lower diffusion in aqueous phase causing generally lower concentrations on the activated carbon felt. Furthermore the FACT liners applied in chalk showed no clear evidence of DNAPL presence, only faint staining occurred. The faint staining can be explained by high aqueous concentrations found during lab experiments with a FACT liner exposed to saturated PCE and TCE solution. Faint staining and/or high aqueous concentrations were found mainly close to the beforehand found fractures during geological analysis (CF1: around 9 m b.s. and between 10.5 and 18 m b.s.; CF2: around 14.5/15 m and 16.5 m b.s.; CF3: around 9 and 14.5/15 m b.s.). Furthermore concentration data of some FACT liners vary highly (as CF1), which is probably due to a varying geology over depth and cracks or a possible contamination with borehole water while installing (mentioned by Keller, 2011).

Comparison with other characterization methods

Water samples taken in the upper chalk showed poor correlation with the FACT results. This can be explained by that water samples are taken from and therefore representing mainly the bigger fractures with higher flow. Whereas the contaminant is known to be mainly present in smaller fractures [Pankow & Cherry, 1996] and the bigger fractures are flushed through with a high ground water flow leading to low chlorinated solvent concentrations with time (also shown in fig. 2 and Jørgensen et al., 2010). In contrast the FACT is shown to represent the concentrations present in the entire aquifer matrix (smaller and bigger fractures, soil). Thus also the upcoming water sampling (in April 2012) is expected to be in poor correlation with FACT results.

However soil and MIP-FID results showed good correlation to FACT results. Where high concentrations in the FACT were observed, also high concentrations in soil or a high MIP-FID values were determined. Small differences between clay till soil and FACT samples can be explained by the different location with a distance up to 1 m between soil cores and FACT installation. Also Keller (2011) tested the FACT in the unsaturated zone in Danish clay till and found good correlation with GEO Probe MIP in April 2010 with up to 3 mg/g chlorinated solvents sorbed to the carbon felt. Furthermore adsorption on carbon felt and transport processes in soil are diffusion controlled leading to an expected good correlation of FACT and soil data.

A summary of maximum PCE concentrations found in soil and FACT samples and the ratio of soil:FACT concentration are given in table 19. In general diffusion is defined as product of concentration gradient and diffusion coefficient. Literature shows an almost 10.000 times higher diffusion coefficient in air than in water [Haynes, 2010]. However the diffusion coefficient in soil is also dependent on the soil characteristics (higher porosity – higher diffusion coefficient). Thus in soil with same/similar properties, the diffusion coefficient is same/similar and the concentration obtained on the carbon felt can be related to the concentration gradient in soil.

When comparing concentrations in soil and FACT samples (table 19), the correlation is indicated when examining the ratio of maximum PCE concentrations on carbon felt and in soil in location 1 and 2 in clay till. Both locations are believed to be of similar soil characteristics and more or less saturated due to both were installed with water. The data show a similar high ratio value of several hundred. When comparing location 2 and 3 in clay till with similar soil concentration, location 3 shows a much lower ratio due to a higher diffusion in vapor phase. Also the locations in chalk show similar results due to similar soil characteristics and therefore similar diffusion coefficient.

Table 19: summary of maximum PCE concentrations in soil and FACT, comparison of ratio PCE in soil/FACT in different zones

Location	Max. PCE in soil [mg/kg]	Max. PCE on FACT [mg/g]	ratio	zone
Clay 1	2000	7	286	Unsaturated, but belived to be water saturated
Clay 2	15000	25	600	
Clay 3	1400	110	13	unsaturated
Chalk 1	40	4	10	saturated
Chalk 2	12	4	3	
Chalk 3	23	2.3	10	

Applicability

Pentane extraction is shown to be useful for analysis of the FACT, due to a high recovery and good comparison with soil samples, which were prepared and analyzed in the same way (addition of water and pentane for extraction and subsequent pentane analysis). Even though the handling of pentane is still an environmental issue, the analysis of water showed no suitable results. However the use of other extractants like acetone or methanol imply addition of the extracting agent in the field, due to addition of water is not suitable, which would preserve the samples.

During sampling and sample handling of the hard chalk material reported by other researchers during the field investigation, unexpected problems rose leading to a more difficult sampling procedure and preparation for analysis. It should be noted that in comparison with soil analysis less pentane is needed for FACT analysis. Furthermore the vials can be prepared beforehand, which simplifies the fieldwork. Also taking out the pentane sub-samples is simple, due to a clear separation between water and pentane phase. In addition the method is not very time consuming showing sampling of 8 m FACT liner in 2 to 10 cm samples and 30 cm backup was carried out in 1.5 h.

Furthermore concentration data of the FACT liner correlate well with MIP-FID and soil data. This implies that the FACT liner is a useful tool to determine locations with DNAPL presence or high water concentration of chlorinated solvents. However the concentration on the carbon felt cannot directly be used to verify DNAPL presence or high aqueous concentrations up to saturation, but soil/soil air or water analysis can give an idea about the exact concentration (ranges) in the matrix. On the other hand different staining (light and DNAPL) was observed leading back to high aqueous concentrations close to or at saturation and DNAPL presence, respectively.

Since testing of small, very discreet samples is unpractical and expensive, staining can be used to give already at the site a clear indication of DNAPL presence. Also high PID values indicate places of interest for high discreet sampling. However less discreet, 30 cm carbon felt samples, analyzed with similar felt to pentane ratio, showed similar results obtained as average of smaller discreet FACT samples. Thus when higher concentrations are indicated with less discreet samples, further discretization can follow. However the risk is high to choose a suboptimal part, thus indication by staining or PID measurement should be used already at the field site for discretization. Furthermore the analysis of the overlapping FACT liner samples (of CTF2) showed the carbon felt reflected one side of the borehole. Even though the FACT can be installed in the way that the carbon felt strip faces the expected contaminant plume, it can still twist in the bore hole. However the difference in concentration can also be explained by different contact to the soil matrix due to overlapping. It should be noted when suboptimal samples (sizes) are chosen, which indicate medium concentration, however a discretization might show one centimeter of very high DNAPL indication (probably due to a fracture), but the rest very low concentration. With observing just the 30cm sample, the high peak value might never be found.

As reported by Keller (2011) potentially contaminated borehole water can absorb on the carbon felt during installation in an aquifer leading to high background data of chlorinated solvents and not distinguishable “real”/peak concentrations. The influence of borehole contamination in this study cannot be excluded totally, since a high background or high variation of data were observed for chalk liner CF1, which could be due to borehole water contamination. However this issue needs to be further evaluated to conclude the cause of highly varying concentration data.

5. Conclusion

General

Focus of this thesis was set on the applicability of the FACT liner in a chalk aquifer. Therefore over 700 filed samples in 6 locations (3 in clay till and 3 in chalk) were taken and compared to other methods applied on the Naverland site (e.g. soil and water samples). First lab experiments were carried out and helped to understand the adsorption process of chlorinated solvents on the carbon felt and therefore interpretation of field data. Furthermore the best analysis method of the carbon felt and the handling of the FACT in the field were discovered.

Pentane extraction was found to be the most suitable analytical method in this study. It showed a high recovery and low detection limits. Furthermore soil samples (which were taken by other researchers during the project) and FACT samples were treated and prepared in the same way, by using pentane extraction, giving comparable concentration results. In contrast to soil or chalk samples, the FACT liner can be discretized in the field and sample vials can be prepared with water beforehand leading to a convenient sampling procedure. Lab experiments showed the carbon felt is preserved in the water and pentane can be added in the laboratory under a fume hood without the risk of losing the volatile compound on the way from field to lab. Furthermore the addition of pentane is less in volume compared to the amount generally used for soil sample analysis due to the smooth pentane-water interface of the prepared FACT samples, which is convenient for sampling of the pentane for analysis.

The application of the FACT liner in clay till during 24 h and in chalk during 40 or 42 h turned out to be optimal, since lab experiments showed a slower adsorption in lower concentration. Furthermore the FACT results correlate well with soil and MIP data, thus the application/contact time of the FACT liner in soil was sufficient. Also faint staining occurred indicating high aqueous concentrations. However to be on the safe side, a contact time of 48 h is suggested for both clay till and chalk for further studies.

The analysis of longer, 30 cm samples was found to be of representative concentration similar to results obtained in average by more discreet samples. Furthermore illustrating average concentration values over depth each 30 cm compared to more discreet (2 to 10 cm samples) showed the concentration trend is still visible. Thus less discreet samples can be used as a first insight of the concentration range. In case some longer samples show high concentrations of a chlorinated solvent, a more discreet analysis will reveal peak values. Nevertheless there is also a risk to choose suboptimal longer samples, which indicate medium concentration. However a higher discretization of that particular sample might show one centimeter of very high chlorinated solvent appearance (probably due to a fracture), but the rest very low concentration.

Saturated vs unsaturated zone- diffusion limitations

Lab experiments determining adsorption of chlorinated solvents from different phases showed highest PCE concentration on the carbon felt (of around 45 mg/g) in PCE saturated air indicating diffusion controlled adsorption on the activated carbon felt. In the field concentrations up to 110 mg/g were determined in the unsaturated zone indicating high concentrations determined in clay till must be present due to high soil air concentrations, also justified by absence of staining at these high concentrations in clay till. Lab experiments showed a drop of DNAPL on the carbon felt results in a concentration around 3 mg/g. In the field concentrations in this concentration range (up to several mg/g) and in combination with staining in clay till and chalk samples justified DNAPL presence in some locations at the site. The carbon felt in saturated PCE, showed around 0.7 mg/g PCE sorbed to the carbon felt and light staining explaining the lower concentrations. Thus light staining the found in chalk in the field are due to high aqueous concentrations close to or at saturation.

The FACT was expected to be helpful to differentiate between DNAPL presence and high aqueous chlorinated solvent concentration. Since concentrations on the carbon felt are not just dependent on the concentration gradient in soil, but also on the diffusion coefficient, which is dependent on soil properties (such as porosity and water saturation), a differentiation between DNAPL and high aqueous concentration is difficult, but possible in soil with similar properties. Furthermore with help of staining on the FACT, DNAPL presence and aqueous saturation in the saturated zone was proven in this study.

Correlation with other characterization methods

Since adsorption on carbon felt and transport processes in soil are diffusion controlled, a good correlation of carbon felt concentrations on the FACT and soil data was expected. This study showed good correlation between FACT liner concentration results and soil concentrations and MIP measurement over depth for most locations. Also PID and staining on the FACT were found to correlate with concentration on carbon felt and in soil over depth. Thus the FACT gives a first insight into the concentration range over depth; however one should be aware that diffusion processes are dependent on the diffusion coefficient, therefore soil properties and location in saturated or unsaturated zone.

Correlation with ground water data over depth will be accomplished soon (April 2012). However first comparison with water samples obtained in the upper part of the chalk showed poor correlation. This is due to water samples represent mainly the bigger fractures with higher flow, whereas the contaminant is known to be mainly present in smaller fractures due to the contaminants are flushed out of the bigger fractures with time. In contrast the FACT results/concentrations on the carbon felt represent the concentrations present in the aquifer matrix (soil, smaller and bigger fractures). Hence also the upcoming water sampling is expected to be in poor correlation with FACT concentration results, due to examination of different matrix fractions.

Perspective of use

Since diffusion is found to be dependent on the diffusion rate (on account of soil properties) and the concentration gradient in the matrix, the FACT is only found to be useful in homogenous soil or with known soil properties to interpret the concentration trends over depth. When also soil or water concentrations are known from other sampling at the site, chlorinated solvent concentrations can be related back (in relative sense) to soil matrix concentrations.

In the unsaturated zone, interpretation of carbon felt concentration data turned out to be even more difficult, since adsorption is diffusion controlled, thus it is dependent on the water content in the soil. With less water content variation over depth the results are expected to be more meaningful, due to similar adsorption over the entire depth. Generally an inhomogeneous subsurface is expected to give highly variable concentration results on the carbon felt. Thus one should be aware of several possible issues leading to a wrong interpretation of the estimated concentrations of field samples, i.e. high concentrations on the carbon felt, do not necessarily indicate a high concentration of chlorinated solvents in the soil since adsorption is diffusion controlled.

On the other hand the FACT as a combination of carbon felt and NAPL FLUTe allows a very discreet screening method to indicate locations with DNAPL and/or high chlorinated solvent concentrations in the subsurface. Therefore the combination of staining and carbon felt analysis on the FACT occurs to be very helpful to differentiate between probable DNAPL presence (due to staining and high carbon felt concentrations) and high aqueous chlorinated compound concentration (due to faint staining, but lower or medium high concentrations on the carbon felt) especially in the saturated zone/ the chalk aquifer, where characterization is difficult with other methods. The combination of carbon felt concentration analysis with staining and PID measurement implies also to find interesting locations to analyze more discreet, already at the field site.

In summary adsorption processes from aquifer material to carbon felt are too complex to obtain a simplified relation between concentration on activated carbon felt and aquifer material. Therefore the FACT characterization method needs to be accompanied and accomplished by other methods (e.g. water or soil analysis). Thus this method does not provide a direct measure of the concentration per unit weight of pore fluid/soil air, but it is a duplicate of the relative amount of contaminant present in the aquifer material and represents concentration trends over depth well. Furthermore it is shown that a combination of staining and concentration analysis on the carbon plus the knowledge about the geological settings and hydrology (in aquifer or unsaturated zone) is crucial in order to interpret the results obtained by the FACT liner.

However the method can be used as screening methods with high flexibility in discretization over depth. Therefore longer samples can be analyzed in a first attempt, and then further discretization can follow giving a very high flexibility, compared to other mostly inflexible characterization methods. Furthermore during the project the analysis of the FACT tuned out to be cheaper and faster compared to many other methods. Sampling of 8 m FACT liner in 2 to 10cm samples and 30cm backup takes around 1.5 h. Therefore the FACT is suitable as first characterization tool giving insight to high chlorinated solvent concentration areas and locations with probable DNAPL presence, especially in chalk. Subsequently another quantitative characterization method can be used to determine actual concentrations in the subsurface.

6. Further work

In case the characterization method wants to be further evaluated, one should test if the concentration analyzed on the carbon felt can be linked to a concentration in the ground water, fractures and soil (pore space). The adsorption and therefore diffusion process is very complex due to numerous dependence and interconnection of parameters and processes. Therefore a real system can be tested bringing contaminated soil with a given concentration of TCE/PCE or DNAPL in contact with the FACT liner screwed in the lid of a vial. An idea for the setup is shown in figure 51.

The followed extraction with pentane and comparison with before done extraction experiments will predict if the concentrations found on the carbon felt can be back calculated to the content of chlorinated solvents in soil/ soil pores and fractures. An estimation of soil properties and therefore diffusion coefficient and the knowledge about the concentration gradient might be helpful for chlorinated solvent determination in the soil matrix. E.g. the soil properties could be kept the same, so just the concentration gradient is changed and later on the concentration gradient can be kept the same, but the soil properties are changed or a fracture is simulated. These extensive experiments are only useful, when the FACT is used in a homogenous or uncomplex subsurface where soil properties are known or they are invariable or consistent. Therefore the concentration on the FACT can be used to relate to the concentration gradient in the subsurface matrix with help of the mentioned experimental setup. However also testing an inhomogeneous subsurface with the setup is conceivable.

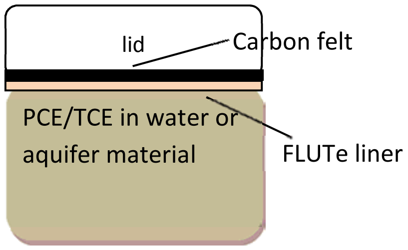

Figure 51: idea for test of real system

The above given setup to study sorption of the chlorinated solvents more intensely also implies the improvement and further interpretation of the obtained field work data in this study and will help to understand the processes and concentrations present in the subsurface. Since it was the first time the FACT was tested in a chalk aquifer further fieldwork could follow, in chalk or another material e.g. sand, comparing the results obtained to improve the interpretation of data obtained with the FACT. Nevertheless testing the FACT in the unsaturated zone with soil containing almost no water, thus implying exposure just from the vapor phase, would be interesting to determine the limit concentrations that can be reached in the unsaturated zone on the carbon felt.

Furthermore other extraction techniques can be further evaluated, e.g. the use of a more environmentally friendly and less harmful alternative to pentane (e.g. methanol or acetone) could be tested as mentioned by other researchers. E.g. Keller reports about methanol extraction and subsequent GC/MS analysis [Keller, 2011] and Erto et al. (2010b) describes a extraction with acetone and subsequent purge and trap GC FID analysis.

Abbreviations

c	concentration
C 1 to 3	soil core in chalk 1 to 3
CF 1 to 3	FACT liner in chalk 1 to 3
cis-DCE	cis- DiChloroEthylen
CT 1 to 3	soil core in clay till 1 to 3
CTF 1 to 3	FACT liner in clay till 1 to 3
(D)NAPL	(Dense) Non Aqueous Phase Liquid
FACT	FLUTe Activated Carbon Technique
FID	Flame Ionization Detector
f_{OC}	Organic carbon content
GAC	Granulated Activated Carbon
GC/MS	Gas Chromatography with attached Mass Spectrometry
K_H	Henry constant
K_d	Distribution coefficient
K_{OC}	distribution coefficient to organic carbon in soil
LOD	Limit of Detection
LOQ	Limit of Quantification
m	mass
m b.s.	meter below surface
MIP	Memebrane Interface Probe
PCE	PerChloroEthylen
PID	Photo Ionization Detector
SIM	Selective Ion Monitoring
TCA	1,1,1-TriChloroEthane
TCE	TriChloroEthylen
V	volume
VOC	Volatile Organic Compound

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Appendix 0 – GC method, standards and controls

The preparation of internal standard, control and standards for calibration curve are described in the following.

Standards

Headspace

A methanolic standard mixture was prepared using 1150µl of methanol, 40 µl of PCE and TCE and 50µl of cis-DCE and TCA (given in table 20). The compounds were added with a Hamilton syringe through the septum (to keep volatilization at a minimum) into a 1.5 ml GC-vial.

Table 20: compounds and amounts for methanolic standard stock solution

Compound	methanol	PCE	TCE	Cis-DCE	TCA
Amount [µl]	1150	40	40	50	50

200µl of this methanolic stock solution is added via a Hamilton syringe to limit volatilization into 1l of tap water (in a 1 l infusion bottle closed with a Teflon septum). The solution (called stam 8, the highest standard) needs to be stirred for 3 to 4 h. The other standards (st 7 to st 1) of volume 10 ml each are prepared according to the following table (21). The prepared standards are filled in 2 ml GC/MS vials. Vials and left over standards are kept upside down in the freezer at -18°C.

Table 21: preparation of st7 to st1 as dilutions of stam 8 in water & final concentration of compounds in standards

	stam 8	**st 7**	**st 6**	**st 5**	**st 4**	**st 3**	**st 2**	**st 1**
Dilution	1	1.25	1.67	2.5	5	10	20	50
water weighed [ml]	0	2	4	6	8	9	9.5	9.8
Standard solution [ml]	10	8	6	4	2	1	0.5	0.2
Concentration of each compound in the standard solutions [µg/l]								
***cis*-1,2-DCE**	9654	7723	5792	3862	1931	965	483	193
TCE	8782	7026	5269	3513	1756	878	439	176
PCE	9762	7810	5857	3905	1952	976	488	195
1,1,1-TCA	10060	8048	6036	4024	2012	1006	503	201

Pentane Analysis

50ul of each compound is added to 50ml of pentane giving standard stock 1. Each standard can now be prepared adding X µl of stock 1 to 50ml of pentane as given in table 22 (upper part) for the first 8 standards. For standard 9 to 14 pentane and stock 1 as given in table 22 (lower part) is used.

Table 22: preparation procedure for standards in pentane

	std 8	**std 7**	**std 6**	**std 5**	**std 4**	**std 3**	**std 2**	**std 1**
pentane [ml]	50	50	50	50	50	50	50	50
Std stock 1 [µl]	325	250	200	125	50	20	10	5
	Std 14	**Std 13**	**Std 12**	**Std 10**	**Std 9**			
pentane [ml]	45	46	47	48	49			
Std stock 1 [ml]	5	4	3	2	1			

Concentration of each compound in the standard solutions [mg/l]

	std 8	**std 7**	**std 6**	**std 5**	**std 4**	**std 3**	**std 2**	**std 1**
***cis*-1,2-DCE**	8.71	6.70	5.36	3.35	1.34	0.67	0.40	0.134
1,1,1-TCA	8.32	6.40	5.12	3.20	1.28	0.64	0.38	0.128
TCE	9.49	7.30	5.84	3.65	1.46	0.584	0.292	0.146
PCE	10.53	8.10	6.48	4.05	1.62	0.81	0.49	0.160
	Std 14	**Std 13**	**Std 12**	**Std 11**	**Std 10**	**Std 9**		
***cis*-1,2-DCE**	134.0	107.2	80.4	53.6	26.8	15.63		
1,1,1-TCA	128.0	102.4	76.8	51.2	25.2	14.93		
TCE	162.0	129.6	97.2	64.8	32.4	17.03		
PCE	162.0	129.6	97.2	64.8	32.4	18.9		

Internal standard

Headspace

First a standard 1 solution (ST1) needs to be prepared in a 1 l infusion bottle. The solution contains 960 ml of tap water and 40 ml of slowly added sulphuric acid and needs to be stirred for 30 min. Afterwards under stirring 0.5 ml of chloroform are added with a 1 ml Hamilton syringe through the septum of the infusion bottle.

Now the internal standard used for analysis (IS2) is prepared using 950 ml of tap water, 40 ml of sulphuric acid and 10ml of IS1, prepared as described above. The solution is stirred for 30 min and kept upside down in the refrigerator at 4 to 5°C.

Pentane analysis

First 1ml of chloroform is added to 10ml of pentane giving IS stock 1. Then 20 µl of IS stock 1 is added to 1 l of pentane giving an Pentane IS as internal standard with a concentration of 2890 µg/l chloroform in pentane.

Control solution

Headspace

To 1000 µl methanol in a screw cap vial 50 µl of TCE and 50 µl PCE are added, making solution 1. 20 µl of solution 1 are added to 2 l of tap water in a 2 l blue cap bottle through the a Teflon septum cap with a gas syringe. The solution needs to be stirred for at least 3 h. With a 1 ml dispenser control vials can be prepared for subsequent analysis of samples. Control samples and left overs are kept in the freezer at -18°C.

Pentane analysis

For pentane analysis standard number 5 is used as control (preparation described below).

GC/MS methods

Headspace GC/MS

Auto sampler (Perkin Eimer Turbo Matrix 40)

Injection volume: 2000 µl
Equilibrium time: 0 s
Syringe temperature: 85 °C

GC (Agilent 6890N)

Column: Agilent 19091P-Q04 (Plot Q). 30 m x 320 µm x 20 µm
Front inlet temperature: 280 °C
Injection: splitless 0 psi, 45 ml/min
Column flow: 45 ml/min helium

MS (Agilent 5973)

Acquisition mode: SIM
Solvent delay: 1.4 min
EMV mode: Gain factor
Gain factor: 1
Resulting EMV: 1412
MS Source: 230 °C
MS quad: 150 °C

Pentane GC/MS

Auto sampler (Combi Pal CTC analysis)

Injection volume: 1 or 0.5 µl
Equilibrium time: 0.5 min
Injection speed: 50 µl/s

GC (Agilent 7890A)

Column: ZB-624. 30 m x 250 µm x 1.4 µm
Front inlet temperature: 250 °C
Injection: split 13.932 psi, total flow 9.6859 ml/min,
Split: ratio 5:1, flow 5.5715 ml/min
Column flow: 1.1143 ml/min helium
Run time: 13.7min

MS (Agilent 5975C, triple axis detector)

Acquisition mode: SIM; EMV mode: Gain factor
Solvent delay: 6.0 min
Gain factor: 1, Resulting EMV: 1718
MS Source: 230 °C
MS quad: 150 °C

Appendix 1 – Phase distribution of chlorinated solvents in subsurface

The phase distribution is given as:

$$c_{tot} = \rho_b \cdot c_s + \varepsilon_w \cdot c_w + \varepsilon_a \cdot c_a[+\varepsilon_{DNAPL} \cdot c_{DNAPL}]$$

C_{tot} as total concentration of chlorinated solvent is given as the product of bulk density ρ_b and c_s the concentration of sorbed DNAPL and the product of water filled porosity fraction ε_w and c_w the concentration of chlorinated solvent in water and the product of air filled porosity ε_a and concentration in the pore air c_a PLUS in case of residual or pooled DNAPL the fraction filled ε_{DNAPL} by a pool multiplied by the concentration of DNAPL in the pool c_{DNAPL} (=1 kg/L, dependent on the density of the DNAPL phase)

According to Henrys law some of the DNAPL volatilizes into the gas phase, where the concentration in the air phase (c_a) is the product of Henry constant (K_H) and the concentration in water (c_w): $\mathrm{c_a} = \mathrm{K_H} \cdot \mathrm{c_w}$ [Cont.Sites]

Furthermore some of the DNAPL dissolves and diffuses from the residual form (from pores and pools, fig. 52) into the water phase reaching an equilibrium concentration or solubility c_w^* With determination of the chlorinated solvent concentration in air c_a or in the groundwater/ porewater c_w, it can be checked if solubility is reached, since at c_a*or c_w* c_t is c_t*:

$$\mathrm{c_t^*} = \frac{R_a \cdot p^* \cdot MW}{R \cdot T} \text{ or } = R_a \cdot K_H \cdot c_w^* = R_a \cdot c_a^* \quad \text{[Cont.Sites]}$$

In case of a mix of 2 or 3 different compounds the solubility depends on the molar fraction X_i of each compound (fig. 53): $c_a = X_i \cdot c_a^*$. The dissolved chlorinated solvent generates a contamination plume the aquifer spreading with the ground water flow. [Cont.Sites]

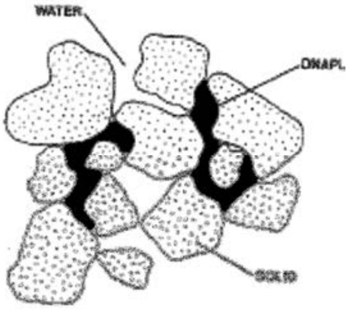

Figure 52: DNAPL residuals in pores of aquifer material [Bedient et al.2004]

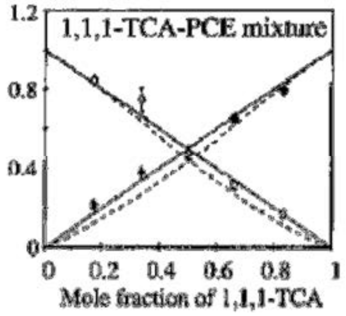

Figure 53: solubility concentration according to mole fraction of given TCA-PCE mixture [Broholm & Feenstra 1995]

Partly chlorinated solvents sorb into pores of the soil particles according to an isotherm. For simplification sorption is assumed to be linear, reversible, with rapid equilibrium in a homogeneous soil [Cont.Sites] giving the retardation of the contaminant when moving with the ground water:

$$\mathrm{c_s} = \mathrm{K_d} \cdot \mathrm{c_w}$$

With K_d the distribution coefficient given as product of organic content f_{oc} and K_{oc} the sorption coefficient to organic carbon in soil. However a recent study including lab experiments by Lu et al. 2011 shows sorption of chlorinated solvents in clayey till is higher than expected from empirical relationships. Moreover they found a good correlation between $\log K_d$ with $\log K_{ow}$ rather than to $\log K_{oc}$, indicating the distribution coefficient K_d might be independent of the organic content f_{oc} of the soil, due to the studied clay till had very low f_{OC} values. [Lu et al. 2011]

Appendix 2 – Estimation of carbon felt sample size for laboratory testing

For estimation of an appropriate size of the carbon felt for adsorption and desorption experiments was done based on the organic carbon distribution coefficient $K_{OC.}$ Specific properties for PCE are given in table 23. Lawrence 1996 and Jørgensen et al. 2010 give an overview of selected physico-chemical properties of PCE, TCE and TCA.

Table 23: selected physico-chemical properties of PCE, TCE and TCA [Lawrence 1996; Jørgensen et al. 2010]

Compound	Solubility [g/L]	K_{oc} [L/kg]
PCE	0.15 (0.2-0.24)	364

To roughly estimate the sorption capacity of the carbon, the distribution coefficient K_d was determined as product of organic carbon distribution coefficient of PCE and organic carbon content of the activated carbon felt ($K_d = K_{oc} * f_{oc}$). Furthermore the relation: K_d = c(sorbed)/c(solved) is valid. In assumption of 90% carbon content of the carbon felt (f_{oc}=0.90) according to literature values [Beyer, 2011] and the specification of PCE from table 24, the capacity of the carbon to sorb PCE is 0.311 mg/g. Furthermore the K_d for PCE for given properties of PCE and activated carbon is estimated to be 311 L/kg (table 24).

Table 24: TCE and PCE sorption capacity estimation on carbon felt

Compound	Solubility [g/L]	K_{oc} [L/kg]	K_d (at f_{oc}=0.9) [L/kg]	Sorption capacity of carbon mg/g
PCE	0.15 (0.2-0.24)	364	311.4	0.311

During adsorption the carbon felt is soaked with PCE solution, thus when transferring the felt into pentane some solution will be carried with it smearing the results. Thus the soaking behavior of the carbon felt has been tested aiming to find the best way to transfer the carbon felt after adsorption experiments or similar to the way as in the field.

Furthermore it has been found to cut the carbon felt always in the same way is impossible, thus weighing out of the carbon felt before or after the experiments is necessary. In addition during the field experiments only the part of carbon felt from the FLUTe liner inside the sewing will was for analysis, thus the weight of used strips cut out of the FLUTe liner needed to be determined as well. This can principally be done either before addition of pentane or after the extraction analysis and subsequent drying of the carbon felt.

Before starting the experiments the concentrations or concentration range of the experiments needed to be thought trough and the ratio of water and carbon felt (checked with sorption calculation). In addition also the size of carbon felt for analysis needs to be discussed, since during the fieldwork the felt was originally planned to be cut into 20cm pieces (according to Gry), which is too big for analysis.

To get an idea about the distribution of chlorinated solvents after adding the carbon felt into the solution is given by the following approach has been used, where in our case the initial concentration is the total concentration of chlorinated solvent added to the system before adding the carbon felt:

$$\mathrm{m_{tot}} = \mathrm{m_{init}} = \mathrm{m_{sorbed}} \cdot \mathrm{m_{solved}} \quad \rightarrow \quad c_{init} \cdot V_{tot} = m_{carbon} \cdot c_s + V_w \cdot c_w$$

However is it known sorption to activated carbon is far more complex as e.g. Shih and Gschwend 2009 describes with linear solvation energy relationships (LSERs), thus this method is used for only a rough estimation.

It has been discussed to determine the amount of carbon felt necessary to reach a concentration change of 30 to 70%, so the error of the analysis does not contribute too much and the concentration change is measurable. Since these calculations are just theoretical, a concentration change of 70% is chosen; due to in reality the concentration change is supposed to be smaller. Furthermore previous calculation showed the amount of carbon felt used will be in g or mg area using a concentration in solution after reaching equilibrium of 30% of the initial concentration (70% change). Furthermore a volume of 20ml will be used, whereas the amount of carbon does not contribute decisively to the total volume, hence the total volume of the solution is set equal to the volume of the solution before adding the carbon felt. The f_{oc} is chosen to be around 90% according to literature values. $\mathrm{c_s = K_d \cdot c_w}$ $\mathrm{K_d = f_{oc} \cdot K_{oc}}$ $V_{tot} \approx V_w \approx 20ml$ *and* $c_w = 0.3\, c_{init}$

Now the mass of needed carbon can be determined just dependent on the concentration difference:

$$\mathrm{m_{carbon}} = \frac{\mathrm{20ml \cdot (1-0.3)\, c_{init}}}{\mathrm{K_d \cdot 0.3}\, c_{init}} = \frac{\mathrm{20ml \cdot (1-0.3)}}{\mathrm{K_d \cdot 0.3}}$$

Results in table 25 show a carbon felt of a minimum size of 0.75cm² is needed, when the carbon felt bulk density is assumed to be 1 g/cm³ and a thickness of 2 mm. These amounts seemed to be practically possible. More precise calculations can be done as soon as real properties and adsorption behavior of the used carbon felt are available.

Table 25: results of amount of carbon felt for TCE and PCE

	K_{oc}	K_d	m_{carbon}	V_{carbon} (ρ=0.1 to 1g/cm³)	A_{carbon} with 2mm of thickness
PCE	346 L/kg	311.4 L/kg	0.1499 g	1.5 to 0.15 m³	7.5 to 0.75cm²
TCE	120 L/kg	108 L/kg	0.4321 g	4.3 to 0.43 m³	21.6 to 2.16 cm²

The distribution of chlorinated solvent follows the subsequent relations, according to assumed linear adsorption (as literature shows in reality rather Freundlich or Langmuir, as more complex adsorption is probable): $c_w = \frac{\mathrm{c_{init}} \cdot V_w}{\mathrm{K_d} \cdot m_s + V_w}$ *and* $\mathrm{c_s} = \frac{\mathrm{c_{init}} \cdot V_w}{\mathrm{m_s} + V_w / K_d}$

To estimate the distribution of PCE in solved in water and sorbed on the carbon felt (figure 54), the highest mass for the carbon felt (0.1499 g), and thereby highest difference between initial and end concentration (c_w=0.3% c_{init}) were chosen.

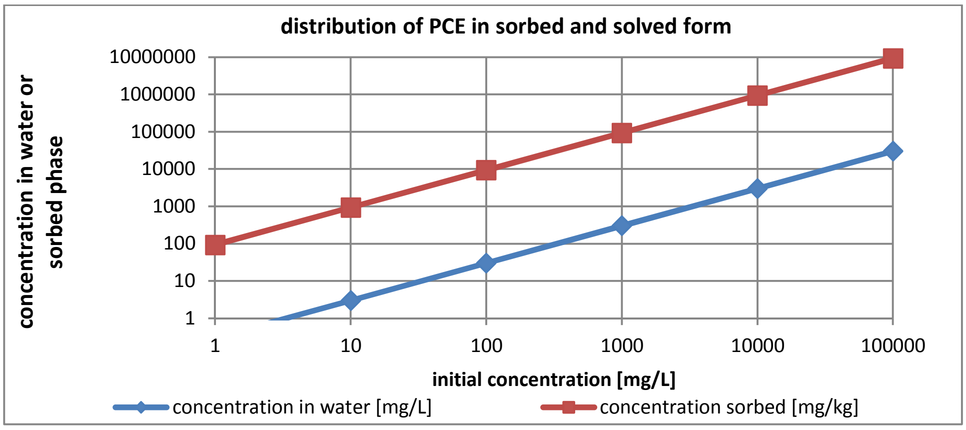

Figure 54: initial concentration and followed distribution of PCE in solved and sorbed phase

Appendix 3 – Field work preparation (max. number of samples & material needed)

During the extraction experiment the highest concentration obtained in pentane was 450 mg/L with use of around 4 cm x 2 cm carbon strips and previous adsorption in saturation (PCE). In the field the stained parts indicating DNAPL presence were planned to be cut into 1 times 2 cm pieces, thus dilution of pentane turned up to be unnecessary. However the concentration ranges of the planned 10 cm or longer strips for unstained parts is unknown, thus just in case a second pentane sample (for potential dilution) was taken. Thus 10 ml of water (which seem to be an appropriate volume to cover the strips) and 3 ml of pentane (2 ml for samples, 1 ml backup) were added to the carbon felt.

The estimation of the maximum durable number of samples to handle per flute was done taking into account financial limitations and the limiting (most time consuming) factor of handling the samples in the lab after the fieldwork. Duplicates of pentane need to be taken out (each 1 ml) and put into small vials plus blanks/controls need to be prepared for analysis. With a length of maximum 7.5 to 8 m in the clay part the maximum number of samples was set to be 450 in total (150 for each flute liner).

Since it was unpredictable how much DNAPL/staining to expect in the borehole, the suggestion was to decide on site how discredited samples were taken. The idea was to take in 1 cm subdivision where the liner is stained (DNAPL indication) and 5 to 10 cm in other cases. E.g. in assumption 1/3 of the whole length will be stained means 125 samples for DNAPL and 50 samples for not stained places, gives in total of 175 samples. In general the carbon will be cut into half. One side is used for further discretization and analysis, the other side is cut into 30 cm pieces to keep as backup (see fig. 32, middle in chapter 4.1).

Clay till: Around 400 vials with 10ml tap water each were prepared, labeled and pre-weight to be ready for the fieldwork. Later 3ml pentane was added, when the samples arrived back at DTU. However since desorption into water is not an issue (shown by pre-experiments); the addition of pentane to the samples does not need to be instantaneously. Afterwards the samples were extracted at least over 2 nights in the rotating box at 10°C. The material needed in the field is summarized in table 26.

Table 26: material needed in the field

for cutting subsamples	table, ruler, scissors, cutter knife, tweezers, gloves
to prepare samples for analysis	20ml vials already prepared and pre-weight with 10ml tap water, racks, cooling bags; labels and data sheets
to prepare flute parts to keep	aluminum foil, diffusion tight bags (75 with 30cm long pieces – take 100)

Chalk: Again over 300 vials were prepared for sampling (labeled, filled with 10ml of water, pre-weight). Since the FACT liners in chalk were up to 13m long, fewer samples were taken per Flute liner to keep the sample number at a practical number. Therefore a priority to interesting sampling locations needed to be set.

Appendix A – Calibration curve headspace analysis

The calibration curve for headspace GC/MS is given below in figure 55 and table 27 gives a summary of the calibration curve data and R^2.

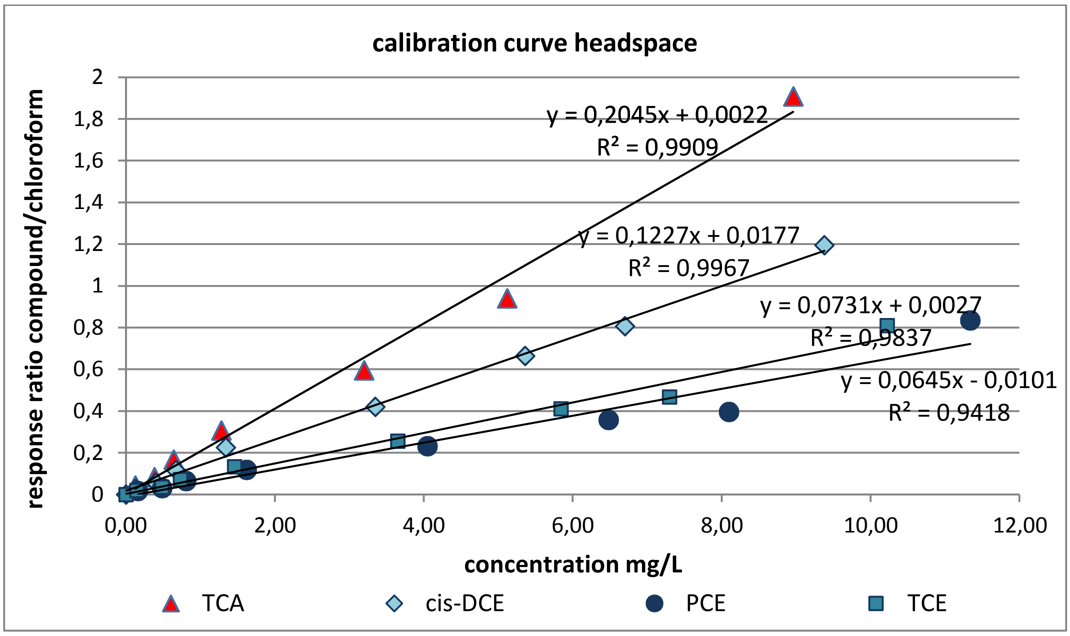

Figure 55: calibration curves of headspace GC/MS

Table 27: summary of calibration data for headspace GC/MS

compound	Linear regression	R^2 [%]
PCE	Ratio=0.0645c-0.0101	94.18
TCE	Ratio=0.0,0731c+0.0027	98.37
Cis DCE	Ratio=0.1227c+0.0177	99.67
TCA	Ratio=0.2045c+0.0022	99.09

Appendix B – Calibration curve pentane analysis - clay till

The calibration curve was prepared in Excel to determine the concentration corresponding to a target response ratio. Standards prepared as in appendix 0 were used and the program Excel to fit a linear regression line. The regression included point (0/0), but was not forced through 0/0, since it had the best R² with the upper calibration points, in which most of the concentration data obtained for PCE and TCE lied. In case smaller concentrations needed to be determined more precisely, just the lower points of the calibration curve with a better fit were used.

The following calibration curve was made for clay data illustrated in figure 56 (table 28 summarizes the found linear regression curves plus R²).

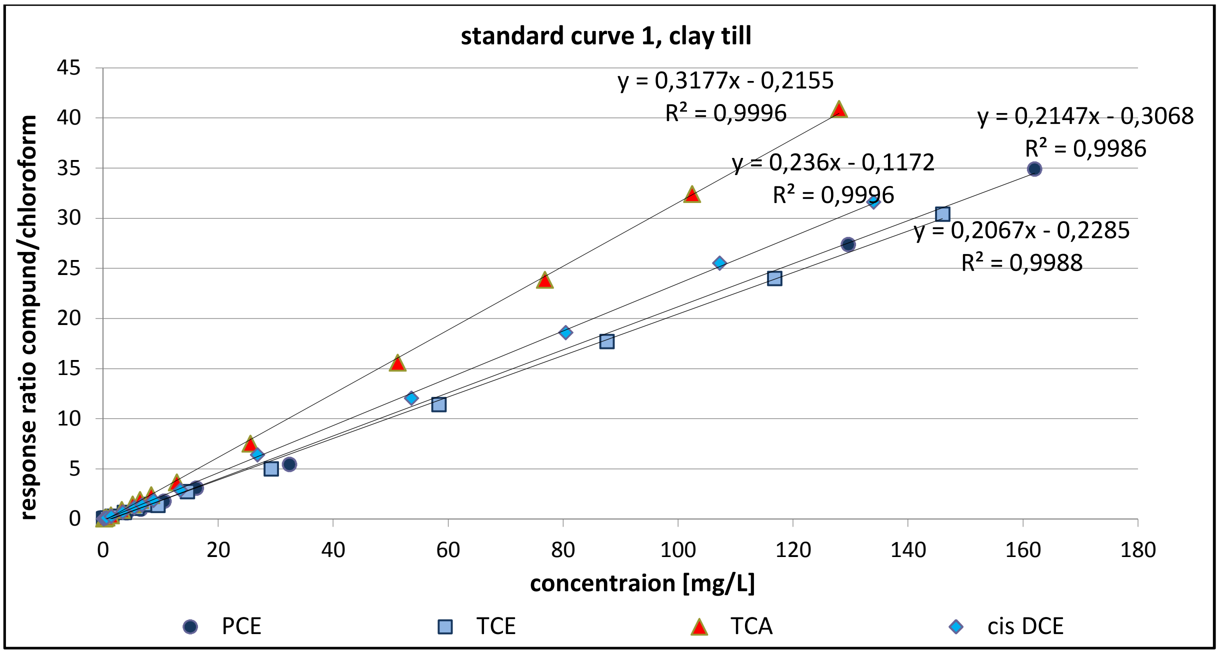

Figure 56: first set of calibration curves (ratio of target response of compound/chloroform over concentration in mg/L

Table 28: linear regression data of calibration curves and R²

compound	Linear regression	R² [%]
PCE	Ratio=0.2147c-0.3068	99.86
TCE	Ratio=0.2067c-0.2285	99.88
Cis-DCE	Ratio=0.236c-0.1172	99.96
TCA	Ratio=0.3177c-0.2155	99.96

Mikael Emil Olsson analyzed the standard error of the calibration curves and found a linear range from about 150 to 18000 µg/l with standard errors for PCE of 0.0966, TCE of 0.0753, cis-DCE 0.0817 and TCA of 0.0976. However since not exact concentration values are used in this study, but trends are determined, the standard error is not further evaluated for higher standards.

However since the GC/MS lost in sensitivity over time, for the last samples in the clay till a new standard curve was determined given below in figure 57 and table 29 gives a summary of the calibration curve data and R².

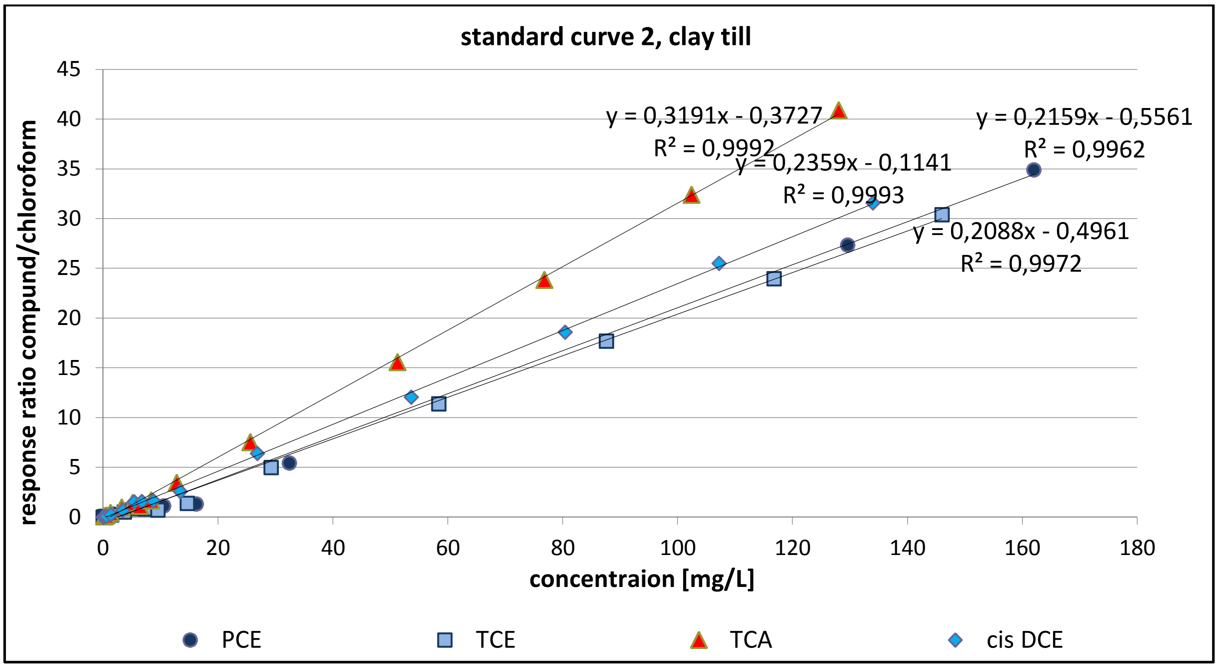

Figure 57: calibration curve 2.nd run of clay till samples

Table 29: linear regression data of calibration curves and R^2

compound	Linear regression	R^2 [%]
PCE	Ratio=0.2159c-0.5561	98.62
TCE	Ratio=0.2088c-0.4961	99.72
Cis DCE	Ratio=0.2359c-0.1141	99.93
TCA	Ratio=0.3191c-0.3727	99.92

Appendix C – Calibration curve pentane analysis - chalk

The calibration curves for chalk aquifer FACT samples with pentane GC/MS is given below in figure 58 and 59. Table 30 and 31 give the summary of the calibration curve data and R².

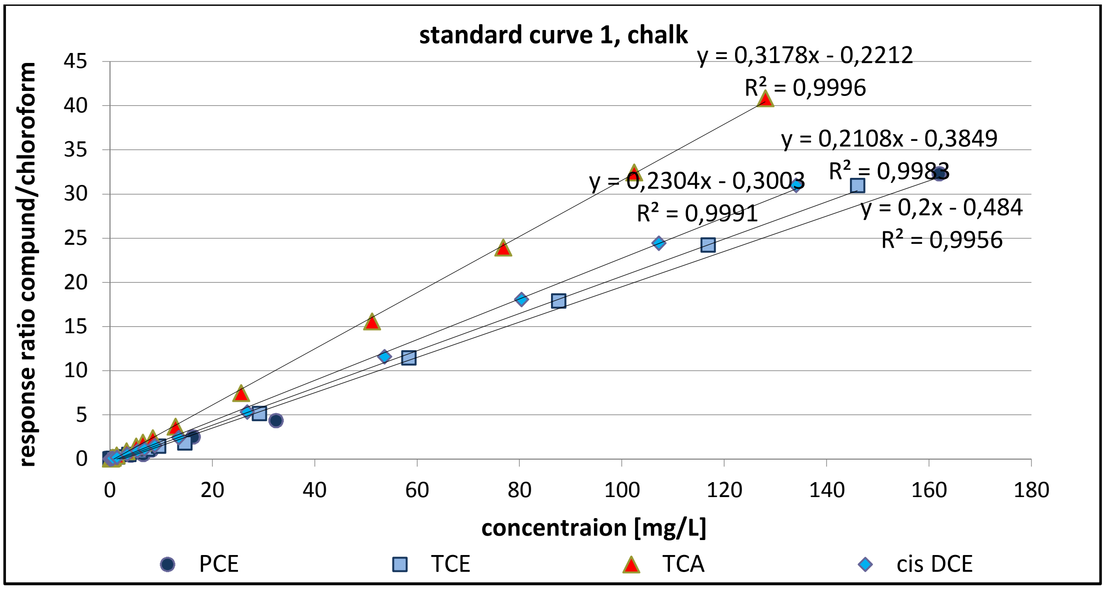

Figure 58: standard curve 1 for chalk samples 1 till 162

Table 30: linear regression data of standard curve 1 for chalk samples 1 till 162, and R²

compound	Linear regression	R² [%]
PCE	Ratio=0.20c-0.484	99.56
TCE	Ratio=0.2108c-0.349	99.83
Cis DCE	Ratio=0.2304c-0.3003	99.91
TCA	Ratio=0.3178c-0.2212	99.96

Table 31: linear regression data of standard curve 2 for chalk samples 162 till 320, and R²

compound	Linear regression	R² [%]
PCE	Ratio=0.2385c-0.4641	99.75
TCE	Ratio=0.2252c-0.5554	99.65
Cis DCE	Ratio=0.2302c-0.3471	99.77
TCA	Ratio=0.3341c-0.2618	99.96

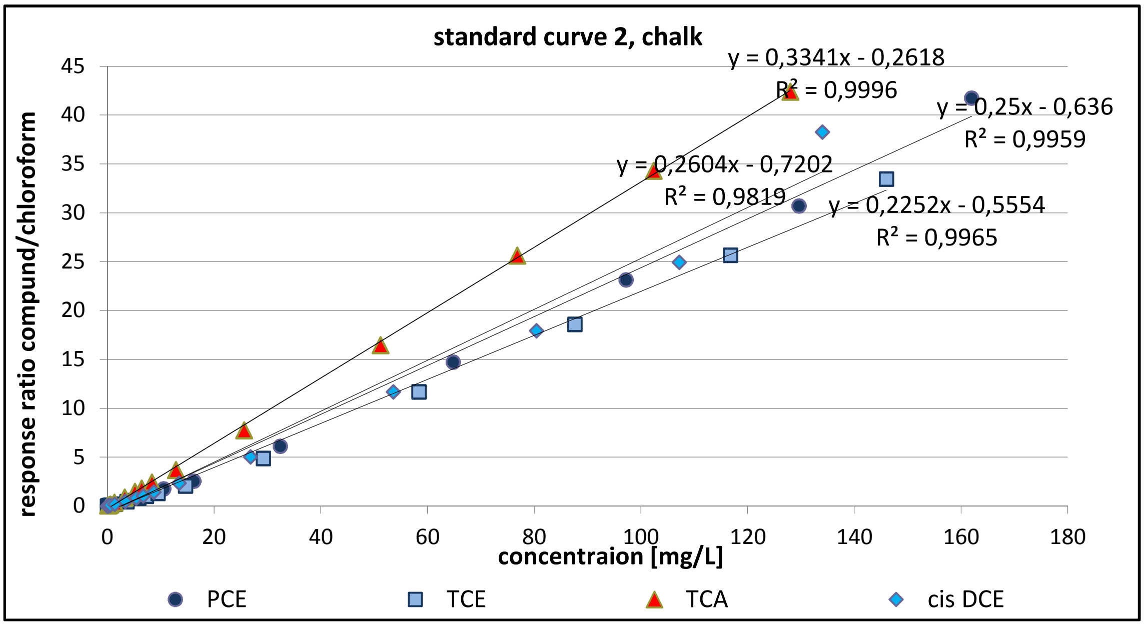

Figure 59: standard curve 2 for chalk samples 163 till 320

Appendix D - Calibration curve pentane analysis - rerun

The calibration curves for the rerun samples, adsorption from different phases and 30 cm samples done with pentane GC/MS is given below in figure 60 and table 32 give the summary of the calibration curve data and R².

Table 32: linear regression data of standard curve rerun/lab experiments for chalk samples 1 till 162, and R²

compound	Linear regression	R^2 [%]
PCE	Ratio=0.282c-0.3225	99.87
TCE	Ratio=0.2387c-0.2448	99.99
Cis DCE	Ratio=0.2204c-0.176	99.92
TCA	Ratio=0.3516c-0.327	99.91

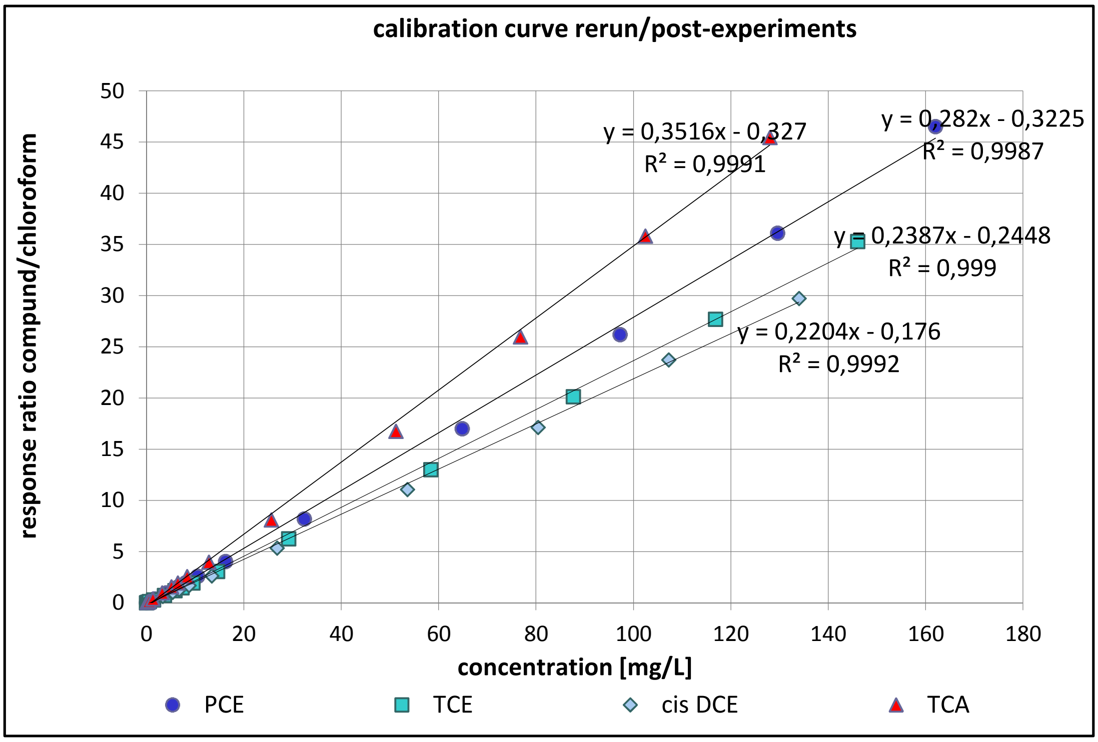

Figure 60: calibration curve for re-reun/post-experiments