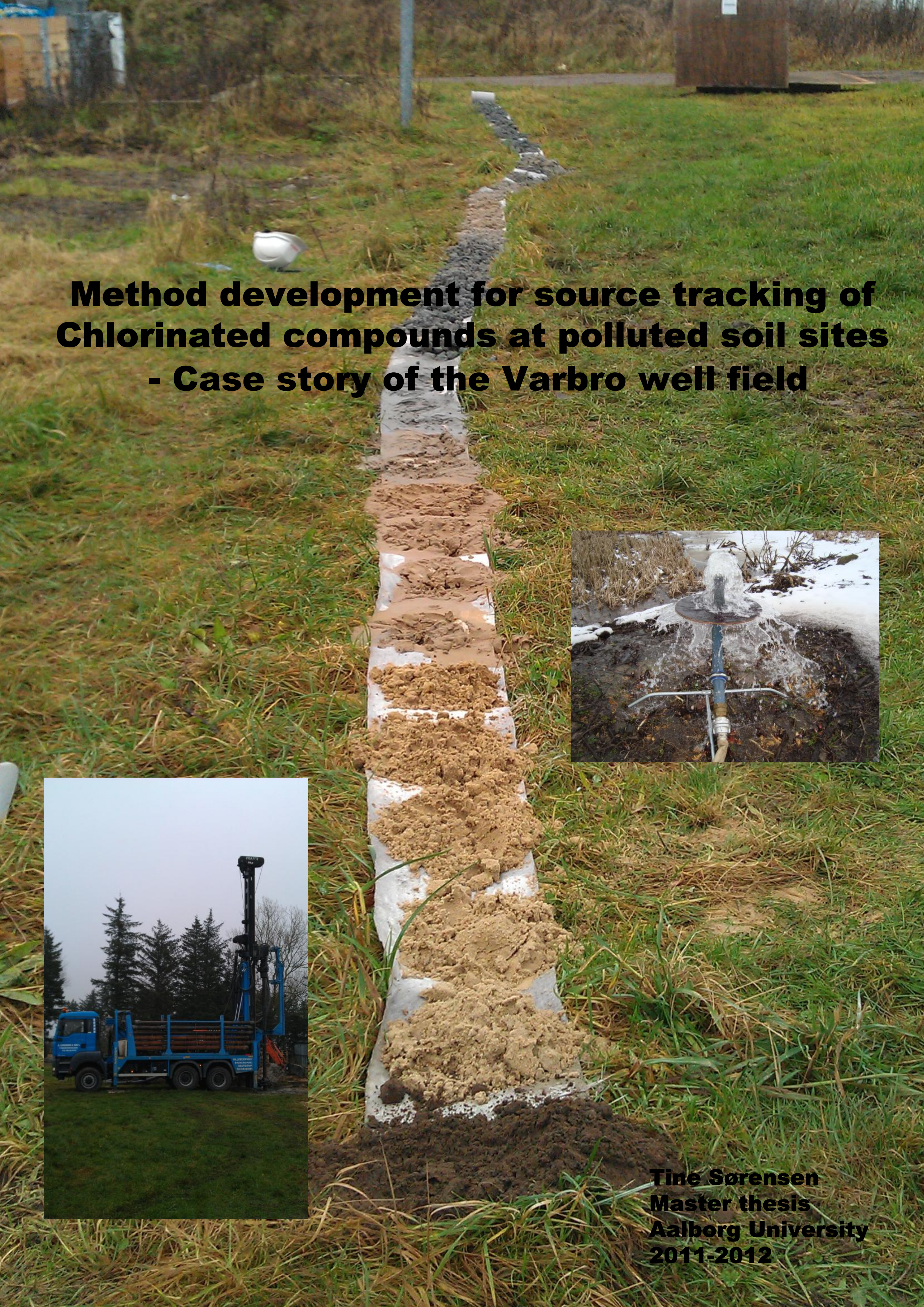


Method development for source tracking of Chlorinated compounds at polluted soil sites
- Case story of the Varbro well field

Tine Sørensen
Master thesis
Aalborg University
2011-2012

overskrift

KANDIDATSPECIALE 2012
TINE SØRENSEN
INSTITUT FOR KEMI,
MILJØ OG BIOTEKNOLOGI
AALBORG UNIVERSITET
DEN 4. JUNI 2012

The Faculties of Engineering,
Science and Medicine
Sohngaardsholmsvej 49 and 57
Telephone number 99 40 84 91
http://www.bio.aau.dk

Title: Method development for source tracking of chlorinated compounds at polluted soil sites: Case story of the Varbro well field.
Theme: Soil and groundwater pollution
Project period: September 1st 2011 - June 8th 2012
Written by:

Tine Sørensen

Supervisor: Jacob Birk Jensen
Supervisor: Per Møldrup

Number of pages: 108
Completion date: 08.06.2012

Synopsis:

In this project is focused on source tracking of chlorinated compounds. For this purpose has a polluted soil site (Varbro well field, Hjørring) been used as case story. At Varbro well field have one well been polluted with TCE since 2003.
A new investigation strategy is set up for Varbro well field. This strategy is based on a solid basic knowledge about pollution history, geology and hydrology of the area. Investigations showed that the geology in the area is complex and that the polluted well not is in hydraulic contact with the other wells at the well field.
Time series is used to estimate the correlation between the concentration and the pumping rates of the polluted well. A delay on 25-90 days between the two time series is observed and tried proved by a simple field experiment. The delay was however not confirmed.
Two other field experiment were conducted at the polluted well. These gave specific informations about the depth of the pollution as well as the hydrogeological properties in the area. From these informations were an area of influence sketched. The pollution should be located within this area. The influence area has been narrowed down by particle tracking in the GMS, Groundwater Modeling System, software package. Two possible sources has been pointed out on the basis of these experiments.
In order to perform a better and more efficient source tracking is a decision tool produces as a flow chart consisting of several steps where the extent of the suggested investigations reflects the complexity of the case. The purpose of the flow chart is to obtain a faster and more efficient source tracking.

Preface

This thesis is a long master thesis in environmental engineering at Aalborg University in the period from September 1st 2011 to June 8th 2012.

The theme of the project is method suggestions for source tracking of chlorinated compounds where Varbro well field, north of Hjørring is used as a case study.

The report consists of a main report, appendices at the end of the report and an enclosure CD, which contains electronic enclosures. The report will also be attached digitally on the enclosure CD together with the model.

The report is produced with the purpose to give the reader an overview of the subject, its problems and solutions. The appendices and electronic enclosures are supplements to the report containing calculations and method descriptions.

The references in the report are given by surname of the author and the year of the publication in square brackets, [surname, year]. All references are clarified in the bibliography, which can be found in the end of the report.

I wish to thank my supervisors Jacob Birk Jensen and Per Møldrup for their supervision during the time of this thesis and Kaj Henriksen for his advices regarding sampling procedures and analysis. I also would like to thank Helle Blendstrup and Kim Mørkholt for their technical assistance with my experimental work in field and laboratory.

Also a special thanks to NIRAS for supervision and lending of equipment, to the Danish Defense Estates & Infrastructure Organisation and not least Hjørring Water Supply for making this project possible and assisting with field work.

Danish summary

Dette projekt omhandler metodeudvikling af et redskab til kildesporing af chlorerede opløsningsmidler. Til dette formål anvendes en forureningssituation på Varbro kildeplads, nord for Hjørring. Fra den forurenede boring på kildepladsen er der i gennemsnit de sidste 8 år oppumpet 1.2 kg TCE (Trichloroethylene) årligt. Ingen andre boringer på kildepladsen er forurenede. Utallige forureningsundersøgelser har været udført ved mulige kilder til forureningen samt ved selve boringen. Forureningen er dog endnu ikke identificeret.

I et sidste forsøg på at spore kilden til forureningen sættes en ny undersøgelses strategi op. Denne er hovedsageligt fokuseret på simple felt- og laboratorieforsøg samt modelberegninger ved brug af GMS.

Gennem projektet er forureningshistorikken for Varbro kildeplads gennemgået, en geologisk konceptuel model er sat op grundvandsstrømningen er kortlagt. Geologien viste sig at være forholdsvis kompleks i området, da den er præget af en delvist begravet dal i den nordlige del af kildepladsen. Dette formodes at være årsagen til at kun en boring er forurenet. Synkronpejlerunder viste at de tre boringer ikke er i hydraulisk kontakt, hvilket understøtter formodningen om en begravet dal.

Tidserier for pumpeydelser of målte koncentrationer i den forurenede boring sammenlignes ved en simpel analyse, og der observeres en usædvanlig god sammenhæng mellem de to datasæt. Stiger ydelsen, stiger koncentrationen. Mellem de to datasæt ses en forskydning, som er estimeret til 25-90 dage, hvilket er en meget kort responstid. Forureningskilden ligger altså tæt på boringen.

Tre feltforsøg er udført med det formål at udarbejde et influensområde hvor kilden til forureningen er lokaliseret. Dette område bestemmes primært ud fra specifikke parametre fundet ved et "Push, drift and pump back" forsøg. Derudover er den dybdemæssige placering af forureningen kortlagt til 58 m u.t. ved niveauspecifikke vandprøver. Dette opnåede influenområde var stort og dækkede flere mulige kilder. Området blev derfor indskrænket ved at anvende en numerisk model i GMS til partiken sporing. Influensområdet blev gjort markant mindre, men det dækker stadig over to mulige kilder. Det anbefales at der udabejdes en specifik stoftransportmodel til nærmere undersøgelse af to mulige kilder efterfulgt af specifikke forureningsundersøgelser.

Som et værktøj til kildesporing er udarbejdet et beslutningsværktøj i form a et flowdiagram. Dette diagram er baseret på de trin som er gennemgået i forbindelse med kildesporingsprocessen på Varbro kildeplads.

Contents

Introduction

1

"Out of sight, out of mind". This sentence seems to describe the waste policy of the early and mid 20^{th} century. At that time the disposal of chemicals to the environment was not of much consideration. This has caused massive soil pollution problems which escalated in the 1960s where the advances in research resulted in the development of new chemical compositions with unknown consequences for the environment. These pollutants spread to the groundwater and are now a threat to both the resources of drinking water and to the indoor environment. There has therefore been a massive attention to chemical spills and groundwater pollution the last 30-40 years which has given lots of experience about the behavior of different compounds and about identification of pollutant sources [Loll and Moldrup, 2000].

When detecting a polluted soil site, it is important to identify the source, in order to provide the best possible treatment of the pollution. The identification is also important regarding determination of responsibility. However, the pollutant source is often unknown and in a polluted area there may be more than just one possible source. If the pollutant source is unknown, the environmental investigation can be a long and comprehensive process which might not even lead to the best and most efficient handling of the pollution [Atmadja and Bagtzoglou, 2001].

Chlorinated compounds are one of many pollutants that have been of great interest in the last decades. These compounds have been widely used and have some distinctive chemical and physical properties which make the occurrence of these compounds harder to predict than for instance oil products. Besides that, most chlorinated compounds are carcinogenic or suspected of being it. Pollutions with chlorinated compounds are therefore seen as a great threat to the quality of the drinking water [AVJ, 2001]. The specific properties of selected chlorinated compounds are described in appendix A.

The consumption of chlorinated compounds was increasing until the 1970s. The casual management of these compounds, caused by lack of knowledge about the environmental and health related effects, has lead to the many polluted sites we know of today. We have attained knowledge and experience about chlorinated compounds but a sufficient tool for source tracking does not jet exist.

Earlier studies of methods for source tracking are mostly based on historical records and model calculations. From the historical records, possible sources in the polluted area may be identified and then investigated further by model calculations. It is proven that groundwater modeling in some cases can be a useful tool in source identification [Jensen et al., 2008]. Inverse modeling has also been a subject for many studies and used for source tracking in the last decades. However, all of these specific mathematical methods of backward simulation have limitations like high sensitivity, no advection, or homogeneous parameters [Atmadja and Bagtzoglou, 2001].

Today comprehensive groundwater models may be used to indicate the source of the pollution and extensive environmental investigations are often performed at locations that, based on historical records, might be the pollutant source. The lack of a good tool for source tracking makes the process difficult and often expensive and prolonged as too many factors are unknown. Figure 1.1 illustrates the difficulties of source tracking of DNAPL (Dense Non-Aquarius Phase Liquid) like e.g. chlorinated compounds and lists some of the many unanswered questions that are important in source identification.

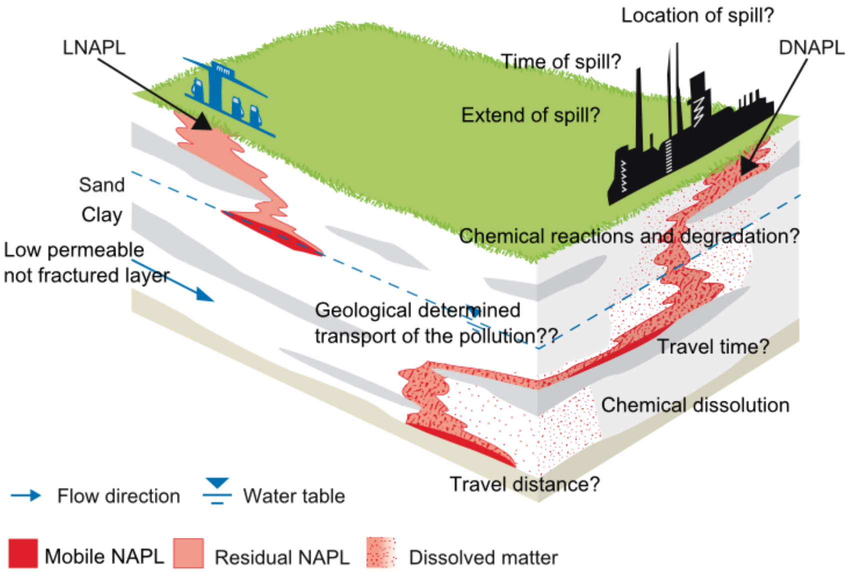


Figure 1.1: *Conceptual model of two polluted soil sites and their different spreading. One with a LNAPL as e.g. an oil product and one with a DNAPL as e.g. chlorinated compounds [Bjerg et al., 2011]. Some of the often unknown questions in source tracking is added to the conceptual model.*

The main objective of this report is to make a suggestion how to improve the existing procedures for source tracking of chlorinated compounds in soil and groundwater systems by using simple tools on the basis of groundwater models. This will differ from earlier studies by combining a sequence of specific field measurement with simple modeling in order to achieve an influence zone for which the pollution in all probability will be located. The purpose is to develop a simple, but still accurate, and faster method for source tracking.

For this purpose, an actual polluted soil site (Varbro well field, north of Hjørring, Denmark) is used as a case story. This will involve an exhaustive description of the geological and hydrological properties of the location as well as several thorough investigations of the location consisting of different specific field measurements followed by sample analysis in the laboratory.

The project will include both field measurement, laboratory measurement, and modeling by own models and the GMS, groundwater model system, software package. The recently acquired results will be compared to the knowledge of the hydrogeological properties of Varbro well field and together form the basis of a comprehensive method for source tracking.

2 Pollution history of Varbro well field

Varbro Well Field is located north of Hjørring in an area with particularly interest of extraction of drinking water. The use of the area is mainly agriculture. Some areas of Varbro well field has furthermore been used for extraction of raw material (e.g. gravel). Varbro well field contains 3 active extraction wells. These will be referred to by the name given by Hjørring Water Supply: B18 (DGU no. 5.631), B19 (DGU no. 5.594), and B20 (DGU no. 5.596). Figure 2.1 shows the location of Varbro well field and the positions of the extraction wells.

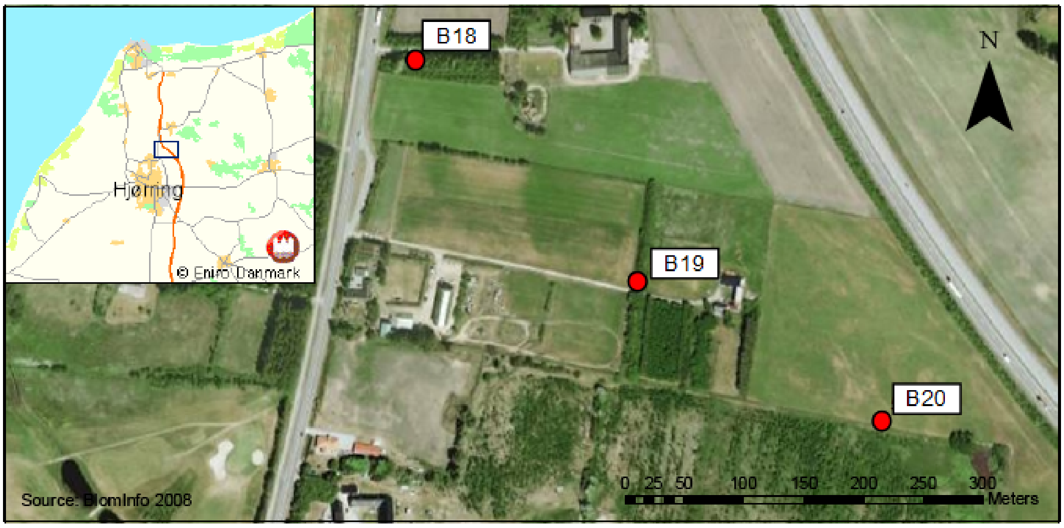


Figure 2.1: *The three extraction wells on Varbro well field where only B19 (DGU no. 5.594) is polluted with chlorinated compounds.*

A pollution with chlorinated compounds was in 2003 detected in one of the boreholes (B19) at Varbro Well Field. Chlorinated compound has mostly been used for textile cleansing and for degreasing of metals which normally makes dry cleaner sites and military areas highly suspects of these pollutions. For more details about chlorinated compounds, their use, and properties refers to appendix A. The pollution consisted mainly of Trichloroethylene (TCE), but contained also minor amounts of Tetrachloroethylene (PCE) and the breakdown product: Vinyle chloride (VC). This lead to several investigations of Varbro well field, but the pollutant source is still today unknown even though the bore hole is continuously affected by a massive pollution of chlorinated compounds clearly above the groundwater limit value. Estimations shows that there in the last 8 years has been an annual pumping of 1.2 kg TCE in B19. The fluctuations of the pollutant concentration measured in B19 over time is presented graphically in chapter 5 [GEUS, 2012].

No other wells in the area of Varbro well field are affected by the TCE concentration, even though, they are placed relatively close. [GEUS, 2012].

After the first measurements of the pollution in 2003 an extensive investigation plan was developed in a cooperation between Hjørring Municipality, Hjørring water supply, and The North Denmark Region. This plan included a general hydrological and geological determination of the area north of

Hjørring as well as screenings of the top soil and exploratory pollution investigations of localities pointed out on the basis of environmental historical reports of Varbro well field [Region Nordjylland, 2010].

Figure 2.2 presents a time line of events that might have caused the pollution. The time line is developed on the basis of environmental historical reports.

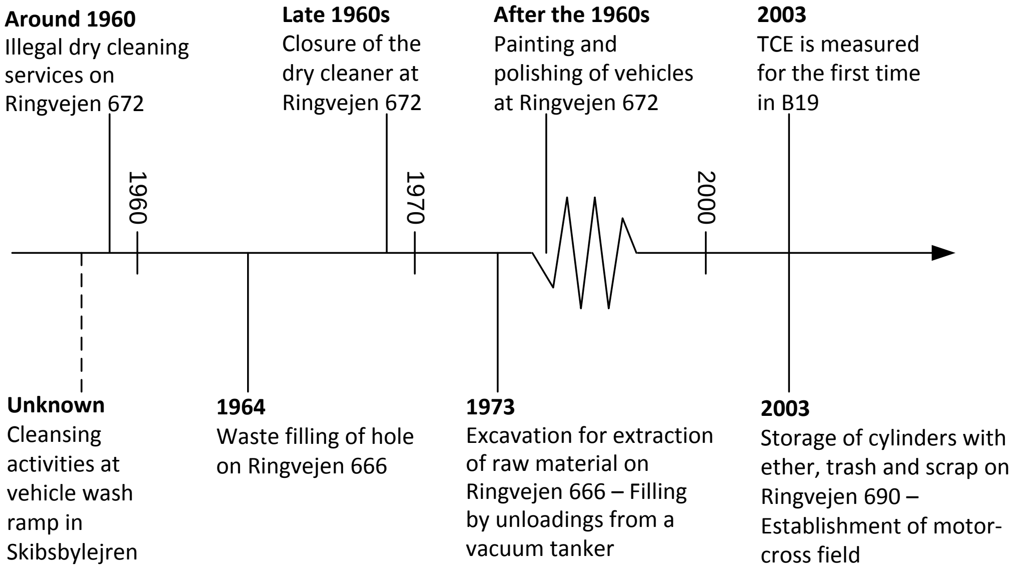


Figure 2.2: *Historical environmental events in the catchment area of Varbro well field that might have caused the pollution of B19. Appendix B shows the position of the referred locations in the figure.*

The locations, which are referred to in the timeline, are showed in appendix B. In the catchment area of Varbro well field there has, since the 1960s, been several activities that could have caused the pollution with chlorinated compounds. The first investigations were for this reason conducted in the immediate area of the polluted well with the purpose of source tracking and using the results for a selection of possible sources for further thorough investigations. The results of the different pollution investigations will be summarized within the next sections.

2.1 Investigations of the polluted area of Varbro well field

The top soil within the catchment area of Varbro well field has been screened for traces of chlorinated compounds, but no notable concentrations were detected and the screening alone does not give rise to further investigations.

Borehole B19 is the only borehole within the Varbro well field which is polluted with chlorinated compounds. Several investigations have therefore been performed on B19 and in the immediate area of B19 to clarify the condition of the extraction wells on Varbro well field and the inflow trails to the polluted well. These investigations comprise:

- Borehole logging (2005)
- Video inspection (2005)
- Level specific water samples (2005)
- MIP-explorations around B19 (August, 2009)
- Level specific water samples from MIP (November, 2009)

2.1.1 Condition assessment of the boreholes on Varbro well field

The boreholes on Varbro well field were all established in 1968, and time has left its mark on the well liner and the screen section. In 2005 investigations were performed on the three boreholes on Varbro well field by Hedeselskabet Environment and Energy A/S (now Orbicon). These investigations should clarify the physical condition of the wells and point out problematic elements, which could influence on the state of pollution, measured in Well B19. The purpose was furthermore to point out the levels of influx through the screen section of the polluted well [Andersen et al., Januar 2006].

A Video inspection was conducted to give a visual impression of the condition of the three boreholes on Varbro well field. The inspection showed that the well liner in every well was sligtly corroded and that the screen sections were heavily coated. Well B18 had several cracks in the well liner whereas the state of the polluted well B19 was less critical. One possible crack with traces of leakage was discovered in the well liner of B19 in the depth approximately 18 m b.s. The crack does, however, not seem to be connected to the pollution as level specific water samples from the well showed that the concentration of TCE and PCE in the top of the screen section (about 53.5 m b.s.) was equally to the regular water samples extracted from the well a few month earlier. The condition of the three boreholes was from the video inspection in general considered being poor [Andersen et al., Januar 2006].

The condition of the screen sections was further investigated using a flow log to clarify the water influx. Because of the conditions of the wells the propeller easily got blocked which made the flow log of well B20 impossible to interpret. The influx to the polluted well B19 seemed to be approximately equally distributed over the 20 meter long screen section. The flow log indicated, however, that the largest influx occurred in the top meters of the screen section and that the lowest influx was in the interval from 59 to 66 m b.s. The logs from the investigations are attached on the enclosure CD [Andersen et al., Januar 2006]. This distribution might have an influence on the level of pollutant influx to the well.

2.1.2 Possible inflow trails to the polluted area of Varbro well field

To clarify the directional trail of the pollution into the polluted well and possible define the source of the pollution, 7 MIP (Membrane Interface Probe) explorations were performed in august 2009 by Ejlskov A/S. By MIP measurements a heated probe with a membrane is pushed down through the soil, where it will bring possible halogenated hydrocarbons at a gaseous phase. The gas is then analysed on a field gas chromatograph using different specific detectors, depending on the solvents of interest. For further informations about MIP explorations is referred to [NIRAS, December 2010].

The placement of the explorations (MIP 1 to MIP 7) around B19 appear from figure 2.3 [NIRAS, December 2010].

Figure 2.3: Placement of the 7 MIP explorations in the area around the polluted well B19 with the purpose of clarifying the directional inflow trail of pollution to the well [NIRAS, December 2010].

For all explorations, effects were observed by analysis on a field gas chromatograph. The most significant effects were observed for MIP 6 in 18-25.5 m b.s. The observed results were in a magnitude which gave an evident indication of the existence of a massive pollution. Ejlskov A/S estimated that the observed effect from MIP 6 corresponded to at least 2 mg/l which was not quite as much as expected considering the magnitude of the concentrations measured in B19 and a given factor of dilution [NIRAS, December 2010].

To confirm the results from the MIP explorations, level specific water samples were extracted from MIP 6 and MIP 2 which had given the most significant effects. The water samples did, however, not show any concentrations of chlorinated compounds. The water samples were extracted 2.5 month after the MIP exploration because a part of the drill stem got stuck in MIP 7. The pumping rate at the closest extraction wells had in that period not been stationary and this might be one reason why the observed effects were not confirmed in the water samples. MIP 6 was therefore repeated April 2010 where an effect again was observed but not in the same depth and not of the same magnitude as earlier. The result was, however, still an evident indication of the existence of a pollution. At the reputation of MIP 6 did the water sample not show any chlorinated compounds either. The reason was now believed to be a result of a geological deviation which indicated that the water sample did not represent the expected level, but rather consisted of water from upper and lower coarse-grained layers where no effects were observed [NIRAS, December 2010].

The results were valued and a guess of the most likely trails to the well was produced. Figure 2.4 gives the result where several areas could be the source of the pollution.

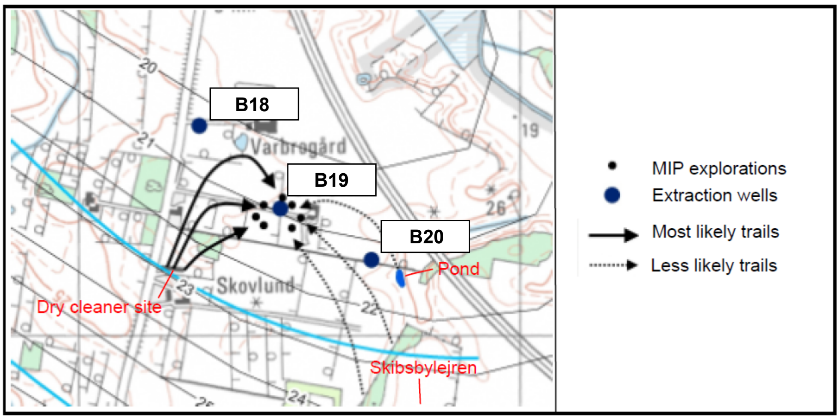
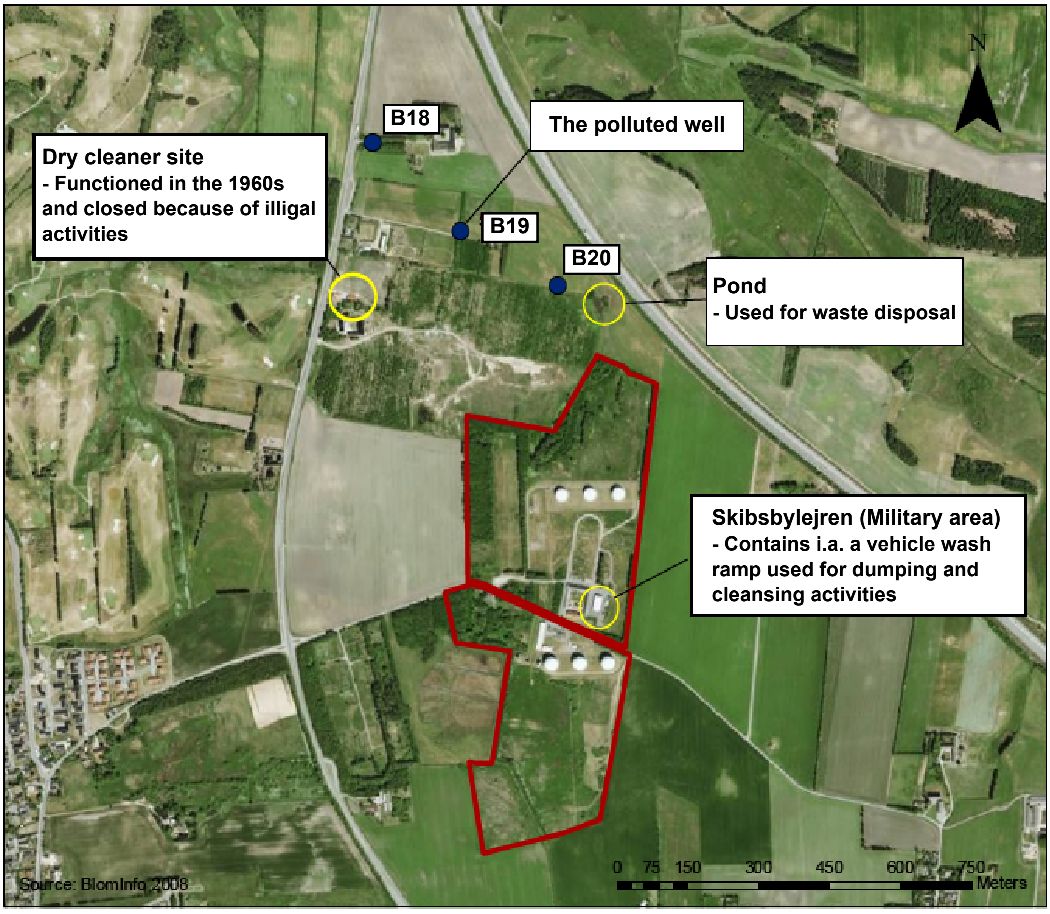


Figure 2.4: Result of the valuations of the most possible inflow trails to match the observation data from the polluted well B19 and the MIP explorations around the well.

From the results of the investigations presented in this section the most possible sources were pointed out and investigated further.

2.2 Investigations of possible sources of the pollution

There are several possible sources of the pollution in the area of Varbro Well Field. The most likely sources has been pointed out for further thorough investigations on the basis of environmental historical reports, screening of the top soil layer, and investigations of the specific area of the polluted well. The most likely sources are a dry cleaner site located roughly 250 m upstream from B19, a pond roughly 350 m east of B19 used for waste disposal, and a military area about 800 m from B19 where there may have been some cleansing activities involving chlorinated compounds. The location of the possible sources are shown in figure 2.5.



Source: BlomInfo 2008

Figure 2.5: *Three possible sources of the pollution with chlorinated compounds were pointed out for further investigations. These are all marked on the map by a yellow circle. The red lines define the area of the military area: Skibsbylejren.*

The possible pollutant sources are in figure 2.5 marked with a yellow circle. At this point, they have all been investigated at some extend. The results of the investigations will be described further in the following sections.

2.2.1 Pond - former used for waste disposal

A small pond, that have been used for waste disposal, is located about 150 m east of well B20; And by the look at the pond it is clear that it still bear the mark of its past. Figure 2.6 shows a picture of the pond in spring 2012 where you on a walk in the area among others could find empty containers, parts of metal, plastic, and broken glass. It is unknown exactly what kind of waste is disposed to the pond, but traces of chlorinated compounds have been found in the pond sediment.

Figure 2.6: *One of the suspected sources of the pollution with TCE at Varbro well field: A pond 150 m east of well B20. The pond has been used for waste disposal in a period of years.*

As mentioned is Only one of the three boreholes on Varbro well field is, as mentioned, polluted, even though, the distances between them are relatively small. The reason of this is expected to be differences in the geology such that well B20 might be protected by a clay layer. This theory makes the inflow trail from the pond to the polluted well possible without contaminating well B20 [Orbicon A/S, 23. oktober 2006]. The differences in the geology will be discussed in chapter 4.

The theory was tested in 2006 by establishing a 22 m deep borehole for investigations (DGU no.: 5.1798) between B20 and the pond. A minor layer of clay was found and screen section were established in two levels below the clay layer. The water samples from 5.1798 showed traces of TCE above the groundwater standard but not of the same magnitude as the concentrations found in B19. It was concluded that the pond was not the source of the pollution or at least not the main source [Orbicon A/S, 23. oktober 2006].

2.2.2 Dry cleaner site

According to 4 independent references was a dry cleaner located in a former chicken farm on Ringvejen 672 in Hjørring. The location is shown in figure 2.5. The dry cleaner service is, however, not documented elsewhere. The dry cleaner services should according to the 4 sources have been active around the 1960s and have had 4-5 employees. The dry cleaner had, however, no authorization and there were several illegal activities. There was no drainage in the dry cleaner, leading to direct discharge on the land. There were though, according to one of the references, a pipe running from the building to a soakage pit placed on the north side of the building [Hjørring Kommune, 24. november 2009]. These conditions make the dry cleaner site an obvious suspect of the pollution of Varbro well field [Region Nordjylland, 2010].

The dry cleaner services was in the late 1960s closed in connection with an increased focus on dry cleaners because of a pollution at a dry cleaner site in Astrup about 5 km from Varbro well field [Hjørring Kommune, 24. november 2009].

The Region of Northern Jutland initiated in 2010 a supplemental pollution investigation of the dry cleaner site based on the informations supplied by the 4 independent references and the screenings of the top soil from 2008 where traces of chlorinated compounds were detected. The concentrations were, however, all below the criteria of evaporation set by the Danish Environmental Protection Agency [Region Nordjylland, 2010].

In an attempt of locating the pollutant source, 14 air probes were established and samples were extracted by coal tubes for analysis of chlorinated compounds. The probes were lead down to 2.7-2.8 m b.s. The result of the analysis showed traces of chlorinated compounds but as in 2008 only in very low concentrations. For further investigations was a 14 m deep borehole established at the location of the former dry cleaner building. Screen sections were established at 3 different levels : 6.5-8.5 m b.s.; 10.0-11.5 m b.s. and 12.5-13.5 m b.s. Soil samples were extracted at every half meter for geological description and pollutant analysis. The drill logs is attached on the enclosure CD. Also, water samples were extracted from every screen section but no traces of chlorinated compounds were found in either water or soil samples [Region Nordjylland, 2010].

The hydraulic yield from the three screen sections was very low and two of the filters were pumped dry which indicates that the water may not have been extracted from the primary aquifer. Even though no chlorinated compounds were measured in either groundwater or soil samples the dry cleaner site can not be completely cleared out as a pollutant source of the pollution. The pollution may be located deeper and possible further away from the building [Region Nordjylland, 2010].

2.2.3 Skibsbylejren - Warehouse and auctioning area

South-east from the polluted well B19 is a military area. The area has been used for different purposes through the ages, but it is not clear whether or not chlorinated compounds have been used. A former employee recalls that the area may have been used for some cleansing activities and finds it possible that chlorinated compounds could have been used for this purpose. The area contains among others a former vehicle wash ramp.

The top soil in the entire military area has been screened and traces of chlorinated compounds have been found several places within the area which confirms that these solvents have been used in Skibsbylejren. Besides that a new groundwater model developed by Hjørring Municipality shows that the catchment area of groundwater formation to Varbro well field may include the military area.

Two new boreholes were established in autumn 2011 as a part of a supplemental pollution investigation within the area. A 6 meter deep borehole, F2, was established by a 6" auger drill right beside the vehicle wash ramp that may have been used for cleansing activities involving chlorinated compounds. All 6 meter consisted mainly of fine silty sand. A two meter screen sectiom was established in the borehole from 4 to 6 m below surface. The journal of F2 is attached as appendix C.

Approximately 50 m north-west of F2 a 50 meter deep borehole, F1, was established. The drilling method used for this purpose was the airlift method. The 50 meters consisted of alternating layers of fine sand and clay. The visual description of the layers in the first 50 m b.s. is applied on the bore hole journal of F1 which, as for F2, is attached as appendix C. Three screen sections were established in F1. This was not done on basis of the visual description alone but was supported by a logging of the borehole. This borehole logging was performed by Orbicon A/S. The logging consisted of natural gamma-log, resistivity-log, and induction-log and showed mostly correlation with the visual description. The screen sections were established at three depths: 6-12 m b.s., 28.5-34.5 m b.s., and 35.5-41.5 m b.s. Screen section 1 and 3 had a diameter of 63 mm whereas screen section 2 had a diameter of 125 mm. From the visual impression and the borehole log it was uncertain whether or not screen section 2 and 3 are separated by a clay layer or are a part of the same aquifer. This will be clarified by investigations of soil samples from the 50 meter deep borehole. Figure 2.7 shows the location of the two boreholes in the warehouse and auctioning area [FBE, December 2011].

Figure 2.7: *Location of two boreholes, F1 and F2, which were established in autumn 2011 as a supplementary investigation of the warehouse and auctioning area: Skibsbylejren. F2 is placed beside a former vehicle wash ramp where there may have been used chlorinated compounds and F1 is placed 50 m downstream of F2 [FBE, December 2011].*

Soil samples were collected for geological description and pollutant analysis, but no chlorinated compounds were detected in the samples. Water samples were also extracted from each screen section in F1 and F2. As for the soil samples, no chlorinated compounds were detected. The result of the survey indicate that the warehouse and auctioning area is not the source of the pollution with chlorinated solvents found in B19, but it is possible that a pollution hot spot could be located elsewhere on the area [FBE, December 2011].

3

Investigation strategy of Varbro well field

Several pollution investigations has been performed during the last decade by different companies in the immediate area of B19, but no pollutant source has jet been identified. Every possible pollutant source has already been investigated and both Hjørring Municipality and The North Denmark Region have put an end to further investigations of the area of Varbro well field which means that the future operation of B19 in all probability will be shut down. This will increase the potential spreading of the pollution to the nearly located boreholes and if these get polluted as well, the entire well field may be closed.

The case of the Varbro well field is a good example of the major problem a pollution with chlorinated compounds may cause and it shows exactly how problematic and prolonged a source tracking can be. This makes the case of Varbro well field obvious as the foundation of this project and in developing an improved tool or method for a faster and more efficient source tracking.

In a last attempt to track the source of the pollution and save the polluted borehole from closure, a new investigation strategy is prepared for Varbro well field. This project will on the basis of three field experiments on the polluted well B19 identify an influence area for which the source of the pollution should be located. These experiments will be founded on a thorough investigation of the geology and water dynamics in the area of Varbro well field, by both existing data from indirect geophysical methods and from new data of direct measurement of the water level and the two new boreholes within Skibsbylejren. Besides that, a profound analysis of the time series of pollution data and pumping rates from the three wells at Varbro well field is performed to achieve informations about the direct effect the changing pumping rates may have on the pollution. If these general informations about Varbro well field does not identify the source of the pollution alone they will at least form the best possible platform for further investigations which in this case is consisting of three different field experiments. These comprise:

1. Level specific water sampling
    - Purpose: To clarify the present depth of the pollution and to identify how broad an interval the pollution stretches over vertically.
2. Push, drift and pump back experiment
    - Purpose: To estimate specific hydraulic parameters in the exact polluted area to give important informations of the water flow direction.
3. Changes of the pumping rate
    - Purpose: To investigate possible effects by the changing pumping rates and thereby find a response time from change to observed effect.

Separately these experiments do not get us closer to a source identification, but together will experiment 1 tell us the depth of the pollution while experiment 2 and 3 will give an estimate of the distance from the well to the pollution. The goal with these three experiments is to track the pollution backwards in time to find the present location of the pollution and not necessarily the original “crime scene”.

The result of the estimated influence area will be supported by model calculations to check if a pollution located in that area fits the observed concentrations in the polluted well. For this purpose will the GMS, groundwater model system, software package be used. The model calculations are expected to be an important tool in the validation of the result from the three field experiments and may finally be used to reduce the area further to get closer to a potential hot spot.

4 Varbro well field - geology and water

The transport of any compound in a polluted soil site is strongly dependent on the water dynamics and thereby the geology of the area. It is therefore important to get an exhaustive understanding of the geological conditions within the area of Varbro well field in order to track the source of the pollution.

The geology can be mapped by different geophysical methods as the 1D Transient Electromagnetic (TEM) explorations and the 2D Multi Electrode profiling (MEP) which are both indirect geophysical methods. By these methods, the general soil type is determined from the resistivity. MEP and TEM explorations are i.a. used in connection with extraction of groundwater.

Deeper drill logs may be used as a supplement to the geophysical methods and is useful in areas with low data quality. Investigations of soil samples from these boreholes gives important information of the soil properties that are significant for the transport of water.

The groundwater flow is beside the geology affected by the extraction wells. As solutes to a great extend are transported by the flow of the groundwater, an explanation of the groundwater stream is important in pollutant source identification. The groundwater potential is often identified by level metering or by using loggers to measure the water level at e.g. boreholes and streams. Other than the directional information, the groundwater may, by its main constituents, give informations about the transport of chemicals from terrain to the aquifer.

The important conditions as the groundwater flow direction, geology, and the chemical composition of the groundwater in the area of Varbro well field will be described in the following sections.

4.1 Geophysical mapping of Varbro well field

Drill logs are often used as a supplement to geophysical methods when the geology of an area is investigated [Jørgensen and Sandersen, September 2009]. Figure 4.2 shows a geological cross section of the boreholes in the area of Varbro well field based on data from the GEUS Jupiter database [GEUS, 2012].

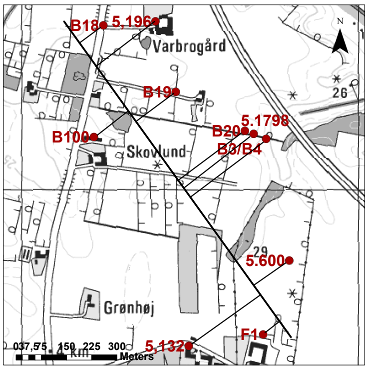


Figure 4.1: *The center line on the geological cross section with the different wells that is included in it.*

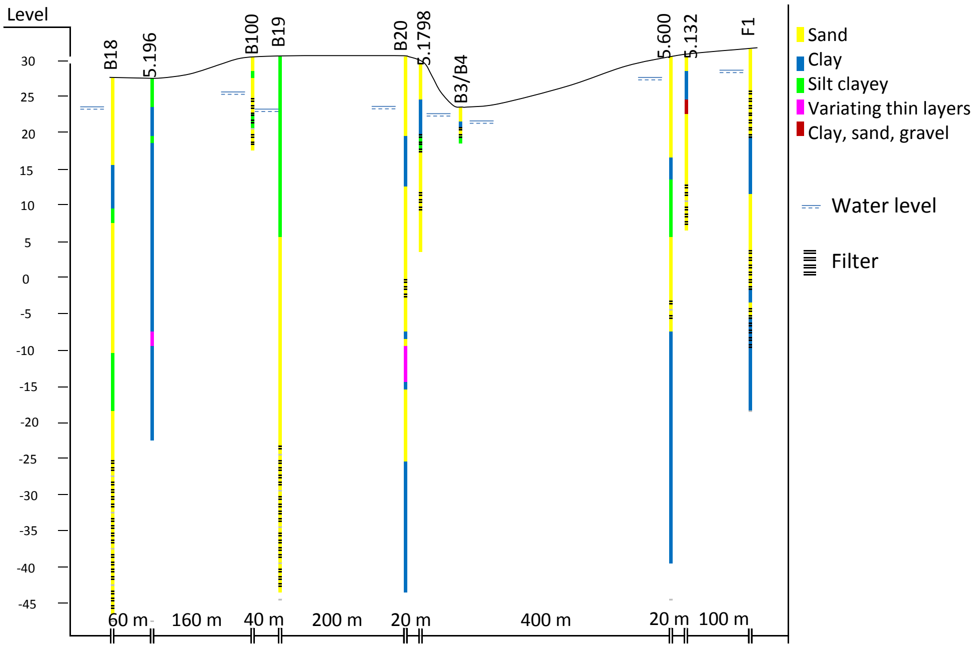


Figure 4.2: *Geological cross section of the boreholes in the area of Varbro well field [GEUS, 2012]. The water level at a steady water table and the screen section of each borehole appear on the cross section.*

From the drill logs, the geology of Varbro well field seems complex as large variations is observed which makes it hard to define specific layers based on borehole journals only. DGU no. 5.196, a demolished well, shows e.g. a geology almost only consisting of clay while the polluted well B19, only 200 m away, shows mainly fine sand and silt. The geophysical mapping by MEP and TEM explorations gives an explanation of this complexity.

4.1.1 MEP and TEM investigation

In the end of 1998 the area of Varbro and Vinstrup well field was mapped by geophysical MEP. A total of 6.1 km was investigated with the spears placed with a 5 m interval. TEM data from another investigation was used as a supplement at points with poor MEP data quality. The result was a two dimensional description of the geology where MEP form the basis of the first 50 m b.s. and TEM explorations primarily form the basis of the next 50 m [Dansk Geofysik A/S, Januar 1999]. The data interpretation is attached on the enclosure CD.

There was in general observed a resistance above 60 Ω in the top 50 m of the soil, indicating sandy and coarse-grained material which account for the primary aquifer. This is broken by a thin low resistance layer primarily observed in 5 - 10 m b.s. This general layer was evaluated to be dominated by clay and silt. The layer is however very thin and at some points non existent according to the geophysical MEP. At borehole B20 no low resistance layer is observed from the MEP data which is not consistent with the drill log of this well as it describes a 6 m thick layer of fertile clay with parts of very fine sand. The reason of this difference might be that the thin and silty layers are hard to register by the geophysical methods. From the geological interpretation of the MEP data seems the clay and silty layer to be disrupted or very thin at the distance between B20 and the polluted well B19. At this distance, the primary aquifer is considered vulnerable to percolating surface water

[Dansk Geofysik A/S, Januar 1999]. The chemical composition of the groundwater can be used for valuing this possible vulnerability and will be discussed in section 4.3.

Below the top 50 m is generally observed low persistences about 5-16 Ω. This bottom layer is presumable forming the lower boundary of the primary aquifer and consists of fertile clay deposits [Dansk Geofysik A/S, Januar 1999].

4.1.2 Mapping of buried valleys by geophysical methods

The TEM and MEP data has together with borehole journals and other geological mappings been used for a nationwide identification of buried valleys in connection with administration of the groundwater resources. A buried valley is an oblong depression that is formed by the meltwater under glaciers and afterwards has been filled with younger deposits. The valleys are subdivided into two categories: a completely buried valley and a partially buried valley, depending on the completion of the valley and whether or not it can be recognised at the present terrain level [Jørgensen and Sandersen, September 2009].

At the north part of Varbro well field was a partially buried valley identified which might explain the variations in the geology found from the drill logs. Figure 4.3 shows the position and extent of the buried valley at Varbro well field [Jørgensen and Sandersen, September 2009].

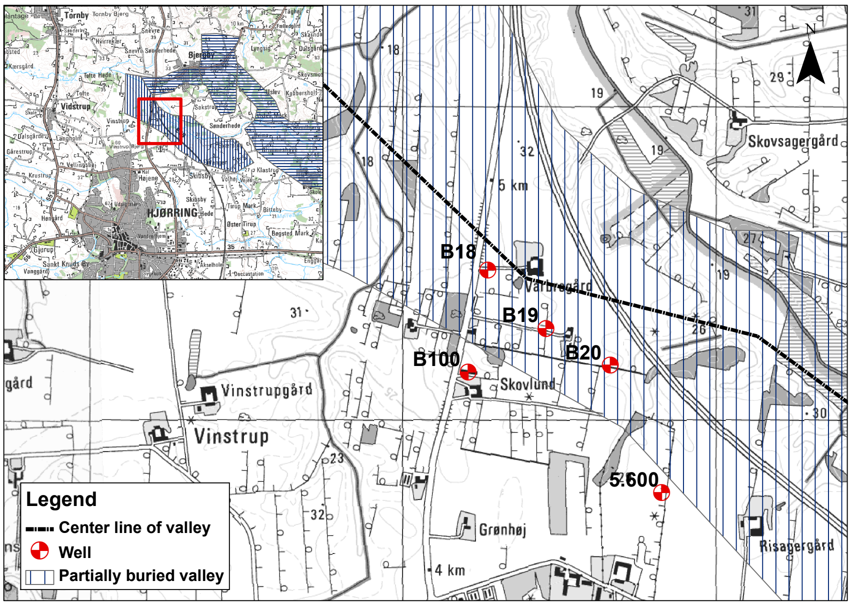


Figure 4.3: *North of Hjørring is a group of buried valleys where a partially buried valley covers the north part of Varbro well field [Jørgensen and Sandersen, September 2009].*

The filling material of the valley was estimated to be mostly coarse-grained deposits while the sides of the valley primarily consists of clay and fine-grained material [Jørgensen and Sandersen, September 2009].

The geophysical mappings of Varbro well field creates an overview and understanding of the geology in the area. The geology consists generally of a primary sand aquifer defined by an upper thin silty clay layer and a lower bottom layer of fertile clay deposits. The buried valley at the north part of Varbro well field partly explains the differences between the MEP data and the drill log. These informations are important to form the basis of a hypothesis regarding the movement of the source of the pollution through the ages and must therefore be taken into consideration in source tracking procedures.

4.2 Geological and physical soil layer description of Varbro well field

The geophysical mapping of Varbro well field defines different geological layers and their approximate extent. But the soil types are only roughly estimated as main soil categories. This description does thereby not tell much about the hydraulic properties of each soil layer. The different layers are therefore investigated further to estimate the hydraulic differences of the layers. The two new boreholes in Skibsbylejren form the foundation of this investigation. The location of the two boreholes is shown in figure 2.7.

Soil samples has been collected from the 50 m deep borehole F1 with a steady interval. The distinctive geological layers has been depicted from the visual impression of the soil samples and from the gravimetric water content. Each soil type have a different porosity and the amount of water, which can be evaporated from a soil sample, can therefore be used for a quick separation of different soil types. From the results and the visual impression was samples in 7 different levels picked out for further investigation. These 7 samples are assumed in general to represent the different layers at Varbro well field. Through a thorough series of experiments was parameters as the saturated hydraulic conductivity and effective porosity, determined along with the phase and grain size distribution. The series of experiments in this physical soil type determination appear from figure 4.4.

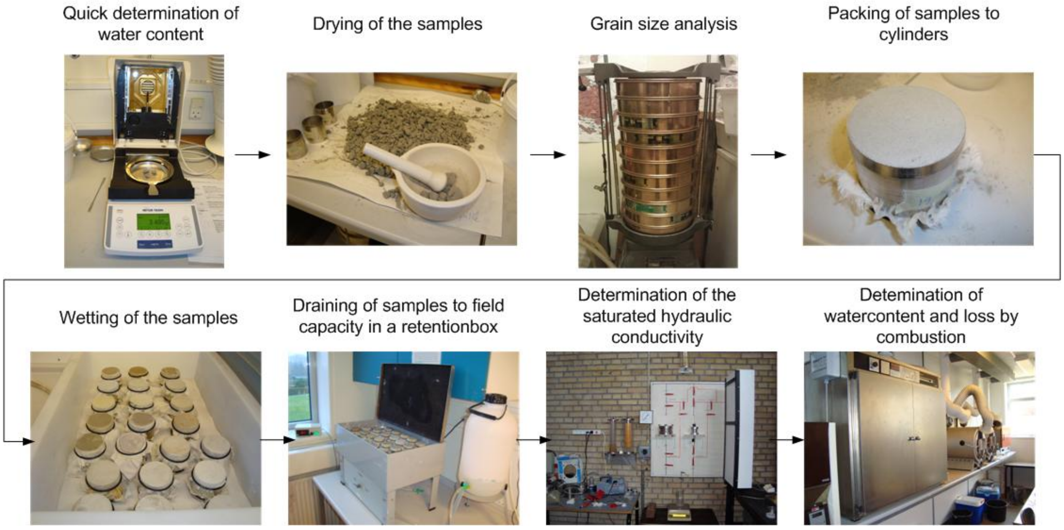


Figure 4.4: Flow diagram of the different steps in the analysis of the soil samples collected from the 50 m deep borehole F1 in November 2011. Several important soil specific parameters were found from the analysis, among others the saturated hydraulic conductivity and the effective porosity.

The experimental procedure of each step in the series of experiments is described in details in appendix F.

The grain size analysis was used for a classification of the textural class of each sample. The analysis were performed as a dry sample analysis which is not a good method for clay samples as it will clump and be registered as larger particles. Samples with more than 10 % of sample mass smaller than the finest sieve on 0.045 mm was therefore assumed to be clay. These samples could then have been analysed further by e.g. a wet grain size analysis og by the hydrometer method which is able to seperate smaller particles and thereby more suitable for clay samples. 4 samples had more than 10 % particles finer than 0.045 mm. This was the samples extracted from 12, 19, 39 and 50 m b.s. Figure 4.5 shows the grain size distribution of the 7 samples graphically.

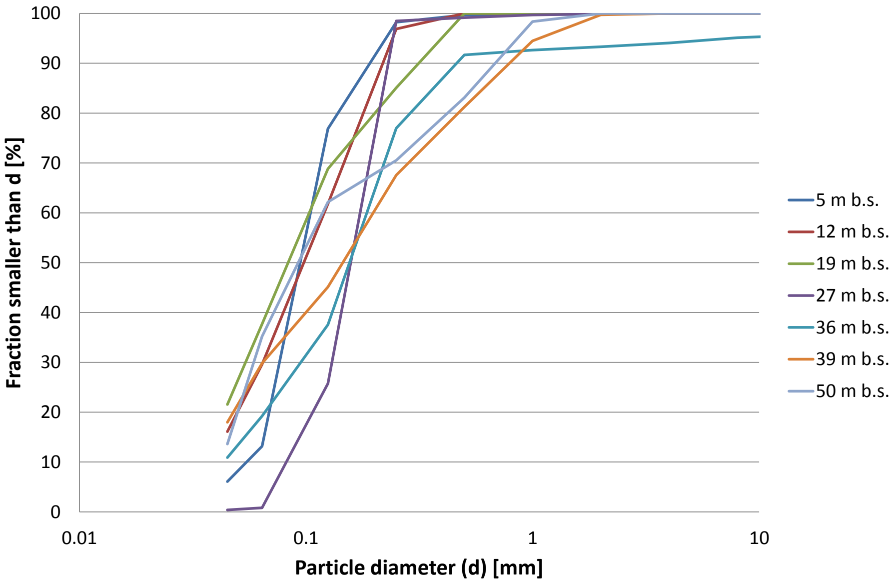


Figure 4.5: *Grain size distribution curves of the 7 samples representing different geological layers in the area of Varbro well field found by dry grain size analysis.*

The sand samples was selected at 5, 27 and 36 m b.s. and might have quite different soil properties. The grain size analysis showed that the samples from 5 and 27 m u.t. was mainly fine and very fine sand while the sample from 36 m u.t. consisted of both some clay, silt, fine sand and coarse sand. This is the only point at the 50 m deep borehole that coarse-grained material was present which might be an important information in connection to pollution investigation as the pollution might primarily be transported in this layer, especially since the layer below according to the soil size distribution and visual impression consists of clay.

The parameters influencing the water and solute transport are determined by the main soil type of the layer and are important in complex 3D models as well as simple calculations. The effective porosity and the hydraulic conductivity was found from each of the selected samples. The result is presented in table 4.1 along with the density of the packed samples, total porosity, and water content at field capacity.

Table 4.1: *Soil parameters influencing the solvent transport determined from the analysis of the 7 soil samples, representing the different geological layers in the area of Varbro well field.*

Sample depth [m b.s.]	Soil type	Bulk Density [g/cm^3 soil]	Density [g/cm^3 soil]	Total pore space volume, ϕ [cm^3 air/cm^3 soil]	Water content at field capacity, θ_{fc} [cm^3 water/cm^3 soil]	Effective porosity, ϕ_{eff} [cm^3 air/cm^3 soil]	Hydraulic conductivity [m/s]
5	Fine sand	1.54	2.75	0.44	0.39	0.05	$3.8 \cdot 10^{-6}$
12	Silt	1.62	2.86	0.43	0.31	0.12	$2.2 \cdot 10^{-7}$
19	Clay	1.59	2.78	0.43	0.40	0.03	$2.7 \cdot 10^{-8}$
27	Fine sand	1.61	2.76	0.42	0.33	0.09	$1.6 \cdot 10^{-5}$
36	Fine sand	1.67	2.60	0.36	0.30	0.06	$7.9 \cdot 10^{-6}$
39	Clay	1.57	2.93	0.47	0.40	0.07	$1.2 \cdot 10^{-8}$
50	Clay	1.54	3.12	0.51	0.40	0.11	$3.4 \cdot 10^{-8}$

The densities found from each soil sample seems a little higher than expected as it will normally be in the interval of 2.55-2.75 g/cm^3. The bulk densities are, however, within the range of typical values of soil on 1.4-1.7 g/cm^3. The measured hydraulic conductivities reflect the degree of compression of the samples and are relatively low, indicating fine particles. This correlates with the drill logs from wells in the area where the samples were selected. There is observed a clear distribution between the samples which proves that different soil types and thereby different layers are represented in the analysis.

The effective porosity of the samples are remarkably low. There was a gradual mass loss through the series of experiments which assumable is the reason of the low measured effective porosities. Method optimizations, by e.g. having fewer transfer steps between the weight measurements, used to determine the effective porosity, will reduce this loss of sample material.

The textural classes of the 7 soil samples, determined by the row of experiments shown in figure 4.4, appear from table 4.1 as well. The same layer distribution as from the geophysical mapping is observed in the samples from the 50 m deep borehole but in different levels. The upper clay and silt layer are placed at a lower level and the clay layer that assumable is defining the bottom of the primary aquifer is at a higher level.

Shell fragments and glitter was observed in several of the samples from the borehole, which is typical in fillings of buried valleys. The buried valley in the northern part of Varbro well field does however not cover the area around the 50 m deep borehole, from which the samples were extracted according to [Jørgensen and Sandersen, September 2009].

The results shows in general that the series of experiments is good for separating and determining soil types and gives god estimates of the specific soil parameters determining the water transport. There may, though, be differences between the estimated results from laboratory soil analysis and the actual values of the parameters as packed samples were used and not intact samples. Cracks and compression are therefore not taken into account, but it is estimated that this type of laboratory analysis can provide valuable informations about the geological profiles as well the potential variations in water transport.

4.3 Groundwater potential and chemistry

Water extraction involves pumping with different rates from different wells at different times. The pumping strategy will have an effect on the water potential in the close area of each extraction well, but the constant local changes will not necessarily change the general flow of the groundwater at a larger scale. The effect of changing pumping rates on the groundwater potential in the area of Varbro well field is investigated further as it will have great influence on the transport of pollutants.

The groundwater table has been measured in several wells in the area of Varbro well field at different pumping situations: with 1 or more active extraction wells and with no active wells, giving a steady water head. Counters has afterward been drawn from the data to make a visual impression of the groundwater flow direction. The result from the steady situation appear from figure 4.6 where the counters made from own measured date is compared to earlier results of synchronous measurements of the water table in that area from 2004 and 2009.

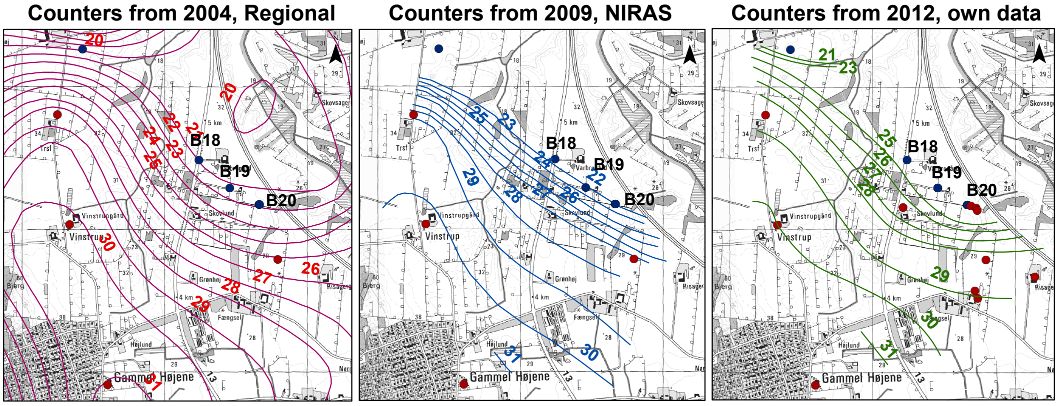
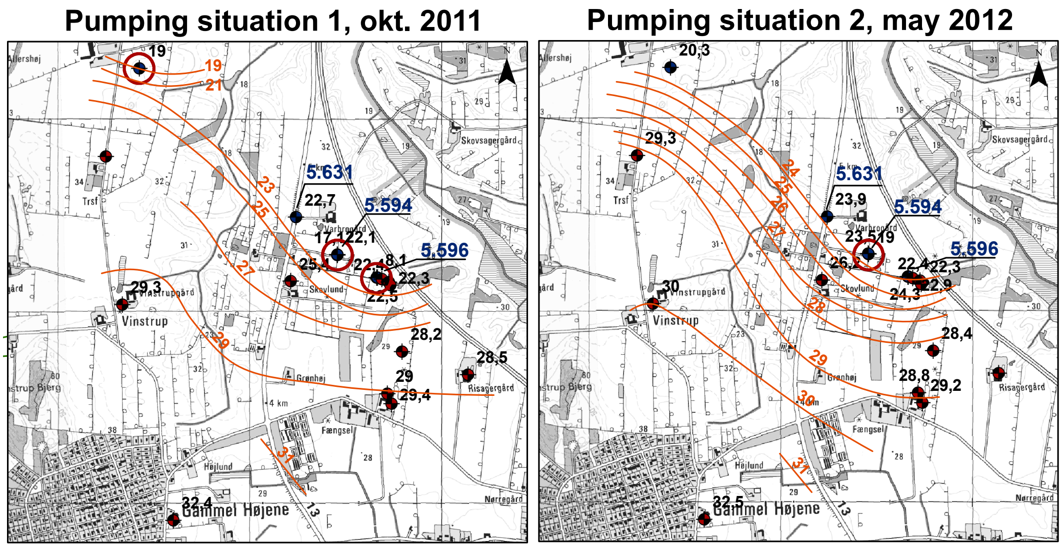


Figure 4.6: Counters made from synchronous measurements of the water table in 2004, 2009, and 2012. The blue points are extraction wells whereas the red points are other measuring wells.

The extent and precision of the counters are depending on the amount of data points that underlie the counters. The new dataset involves 3 more points in the south-east part of the investigated area near Skibsbylejren which in that area gives a quite different picture than the counters from 2009, but is consistent with the counters from 2004. Another difference is the gradient which from the new data seems to be lower. This variation is probably caused by seasonal changes. In general seems the direction of the groundwater flow however to be similar in 2004, 2009, and 2012.

Figure 4.7 shows examples of 2 different pumping situations at Varbro well field with 1 and 3 active extraction wells respectively. The active wells are marked with a red ring.



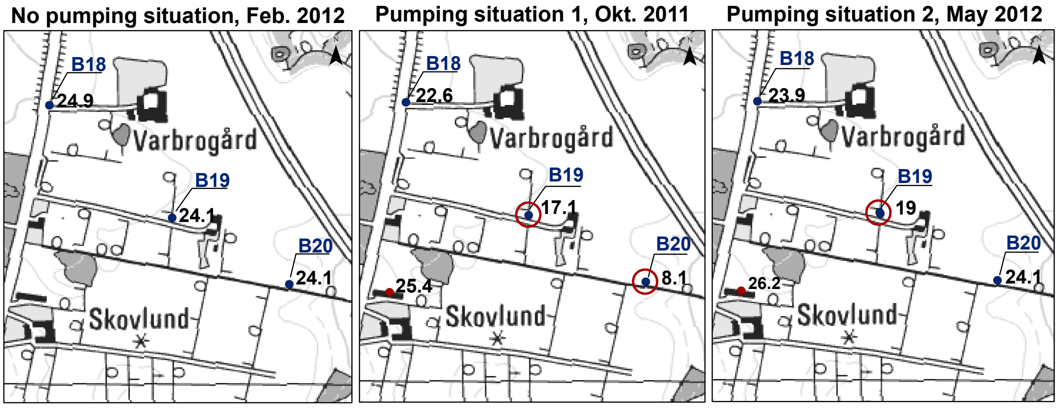
Pumping situation 1, okt. 2011

Pumping situation 2, may 2012

Figure 4.7: Counters made from synchronous measurements of the water table at two different pumping situations. The red rings marks the active wells. The blue points are extraction wells whereas the red points are other measuring wells.

By comparison of the 2 situations illustrated in figure 4.7 and the contours sketched from, data measured at a steady water table, no significant changes is observed in the groundwater flow direction at a larger scale. In a smaller scale, the local cone of depression at the active extraction well might however be of influence. Also the gradient changes depending on the time of the year and possible on how many wells are active and with what pumping rate.

The local cone of depression by active pumping wells is investigated further by focusing only on the three wells at Varbro well field at a steady water table, with 1 active pump, and with two active pumps respectively. Figure 4.8 shows a zoom on the three extraction wells at Varbro well field in the different pumping situations.



No pumping situation, Feb. 2012

Pumping situation 1, Okt. 2011

Pumping situation 2, May 2012

Figure 4.8: The specific area around the three extraction wells at Varbro well field at different pumping situations. The red ring mark the active wells in each situation. The blue points are the extraction wells while the red point is well B100. At each well is the level by metering noted.

By comparison of the different pumping situations the local cone of depression from the active wells does not seem to affect the non pumping wells. The general changes is more likely a result of seasonal variations. This means that the three wells at Varbro well field possible are of very low or non hydraulic contact with each other which explains why only B19 is affected by the pollution.

Besides the synchronious measurements of the water table loggers has been installed in 4 wells in the area of Varbro well field to a continuously determinations of the pressure and the temperature. The loggers were placed in the monitoring wells beside B19 and B20 plus at the well at the dry cleaner site, B100, and one of the wells in the military area, 5.600. Also, a logger was placed in the top of the monitoring well beside B20 as a atmospheric pressure reference. The loggers were started the 12th of October 2011 and stopped 7 month later the 11th of May 2012.

From February to June 2012 was B19 the only active well because of the experiments discussed in chapter 6. These experiments involved pumping on B19 of different magnitudes that clearly shows on the pressure measured by the logger in the monitoring well beside B19. If B19 and B20 is in direct hydraulic contact would these variations at some extend show as changes in the pressure measured by the logger in the monitoring well beside B20 as well. This is however not the case which clearly shows from figure 4.9.

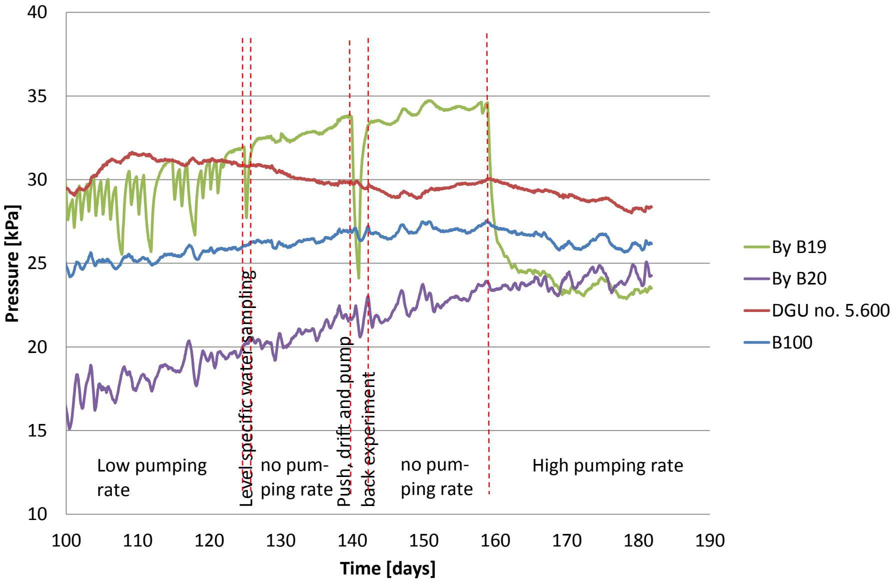


Figure 4.9: *The variations in pressure measured by loggers installed in different wells in the area of Varbro well field from February to June 2012.*

At a very few points seems the logger data from B20 to show an effects on the changes in pressure at B19. This is e.g. at the point of the “Push, drift and pump back” experiment. The effect is, however so small that it can not be separated from general noise. The water level in B20 seem in the entire period to be increasing, even at the last part where the depth at B19 drops with approximately 10 m.

The depth in B100 and 5.600 seems relatively stable and react with great possibility mostly on seasonal changes. For both of them is, however, observed a remarkable change in the general tendency of the curves in figure 4.9 at the exact point of the large and constant pressure drop in B19. Where the depth in B20 still seems to be increasing, is a minor decreasing tendency of the depth in B100 and 5.600 observed.

The logger data support the theory regarding a missing hydraulic contact between the wells, based on water level metering. It does not seem like there is any hydraulic contact between B19 and B20. It does however seem like the pumping at B19 has a minor effect on both the water level in B100 at the dry cleaner site and in 5.600 at the military area. This was not expected as especially 5.600 is located relatively far for the well. This remarkable correlation explains why only B19 is polluted and is a very important information in the conceptual modeling of solute transport. Also, it makes both the dry cleaner and the military area highly suspects in the source tracking.

4.3.1 Determination of surface impact on the groundwater by its chemical composition

The flow direction of the groundwater is of great importance of the horizontal transport of pollutants but does not tell much about the vertical transport of a possible spill from the top soil down to the primary aquifer. The chemical composition of main components in the groundwater at different depths can, however, indicate in which extent the aquifer is affected by the surface. For both the polluted well and the two closest extractions wells has the concentrations of nitrate, chloride and sulfate been relatively constant since the 1990s, indicating that the influence from the surface has been constant in that period [Andersen et al., Januar 2006] [GEUS, 2012]. Concentrations of sulfate higher than 50 mg/L is furthermore an indication of an indirect influence from the surface. In 2005 was level specific water samples extracted from the top and bottom of the screen sections in the three extraction wells at Varbro well field. The analysis of the samples showed a concentration of sulfate on 91 mg/L in the top of the screen section in the polluted well, B19. The concentration drops by the depth of the screen section to 49 mg/L in the bottom sample, showing that the indirect influence from the surface, as expected, is highest at the top of the aquifer. The concentrations of the samples from the two other boreholes showed concentration around 50 mg/L [Andersen et al., Januar 2006].

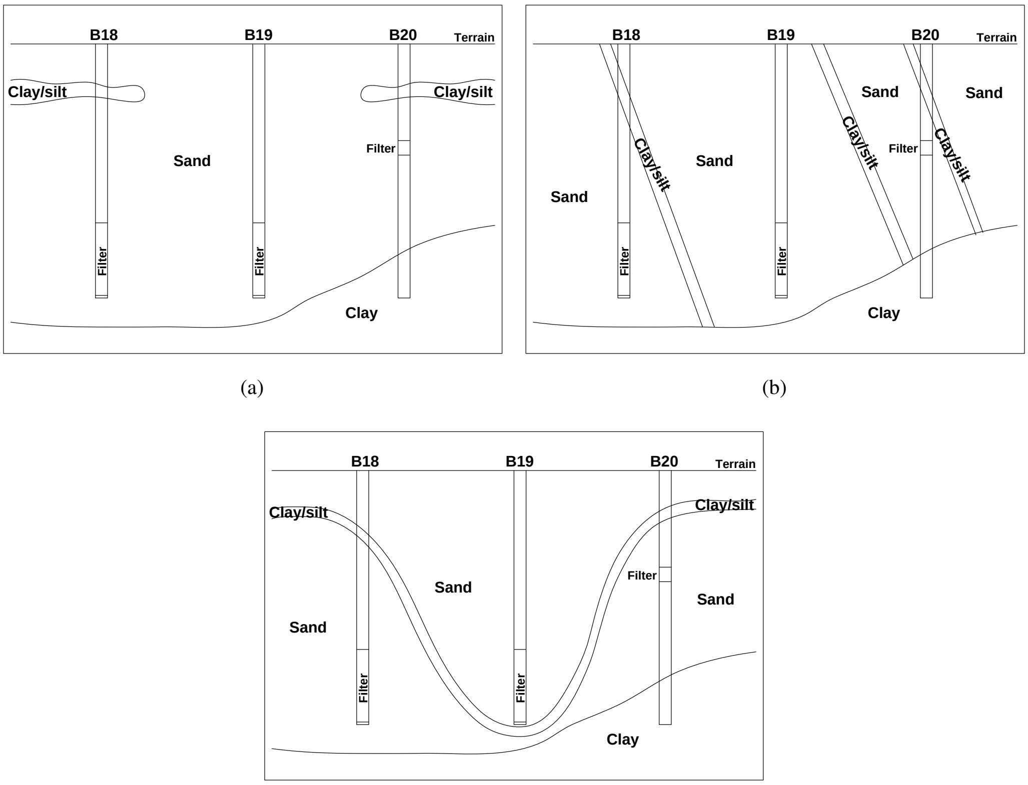
4.4 The geological influence on the pollution of Varbro well field

The transport of the pollution is depending on the geology. In order to understand the transport a geological conceptual model must be set up. This is done by gathering all the results discussed in the previous sections of this chapter.

Geophysical mapping showed 4 general layers consisting of sand, an upper clay or silt layer, then sand again, and a lower fertile clay layer [Dansk Geofysik A/S, Januar 1999]. The upper low permeable clay or silt layer may, however, be missing in the area near B19. The 4 general layers are verified in the analysis of the soil samples from the 50 m deep borehole, F1, 800 m south-east of the polluted well. The location of F1 appear from figure 2.7. The drill logs from the area of Varbro well field shows, however, changes in the geology indicating that the geology is not as simple as the 4 general layers, but may be highly affected by the buried valley that covers the northern part of Varbro well field or other geological variations.

From the groundwater composition, the polluted well seems to be more vulnerable to surface impacts which correlates with the theory of a missing upper clay or silt layer in that area. Besides that, the potential of the groundwater tell us that the pumping of the three wells does not have a greater impact on ground water level at a larger scale and that the polluted well might not be hydraulic connected with the two other extraction wells at Varbro well field.

By combining these information, several suggestions for a geological conceptual model can be made. In figure 4.10 is three different possible geologies of Varbro well field sketched.



(a)

(b)

(c)

Figure 4.10: *Three different conceptual models of the geology at Varbro well field presented as a geological cross section with the three extractions wells.*

Figure 4.10(a) is the most simple model suggested by the geophysical data alone. This model does, however, not seem realistically as the three wells would clearly be in hydraulic contact with each other which from the direct hydrogeological investigation methods (level metering and logger measurements) is not the case. The conceptual model sketched in figure 4.10(b) allow for the missing hydraulic contact between the wells and explains why the drill log of B19 only shows sand for 74 meters. This would also disable the hydraulic contact between B18 and B20.

Figure 4.10(c) takes a starting point in the buried valley by suggesting that B19 is the only extraction well at Varbro well field that is actually in the valley. This suggestion correlates better with the geophysical mapping of the area than figure 4.10(b) and does separate B19 from the other wells hydraulically. The direction of the valley suggested by geophysical methods does, however, not quite match the constructed conceptual model. Figure 4.10(c) suggest thereby a branching of the buried valley. Branchings are observed at several of the other groups of buried valleys north of Hjørring and is therefore not unrealistic. This would also match with the observation of shell fragments and glitter in the soil samples from the military area.

Figure 4.10(c) seems to give the most likely estimate of the geology of the three sketched conceptual models and will therefore be used to describe the geological influence of the solute transport on Varbro well field.

A surface spill of chlorinated compounds as a DNAPL (Dense Non-Aqueous Phase Liquid) will due to the high density seek downward but is slowed down by less permeable layers. On the top of low permeable clay layers, the DNAPL might gather in a pool and as the pressure increases it will spread further vertically as branching “fingers”. This behavior is described in details in appendix A.

From the DNAPL pool, an amount of dissolved chlorinated compounds will be transported with the groundwater giving the concentrations pumped up through the extraction well.

Assuming that the geology at Varbro well field is as sketched in figure 4.10(c), a hypothesis of the movement of the DNAPL can be made from the day of the spill until now.

4.4.1 Hypothesis on the historical movement of the pollution plume

If the pollution is assumed to be caused by a surface spill it would dive and at some point reach the upper clay layer and create a pool. Depending on the slope of the clay layer the DNAPL may be assumed to move with the slope until it hit an end. This could be either by the end of the clay layer or by hitting a hollow from where the DNAPL eventually would spread as branching “fingers”.

At some point the pollution must, however, has dived and possible gathered again at a deeper level as specific water samples indicates a present deep location of the DNAPL.

With a starting point in the geological conceptual model sketched in figure 4.10(c) is the hypothesis of the solute spreading and transport as follows:

A surface spill of a larger amount of chlorinated compounds has caused the DNAPL to dive until it meets a clay layer. From here it is transported in the direction of the polluted well where it dives down into the valley on the low permeable sides until it reaches a less permeable fracture in the valley or the bottom of the valley, defining the present location of the pollution. From this point it might dive even deeper.

According to the flow direction of the groundwater is the DNAPL assumable placed either south-east or south-west of the polluted well. It might, however, also be at the location where the highest effect from the MIP, described in section 2.1, was detected. In that case the DNAPL would be assumed to be located relatively close to the well making the cone of depression by pumping the reason of pollution influx to the well. This might be clarified by a closer look on the time series of pollution and pumping rates.

Time series analysis - water and chemistry

5

The complexity of the geology is likely to be the explanation why only one well at Varbro well field is effected by the pollution. Another part of the explanation might be found in the pumping strategy through the ages. The pumping rates from the different extraction wells and the time series of pollution data might give an understanding of this and will be discussed in this chapter.

5.1 Time series of pumping rate from the wells at Varbro well field

Depending on which extraction wells have been active and with what pumping rate the pollution might have been dragged in different directions. The yearly extraction from each well at Varbro well field has therefore been compared to each other. The changes is shown graphically in figure 5.1.

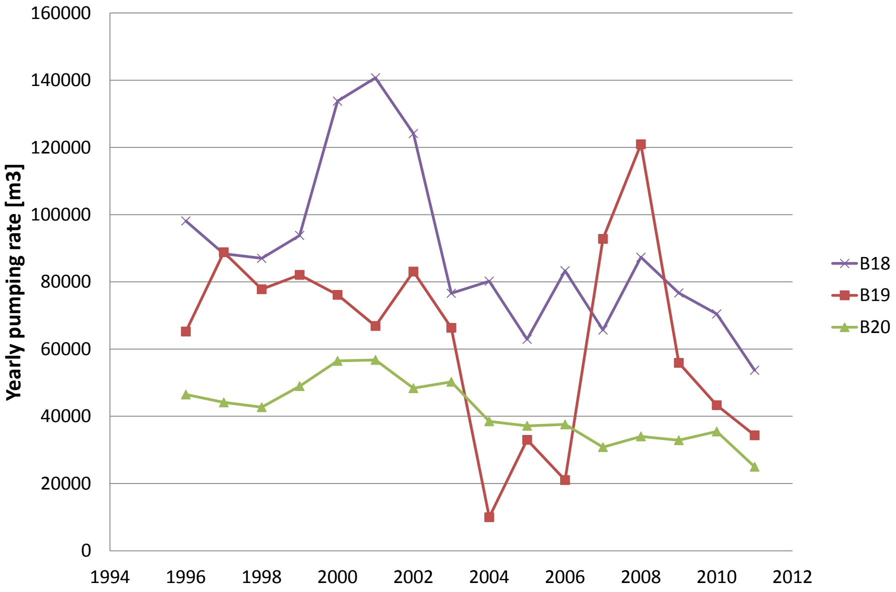


Figure 5.1: *The yearly yield from the three extraction wells at Varbro well field from 1996 to 2011.*

The rate has very roughly been constant for the polluted well B19 until 2003 where chlorinated compounds first were detected for the first time. The pumping rate was the following years lowered considerable and after a few years of almost no activity, the rate was again increased. There were two reasons of that increase: one was the fear of the pollution spreading to other wells and the other was that the concentrations in that period was dropping and it was assumed that this tendency would continue. This was, however, not the case which will be mentioned further in the following sections.

The yearly extraction from B20 has in general been lower and more stable than the two other wells, but has gradually decreased since 1996. The highest yearly pumping rate is on the other hand found in B18 where the extraction was remarkably increased in the 5 years before the discovering of the pollution in well B19.

The yearly pumping rates gives only a general impression as it is the total amount for one year, but at a smaller scale, the rate is in constant change. An example of the daily variations over a couple of month in the polluted well B19 is shown graphically in figure 5.2.

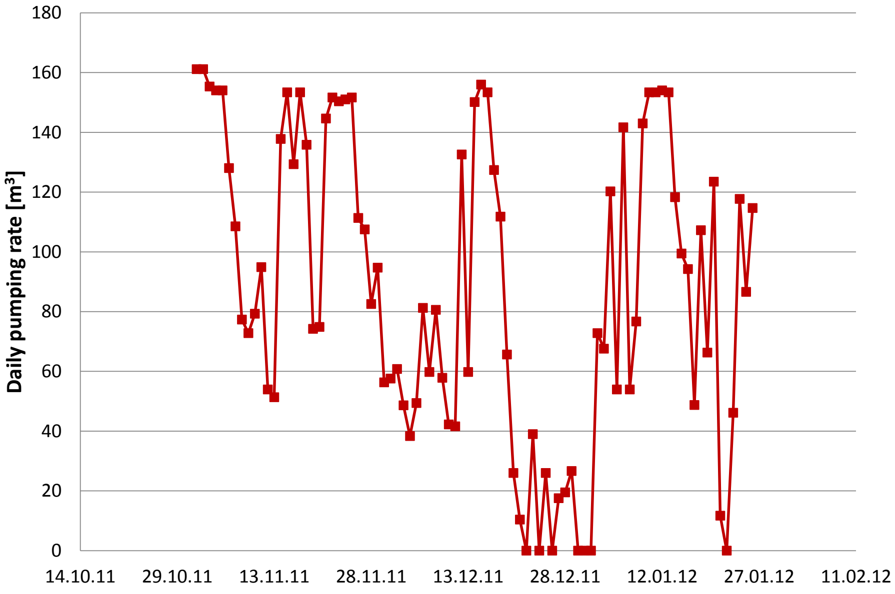


Figure 5.2: *The daily variations of the pumping rate in the pollutede well, November 2011 to January 2012*

The pumping rate in B19 varies quite a lot over a couple of month. This should, however, not have any influence on the pollution as the pollution is expected to react on the general tendency only, if any at all.

5.2 Time series of chlorinated compounds from the wells at Varbro well field

Since 2003, samples has been extracted from the three wells at Varbro well field for analysis of chlorinated compounds on a regular basis. Chlorinated compounds has at every analysis only been observed in B19 except from one time where a very small amount (0.024 μg TCE/L) was measured in B20 in 2006, immediately after the relatively stagnant period of the pump in the polluted well B19. This gives reason to believe that a spreading to the other boreholes at Varbro well field will occur if B19 is taken permanently out of operation.

Figure 5.3 shows the concentrations of TCE, PCE, and VC found in B19 from 2003 to 2011 [GEUS, 2012]. Notice that the concentration of TCE is much higher than PCE and VC and is therefore shown on a secondary axis within the graph. The groundwater limit value for chlorinated compounds is 1 μg/L. The groundwater limit for VC alone is, however, only 0.2 μg/L as VC is considered much more toxic than the other chlorinated solvents.

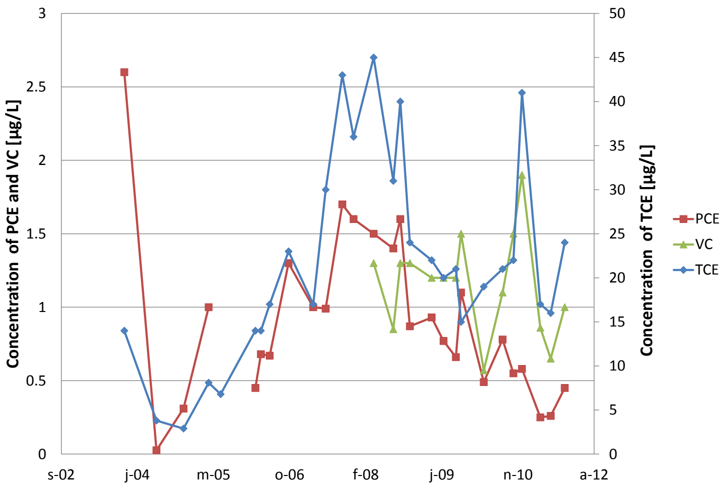


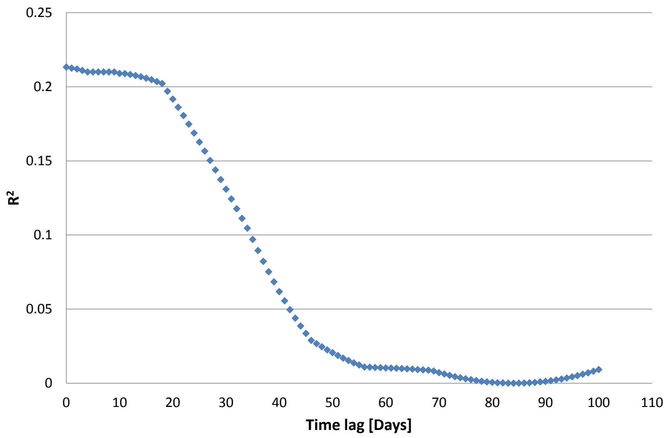
Figure 5.3: *Time series of concentrations of the chlorinated compounds TCE and PCE and the breakdown product VC, from 2003 to 2011.*

The time series of VC is much shorter than for the other two solvents as the samples before 2008 not were analysed for the breakdown product. At the first look at the data it could seem like a plume of pollutants passing the well with a peak in 2007-2008. But in 2010 seems the concentration to be increasing again. In general the concentration of all three compounds has been variating quite a lot the last 9 years but they does, however, seem to follow the same trail and the variations seems similar. According to appendix A, TCE and PCE has very similar and poor retention properties in soil and should therefore undergo the same variations whereas VC have slightly lower sorption qualities and is much more volatile. This might displace the time series of VC in proportion to the time series of TCE and PCE. This is be investigated by a simple analysis.

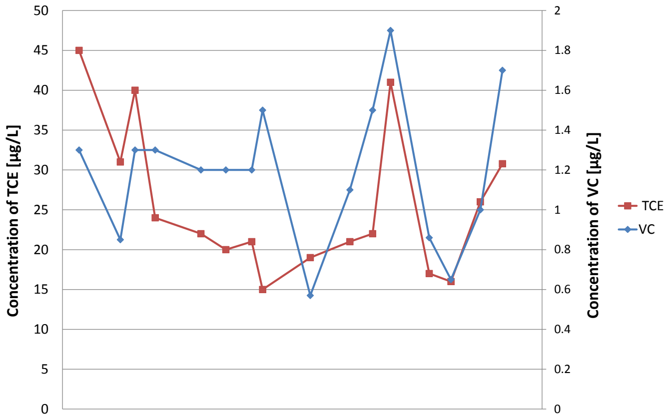
5.2.1 Time lag analysis - TCE and the breakdown product, VC

TCE and VC has different retardations in soil and VC should therefore in theory reach the well before TCE. This would be reflected in comparison of the time series of TCE and VC respectively as a delay between the curves. If the source is located close to the well a delay caused by the sorption properties will not be expressed. The purpose of a time lag analysis of the time series of TCE and VC is then to identify a given delay time between TCE and VC that could indicate whether or not the pollution is located close to the polluted well.

For the analysis is daily points needed of the pumping rates. Therefore has a daily value of the pumping rates been calculated by interpolation of the original time series. The time series of VC was restraint in time while the time scale of the pumping rates was moved one day at a time. The correlation between the two datasets are, at every time lag, compared in order to determine how well they match at a given time lag. The result appear from figure 5.4 as the linear correlation between the two datasets, R^2, as a function of the time lag in days.



(a) The correlation between the concentrations of TCE and VC as the coefficient of determination, R^2, of the linear correlation between the two datasets as a function of the investigated time lag in days.



(b) The two datasets with no displacements between the curves.

Figure 5.4

The correlation between the two datasets is not remarkably good at any point but it does however peak around zero days of time lag indicating no difference in the transport of TCE and VC. This could indicate that the source of the pollution is located so close to the polluted well that the different physical and chemical properties of these compounds does not manifest itself. By a longer transport distance between the pollution and the well a difference between the time series might be observed.

5.2.2 Analysis by time series of degradation potential

Another interesting point of view is how the ratio between the different compounds has developed for the last 9 years as dechlorination will take place under certain conditions. Under anaerobic conditions, PCE can be dechlorinated to TCE and then further dechlorinated to VC which often will accumulate at polluted soil sites [Bjerg et al., 2011]. Anaerobic dechlorination is described further in appendix A. The ratio between PCE and TCE plus TCE and VC is investigated by graphically putting the ratio against time and determine the tendencies, if any. The result appear from figure 5.5.

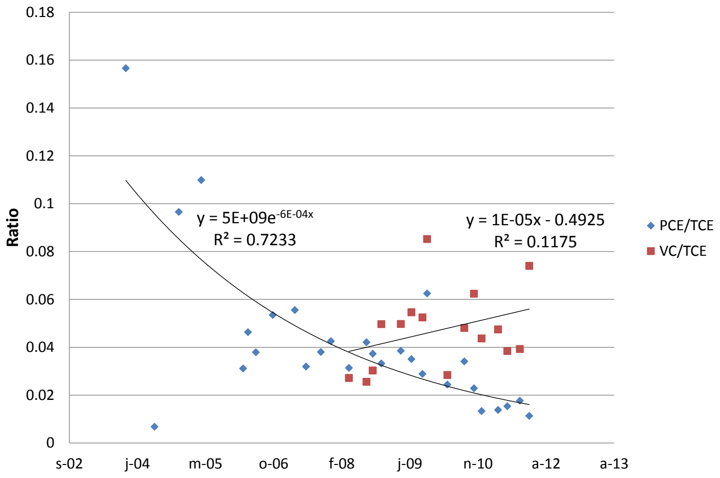


Figure 5.5: *The ratio between PCE and TCE plus VC and TCE as a function of time. PCE seem to account for less compared to TCE while VC seem to account for more by time.*

It seems from figure 5.5 that PCE account for a decreasing amount compared to TCE. The ratio between the two compounds is approximately exponentially decreasing and indicates a dechlorination over quite a long time. VC seems however to account for an increasing part compared to TCE which indicates a slowly accumulation of VC. VC is seen as a greater threat to the groundwater quality than TCE and PCE as it is highly toxic and carcinogenic. An accumulation of VC would therefore intensify the situation even further.

By the use of an exponential function, the first order degradation rate of PCE is determined to $K_1 = 6 \cdot 10^{-4}\ d^{-1}$. [Loll and Moldrup, 2000] suggests a very similar first order degradation rate for TCE on $K_1 = 9.5 \cdot 10^{-4}\ d^{-1}$.

The time series analysis of TCE and VC has turned out to be a useful tool in source tracking. The analysis implies that the present location of the pollution is relatively close to the polluted well as no delay between TCE and VC is observed. Furthermore indicates the analysis naturally degradation of PCE and accumulation of VC that is considered even more toxic.

5.3 Changes of pumping rates and pollution in time - Is there a connection?

The concentration of TCE and PCE seems, from figure 5.3, to be decreasing from 2003 to 2004 where the lowest concentrations in the time series are observed. This is the same period that the pump in the polluted well B19 was taken out of operation for a longer period of time. Contrary, when the pumping rate was at its highest in 2007 - 2008, the highest concentration in the time series was observed. The time series of TCE and pumping rates from B19 are compared graphically in figure 5.6.

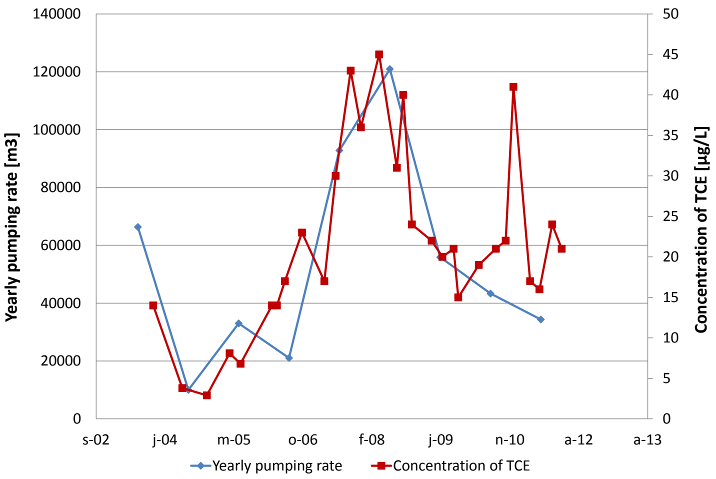


Figure 5.6: *The time series of pumping rates of the polluted well B19 and the concentrations of TCE. The two time series seems to follow the same pattern.*

The agreement between the two curves is extraordinary and against all expectations. If a pollution is affected by the pumping would an increased pumping rate assumable mean a larger dilution of the pollution because more pure water is dragged to the well. The effect would be a decrease in concentration when the pumping rate is increased. This agreement is an important information in the identification of the source location. Figure 5.7 shows a zoom on the period from 2006 to 2010 as more data is available for this period.

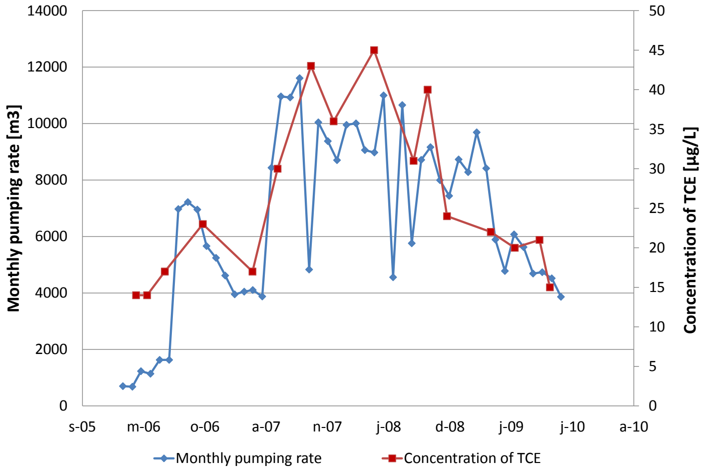


Figure 5.7: *Time series of the TCE concentration and monthly pumping rates in B19 in the period from 2006 to 2010 where most data is available.*

From figure 5.7 it seems that the pollution dataset is slightly displaced compared to the time series of the pumping rates, which means that there is a response time from the change of the pumping rate to a change in the concentration is observed. This response time is investigated further in the same manner as for the time lag analysis of TCE and the breakdown product VC, described in section 5.2. An interpolation of the time series of pumping data has been performed to achieve a dataset with daily data points which are then pushed forward in time by adding one day at a time and then compare with the time series for TCE. The correlation between the two datasets are shown in figure 5.8 as the coefficient of determination, R^2, of the linear correlation between the two datasets as a function of the time lag in days.

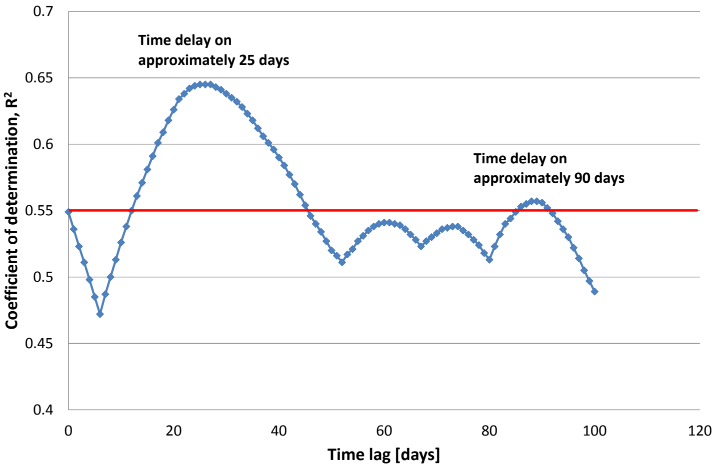


Figure 5.8: *The correlation between TCE concentrations and monthly pumping rates for period 2006 - 2010 when using different time lags. Two peaks stand out as the coefficient of determination is higher than when using no time lag. The red line mark the coefficient of determination at zero lag time.*

At zero lag time is the coefficient of determination relatively high and the best correlation between the two time series should therefore have a correlation coefficient higher than the point of origin on 0.55. The red line in figure 5.8 mark that level. Two peaks appear above the red line; one at a lag time of approximately 25 days and one at approximately 90 days. These are both very short lag times and indicates clearly that the location of the pollution is located close to the polluted well.

There will of cause be some uncertainties connected with the large intervals between the data points in the TCE time series. The same analysis has therefore been made with own measured data for the period from October 2011 to January 2012. The data was in that period sampled with a 2 week interval. An interpolation of the weekly pumping rates from June 2011 to January 2012 was used in the analysis. The two data series without any time delay appear from figure 5.9.

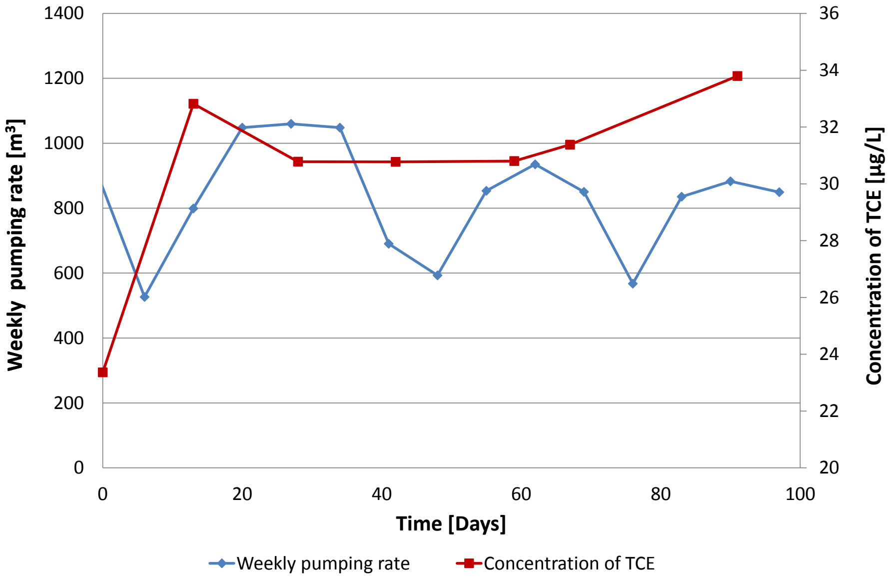


Figure 5.9: *Time series of weekly pumping rates and concentrations of TCE by own measurement, October 2011 to January 2012. No Time delay has been used in this graph.*

As it appear from figure 5.10, the clear result from the analysis of the rough time series is not achieved with the more detailed dataset. The result is, however, shorter and based on fewer points than when using the more rough time series for TCE and this might have en impact on the result. Besides that, only minor variations of the concentration of TCE was observed in that period which makes the unambiguity of the correlation between the data series less significant.

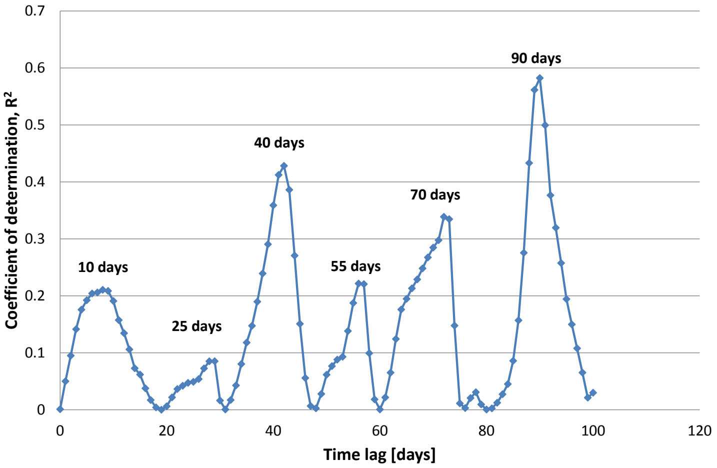


Figure 5.10: *The correlation between TCE concentration and monthly pumping rate in the period from October 2011 to January 2012.*

The result of the analysis is almost periodic with a peak approximately 15-20 days apart. The pumping rate is as mentioned variating from day to day and this behavior might be reflected in the time series of own measured TCE concentrations which shows small variations up and down from time to time. This could indicate that the short termed changes in pumping rate has more impact than expected. This is, however, also an explanation of the periodic result shown in figure 5.10 as two zigzagging datasets are compared, which must give either a very good correlation or a very pure correlation. The variations in concentration and pumping rate must therefore be at a larger scale to get the optimal results of this analysis. The cycles of the periodic graph is, however, close to the 25 days which was the most significant result of the analyses of the larger and more rough time series for TCE. By this analysis is the most significant peak observed at a lag time on approximately 90 days which correlated with the less markable peak from figure 5.8. The result of this analysis will therefore be a delay between the two time series of 25 to 90 days.

Full scale experiments conducted on B19

6

Three different full scale experiments have been conducted at the polluted well, B19:

1. Controlled changes of pumping rates
2. Level specific water samples
3. "Push, drift and pump back" experiment

The general purpose of these experiments is to identify the present position of the pollution hot spot.

The two nearest extraction wells has been kept out of operation at all time to avoid hydraulic disturbances during the experiments. The nearest active extraction well is thereby a private borehole at a farm roughly 1 km south-east of the polluted well, B19.

This chapter will describe each experiment by purpose, method, and result. All raw data and spreadsheets for calculations are attached on the enclosure CD of this report.

6.1 Changes of the pumping rate

A remarkable correlation is observed by comparing the historical time series of pollution and pumping rates. Section 5.3 describes the specific correlation of these two data series. It was estimated that the delay of a decrease or increase of the concentration of TCE, as a response of changing pumping rates, is about 25-90 days. The relatively large time steps between each point in the pollution time series does, however, make this estimate uncertain. A specific experiment of persistent changes of the pumping rate in B19 will support and specify the estimate of the time delay between pumping and concentration changes.

Purpose of the experiment

The purpose of the experiment of changing pumping rates is to investigate the effect of the changing rates may have on the concentration of chlorinated compounds in B19 and thereby estimate a more specific response time. The result will then be used in a simple estimation of the distance from the polluted well to the present hot spot of the pollution.

Procedure of the experiment

The first step of the experiment was to decrease the pumping rate in B19 to a minimum level of extraction for a period of approximately one month. The two other field experiments was conducted afterward which resulted in periods of no pumping from the well and some short-duration intense pumping. After the other experiment, the rate was increased to a high constant level. The changes in pumping rates appear graphically from figure 6.1.

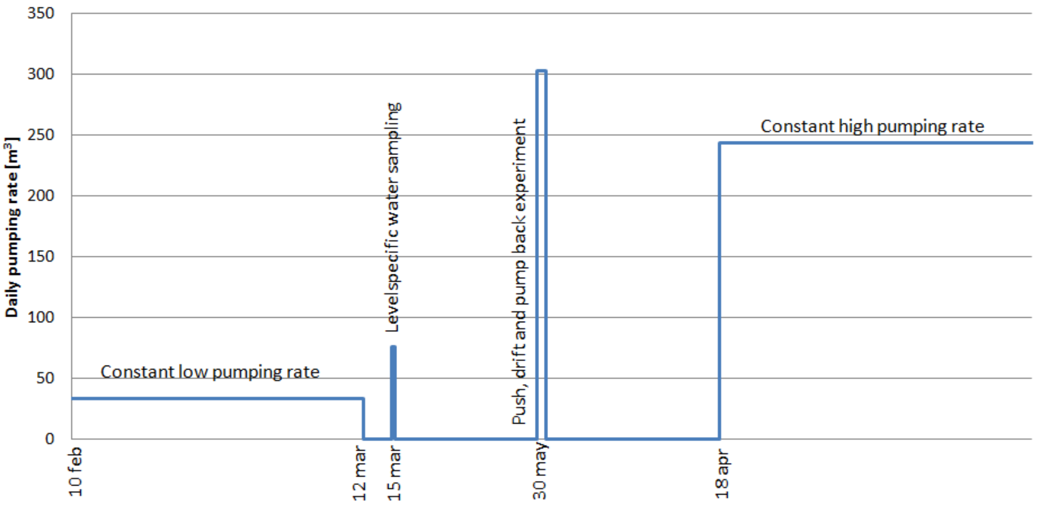


Figure 6.1: *Changes of the pumping rates for B19 at the time of the experiments from February to June 2012.*

It was expected that the concentration of chlorinated compounds would undergo the same variations as the pumping rate but with a certain time delay. It was however uncertain whether or not the pollution would react on sudden short-duration changes. The time delay is expected to be in the area of 25-90 days according to the time series analysis described in chapter 5.

The magnitude of the expected effect by the changes has been estimated from the time series of pumping rates and concentrations. Different points of the time series has been picked out for this estimation. The calculations of the selected parts of the series showed an increase of roughly 100% by the doubling of the pumping rate. A significant effect of the concentration of chlorinated compounds is therefore expected as a result of this experiment as the pumping rate from start towards the end of the experiment is increased by a factor 7.

6.1.1 Results from the experiment

To investigate possible effects of the changing pumping rates, water samples were extracted from the polluted well with a 1 week interval. The sampling period started February the 10th 2012 and went on to June the 1th 2012. In the period of the conduction of the other field experiments, the pump was not active most of the time. No water samples has been extracted in that period. The result of the experiment of changing pumping rates appear graphically from figure 6.2 as the concentration of TCE and the daily pumping rates as a function of time.

Minor changes in the concentration has been observed in the period of the experiment but not of the magnitude which was expected. The concentrations measured in the period of the experiment are, though, in general high compared with the entire time series from 2003 until today. It is possible that major changes in the pumping rate will not give quite as significant increase in concentration as expected. Most likely the effect have not showed jet. Some kind of effect is, however, proved as the concentration at 1 point decreases by 10 μg/L within 2 weeks. The observed variations of the concentration indicates that short-termed intense pumping is of more importance than expected. The increase by the two last points in the data series of TCE concentrations might be the beginning of the response of the constant high pumping. The delay time on 25 days can not be confirmed by the analysis; Nor can it be disproved as the small changes in concentration might be a response to changing pumping rates. No exact and precise tendencies has after 45 days with a constant high pumping rate appeared. The time series of concentrations measured from January to June 2012 and

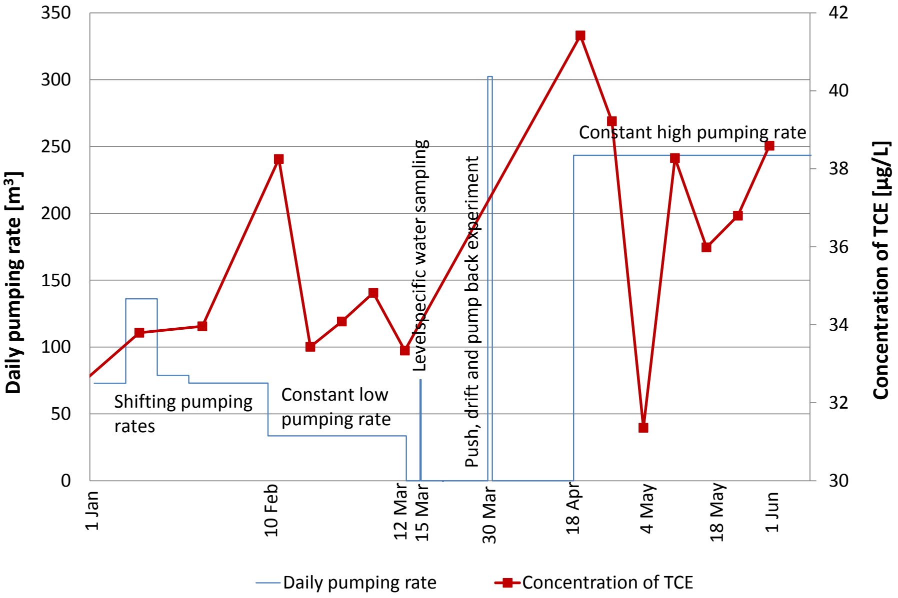


Figure 6.2: *The concentrations of TCE measured in water samples extracted with a 1 week interval from B19 in the period of the experiment with changing pumping rates. Pumping rates and measured concentrations from January to June 2012 is compared.*

the pumping rates of that period could be analysed by the time series analysis but the result will undergo the same uncertainties as the previous analysis described in section 5.3. More samples are necessary to achieve an unambiguous result of this experiment.

6.2 Level specific water samples

Knowledge of the depth of the pollution may be an important parameter in source tracking and is useful information in the discussion of possible removal procedures. Chlorinated compound has a higher density than water and will therefore dive deep into the aquifer. The vertical spreading of a spill with chlorinated compounds as a DNAPL (Dense Non-Aqueous Phase Liquids) will primarily be limited by the heterogenius geology. For further informations about the specific transport and spreading mechanisms of chlorinated compounds refers to appendix A. The geology in the immediate area around the polluted well B19 consists mainly of fine sand. Small variations as lenses of a low permeable material is therefore of vital importance of the vertical distribution of the pollution, which might be very wide or limited to a narrow interval.

Purpose of the experiment

The purpose of level specific water sampling is to identify the inlet of the pollution to the well by measuring concentrations of chlorinated compounds in different levels in both the screen section and the well liner. From the result will the vertical location and distribution of the pollution in the aquifer be estimated.

Procedure of the experiment

The experiment of level specific water sampling was conducted twice; both times by the same method and sampling procedure. The entire well was investigated the first time to clarify whether or not a crack in the 40 year old steel pipe is the inlet of the pollution to the well. Water samples was, in the first execution of the experiment, extracted with a 5 meter interval stretching from the lower part of the screen section 69 m b.s. to the middle of the well liner 35 m b.s. plus one at 16 m b.s. The levels of water extraction was selected on the basis of the video inspection of the well from 2005, described in section 2.1. The video inspection showed among others a possible crack in the well liner approximately 16 m b.s.

It was, at the time of the first execution of the experiment, uncertain how closely the sample could be extracted without disrupting the levels above and underneath it. Such a disruption would mean that the samples does not only repressent the desired level, but are a mix of the surrounding water from other levels as well. The first execution of the experiment indicated, however, good separation between the samples in different levels. It was therefore decided to investigate the screen section in the polluted well even further with a sampling interval of only 1 meter from 50 m b.s. to 69 m b.s.

The water samples were extracted by the use of a two pump system. This system consisted of a master pump to provide a constant stationary flow through the filter and well liner, and a smaller pump for the actual sampling. The water sample from a certain level represents the water below the small sampling pump. The concept of this method and its pros and cons is described further in appendix G.1. The master pump was placed above the screen section 20 m b.s. and worked with a rate of 11.5 m^3/h during the entire experiment. The water, which was extracted by the master pump, was discharged to the pond about 350 m from the well. Before the discharge to the pond, the water was lead through a simple aeration system to minimize the discharge of chlorinated compounds to the already polluted pond. Figure 6.3(a) shows the aeration system where the water splashes down on a board that splits the water into smaller drops and increases the evaporation of chlorinated compounds.

(a) Aeration system before outlet of the water from the master pump to the pond approximately 350 m east of the polluted well.

(b) Set up of the experiment. The black hose was used for the actual water sampling and the blue fire hose was used to transport the water from the master pump to the location of the water discharge.

Figure 6.3

At least 15 min passed between each sample extraction to ensure that each sample actually represented the level of the small sampling pump. The samples were extracted, treated, and analysed cf. the sampling procedure described in appendix E.

6.2.1 Results from the experiment

The concentration in each sample was found by analysis of the water samples by gas chromatography. The result is presented graphically in figure 6.4.

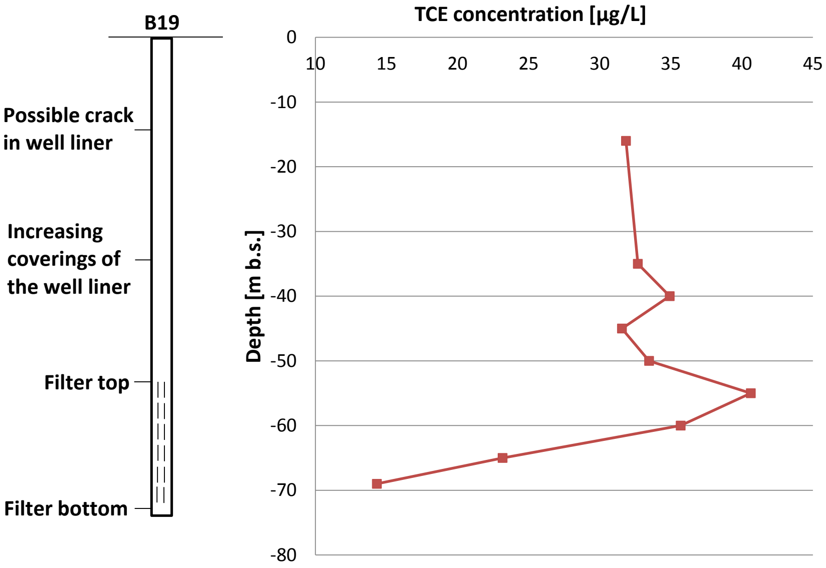


Figure 6.4: The concentrations found from the first execution of level specific water sampling the 8th of February 2012.

The concentrations of TCE increases from the bottom towards the top of the filter. Here, a small decrease in concentration is observed. The concentration of TCE in the other samples extracted above the Screen section is relatively constant. The minor variations are likely to be caused by uncertainties connected to the sampling and analysis procedure. This disprove that the crack, observed in the video inspection from 2005 about 16 m b.s., is the inlet of the pollution to the well. The pollution must therefore be assumed to be located at a deeper level than the crack but above the bottom of the screen section, as the concentration increases in the screen section. The concentrations of PCE was also measured in each sample and shows approximately the same tendency as for TCE. But because of the very low concentration in especially the screen section, the data quality is uncertain due to the sensitivity of the analysis. The concentrations of PCE in the level specific samples is therefore not taken into consideration in the valuation of this experiment. The concentrations and graphical representation are attached on the enclosure CD though.

In order to specify the level with the highest inflow concentration was the results compared with a flowlog from 2005, as the influx of water rarely is evenly distributed in the screen section interval. This means, that a high concentration of TCE in the influx water in an area with a low water inflow may show as a small or no increase in the concentration measured in the samples. The direct result from the water samples does therefore not represent the concentrations of the pollution in the inflowing water. The final result of the first execution of the level specific water sampling experiment is presented graphically in figure 6.5.

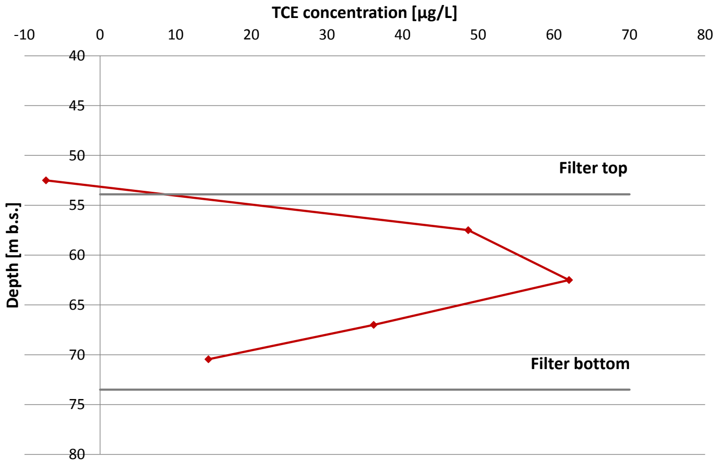


Figure 6.5: *The calculated concentrations of TCE in the inflowing water found from the first execution of level specific water sampling the 8th of February 2012.*

The calculated concentration in the inflowing water in the top of the filter turned out to be negative which is of course not possible. At that point should the concentration be zero and the negative value is assumed to be a reflection of the uncertainties in reading and using the flow log as only a graphical result of the log is available. The error is, however, small and the quality of the data is acceptable.

By comparison with the flowlog with the concentrations from the samples, a peak is clearly observed around 60 m b.s. which is within the filter interval. The second execution of the experiment makes this peak stand out even more. The result, by comparison with the flowlog, is shown in figure 6.6.

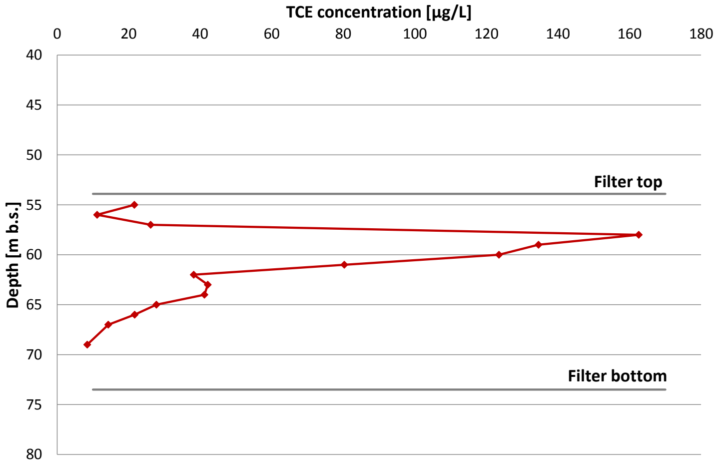


Figure 6.6: *The calculated TCE concentrations in the inflowing water found from the second execution of level specific water sampling the 15th of Marts 2012.*

The pollution seems to be stretching vertically over at least 15 m and the concentration in the inflowing water to the well is clearly peaking at 58 m b.s. The concentration at this point is calculated to 3 times as much as the concentration measured in the water samples. The magnitude, form and width of the peak should however be taken into more consideration than the exact calculated values because small changes in the reading of the flow log, used for the calculation, may give a great difference in the calculated concentration, as no exact values from the flow log is available. The position and the width of the peak do however not change.

The flow log from 2005 showed that the water influx was low in the interval from 59 m b.s. to 66 m b.s. This is right below the level where the highest concentrations of TCE was measured. The reason of the lower influx of water in that area may be that the blocking of the screen section increases in that area but could also be a result of geological lenses consisting of finer particles in that level. A natural gamma log is often used to clarify the changing geology from wells and was also conducted at B19 in 2005. The flowlog and the natural gamma log is attached as appendix D. Notice that the scale is in m below reference and not terrain. From the reference point up to terrain is 1.6 m.

The natural gamma log shows a very small effect in the same area as the low influx was observed by the flow log. It is not possible to predict whether or not a low permeable layer is the reason of this effect from the natural gamma log alone but the fact that the influx is low in that same area and the concentration of TCE in the inflowing water peaks just above gives strong indications of the existence of a low permeable layer in that depth. The pollution might for now has stabilised on this layer of finer particles.

The results from the level specific water samples proves, that the chosen method, in this case, is useful in the level specification of pollution influx to the well. Also, it is shown that it is possible to use sample intervals as small as 1 meter. The short intervals between the sample extraction levels has been very useful in this case as they show a significant peak of TCE in the inflowing water.

6.3 Push, drift and pump back experiment

In chapter 4 the complex geology in the area of Varbro well field was described. The uncertain geological changes makes it difficult to predict the transport of water and pollutants. Besides that, the connection between pumping rates and measured concentrations in the polluted well, described in chapter 5, indicated that the hot spot of the pollution is located relatively close to the well. Knowledge of local hydraulic parameters is therefore, especially in this case, extremely useful in the process of source tracking.

Purpose of the experiment

The “Push, drift and pump back” experiment is a single well tracer test which makes the geology near the well decisive in the estimates of the local parameters. The purpose of this experiment is to determine the specific pore water velocity of the area around the polluted well by injecting a non toxic conservative. This experiment will by numerical model calculations give a close estimate of the gradient, effective porosity, and the hydraulic conductivity. The pore water velocity can be estimated by equation 6.1.

$$v_p = -\frac{T}{b} \cdot \frac{dh}{dx} \cdot \frac{1}{n_{eff}} \text{ , where } K = \frac{T}{b} \tag{6.1}$$

where:

v_p	Pore water velocity [m/s]
T	Transmissivity [m^2/s]
b	The depth of the aquifer [m]
dh/dx	The gradient, I, (Change in hydraulic head by the distance) [-]
n_{eff}	The effective porosity [-]
K	Hydraulic conductivity [m/s]

Procedure of the experiment

The principle of the "push, drift and pumpback" experiment is to inject a chloride tracer into a well, let it drift in a period of time, and then pump it back to the same well while continuously measuring the chloride concentration. At this experiment is used Sodium Chloride as a tracer.

A logger was used for measurements of the pressure and the conductivity, which afterwards was recalculated to a chloride concentration using a standard curve. The logger was placed in the top of the screen section. where the water influx cf. the flow log from 2005 [Andersen et al., Januar 2006] is high.

4 kg of Sodium Chloride dissolved in 2000 L water, equaling 1213 mg chloride/L, was injected to the polluted well B19 with a pumping rate of 2.2 m^3/h. 2000 L pure water was hereupon injected to the well with the same rate to insure that the saline solution was pushed out from the filter and into the aquifer. This will leave the injected chloride in a ring around the filter. From this point, the solution was left to drift naturally in a period of time. These steps of the experimental procedure are sketched in figure 6.7. Notice that the size and shape of the peaks in figure 6.7 is determined by the factor of dissolution and the rate of pumping.

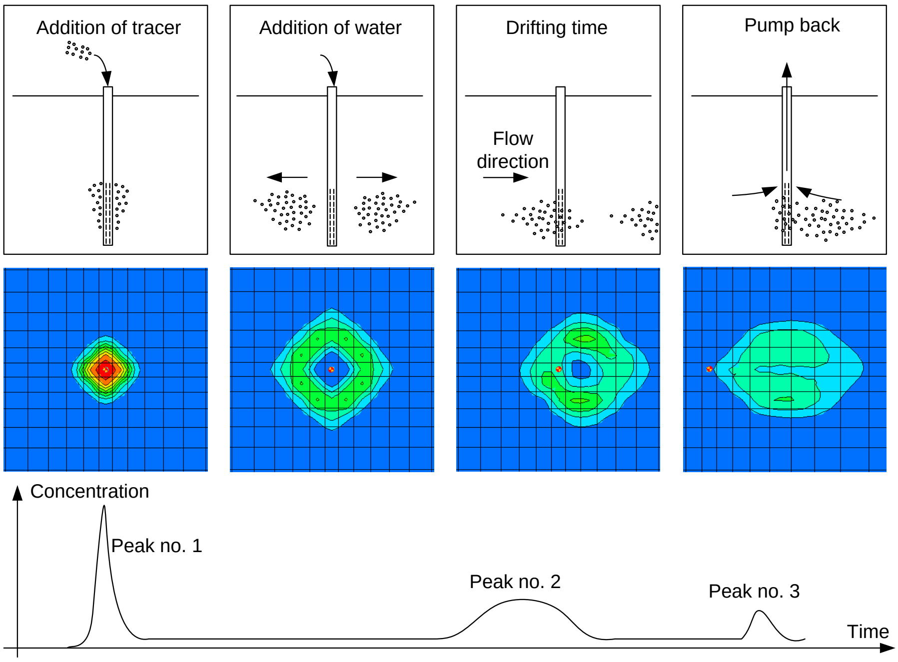
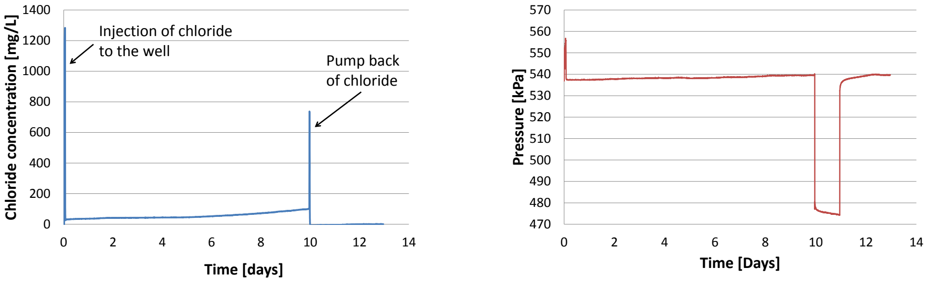


Figure 6.7: *The experimental procedure of the "Push, drift and pump back" experiment shown by an illustration sketch, a model simulation of the same situations, and the expected result of the experiment.*

The drifting time is normally determined from the time that the ring of chloride passes the logger in the well by drifting. In this case, that is expected to take a long time as the soil material primarily is expected to be very fine sand. A to long drifting time will result in higher dilution of the chloride and the possibility of losing it before pumping it back. After 10 days of drifting was the chloride tracer therefore pumped back with a rate of 12.6 m^3/h even though the chloride ring had not jet passed the logger. The pumping continued until the conductivity measured by the logger was equal to the background concentration measured before the injection of the salt.

6.3.1 Results from the experiment

The chloride concentration was by a standard curve calculated from the conductivity measured by the logger. The result appear from figure 6.8(a) along with the pressure.



(a) Calculated concentration of chloride throughout the experiment.

(b) The pressure measured by the logger throughout the experiment.

Figure 6.8: *The observation data from the "Push, drift and pump back" experiment on B19.*

Two peaks appear from the data; one at the injection point and one at the time of the pump back. The total mass, which has been pumped back, can be calculated by numerical integration of the concentration curve. This calculation shows that approximately 70% of the chloride has been pumped back. The chloride ring around the filter has presumable not moved much after the injection which verify the fact that the well is surrounded by fine-grained material and that the pore water velocity therefore is low.

The two nearest boreholes has been shut down in the period of the experiment which clearly shows on figure 6.8(b) as no interruptions of the pressure is observed in the drifting period of the experiment.

A numerical model by the GMS, groundwater model system, software package is used to simulate the different states of the experiment. The model is simply structured as a 100 x 100 m square with 20 layers of 5 m each. A well is placed in the middle of the grid. The grid is refined around the well down to a cell size on 0.2 x 0.2 m. The model consists of just one geological material, assuming that it is one uniform aquifer. To keep the gradient constant, the pressure is fixed to a constant level at the boundaries.

During the experiment the chloride is injected to the top of the well and then pushed out into the aquifer by an amount of pure water. The chloride will thereby be pushed out in the screen section of the well with a time delay depending on the pumping rate. This may be modeled by setting the hydraulic conductivity equal to 0 in the cells surrounding the cell in every layer of which the well is located. This will consequently "isolate" the well cells in every layer with the exception of those layers corresponding to the screen section. Furthermore, the well cells above the screen section should have an effective porosity of n_{eff}=1, which means that there is no solid material in the cells, only water. This would give a time delay before the chloride reaches the observation point at the level the logger was monitored. The principle of this conceptual model is sketched in figure 6.9.

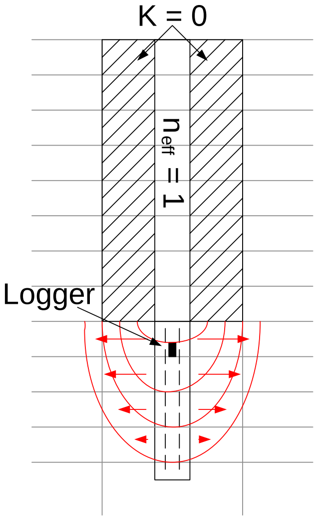


Figure 6.9: *A model simulation of the actual event could be put up in this way by "isolation" of the well cells which will have a effective porosity on 1. The red lines in the bottom illustrates how far the tracer has reached at different times after the injection as it will not flow equally from the entire screen section.*

The conceptual model may describe the progress well but is, however, also quite complex and time demanding. It is assumed that it is reasonable to model the operation by adding a concentration directly to the well cells in the layers corresponding to the filter interval. The chloride will be injected with a delayed starting point calculated from the observation data.

The injection and the pump back step in the experiment, results in a certain change of the pressure. Since whether the gradient or the effective porosity has any effect on that change in the model,the hydraulic conductivity is estimated by calibrating to the pressure measurements from the logger. Figure 6.10 shows the variation of the pressure compared to the point of origin for the measured data and the model output of the best fit. The model does not take certain reservation to possible clogging of the screen section. The estimated hydraulic conductivity might therefore be a little too low as a clogging would result in an extra increase in the pressure by the injection and a larger pressure drop by the pump back. The gradient will allow for this uncertainty.

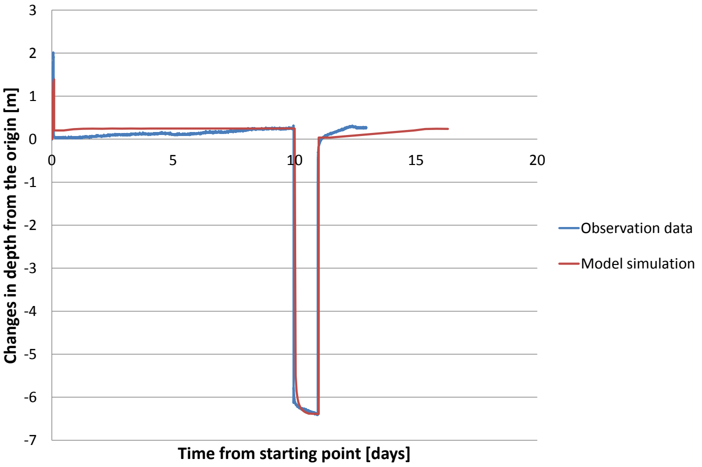


Figure 6.10: *Changes of the water level from its origin during the "Push, drift and pump back" experiment with observed data and model simulation. The best fit was achieved when using a hydraulic conductivity on* $K = 2.6 \cdot 10^{-5}$ *m/s.*

Using the estimated hydraulic conductivity on $K = 2.6 \cdot 10^{-5}$ m/s, the model was calibrated on the basis of the measured concentrations of chloride by changing the gradient and the effective porosity one at a time. There will, in the calibration, be focused on the peak from the pump back of the chloride. The gradient influence primarily on the width of the peak whereas the effective porosity influence on the hight. The sensitivity of these parameters appear from figure 6.11 and 6.12.

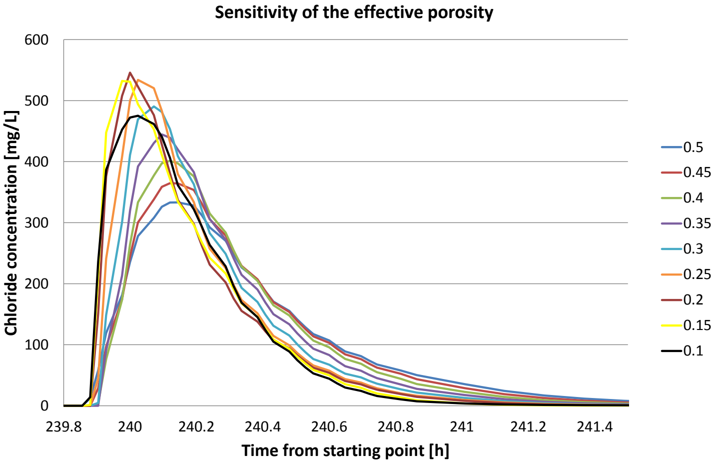


Figure 6.11: *The sensitivity of the effective porosity was investigated by changing the effective porosity while keeping every other variable parameters fixed.*

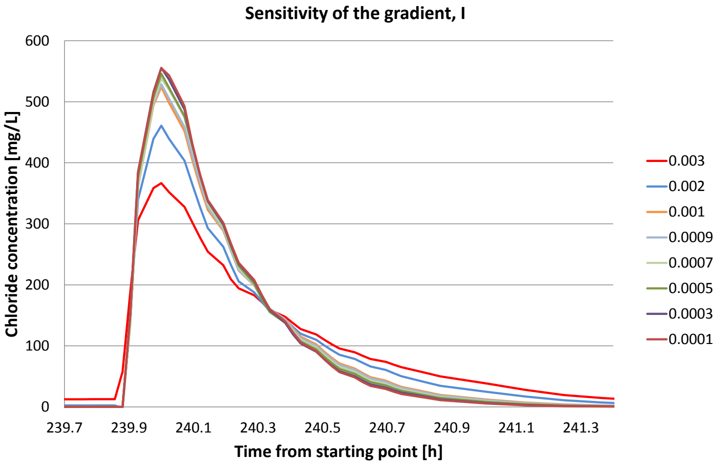


Figure 6.12: *The sensitivity of the gradient was investigated by changing the gradient by the boundary conditions while keeping every other variable parameters fixed.*

As a point of origin, an estimate of the gradient was made by using the groundwater potential map from chapter 4. The gradient was estimated to 0.0052 and the best fit by modeling to the observed data was then found by comparing the shape of the peaks, the difference in mass in percentage, and the hight of the peaks. In order to get a reasonable fit was both the effective porosity and the hydraulic conductivity changed. The best fit, using a gradient on I = 0.0052 appear from figure 6.13.

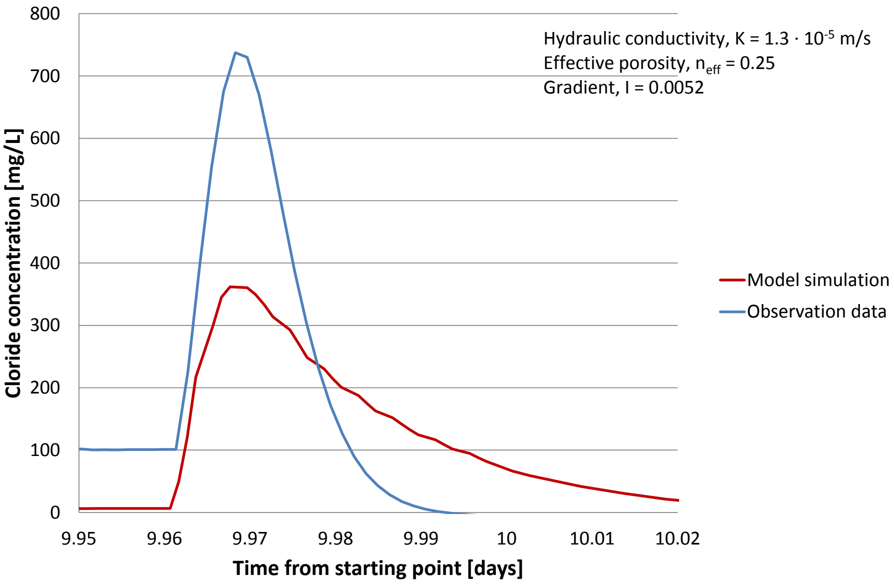


Figure 6.13: *The best fit between model simulation and observed data when using the estimated gradient on I = 0.0052.*

By the visual point of view the model simulation does not match the observed peak very well. A better fit was therefore tried by changing the gradient and keeping the hydraulic conductivity fixed at K = 2.6 · 10^{-5} m/s, but still using values for the gradient that seemed realistic according to the estimate of the groundwater potential of the area. The best fit was found by using a lower gradient. Figure 6.14 shows two attempt of fitting the model simulations to the observed data using "normally expected" values, where one is giving the lowest percentage difference in mass and the other i giving the lowest difference in the hight of the peaks.

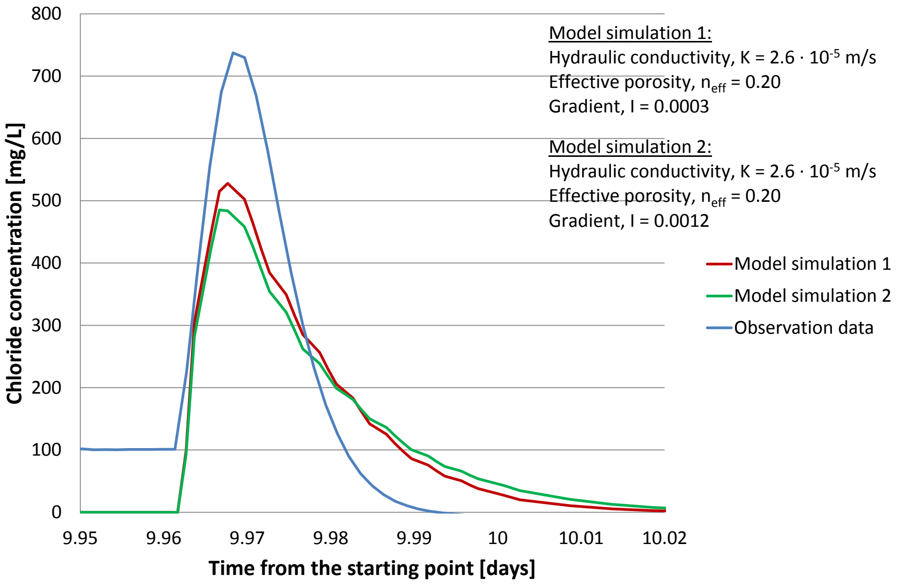


Figure 6.14: *The best fit between the model simulation and observed data, found by keeping the hydraulic conductivity fixed from the calibration to the pressure changes and using different values of the gradient and the effective porosity.*

From the visual point of view the simulations still does not give a good match but better than when using a higher gradient. A last attempt was made by letting all parameters, including the hydraulic conductivity, change to the extreme to achieve the best fit. But because the gradient was already very low, only small changes were observed and an even lower gradient would only slightly improve the shape of the peak. It has not been possible to achieve a better fit with this model set up.

The values used for the different fits are all listed in table 6.1 along with the calculated pore water velocity of each calibration attempt.

Table 6.1: *The values used in three different attempt of fitting the model simulation to observed data.*

	Hydraulic conductivity [m/s]	Gradient	Effective porosity
Fixed gradient	$1.3 \cdot 10^{-5}$	0.0052	0.2
Fixed hydraulic conductivity	$2.6 \cdot 10^{-5}$	0.0003-0.0012	0.2
No fixed values	$2.6 \cdot 10^{-5}$	0.00005	0.18

The different calibration attempts gives more than one result. The gradient should have an value near the estimated value from the measurements of the water levels in the area of Varbro well field.

But using that value means that the hydraulic conductivity has to be lowered to achieve a good fit which consequently give a mismatch between the simulated and observed pressure changes. Using lower values of the gradient is a better visually fit achieved with a lower hight and mass difference between the observed data and the model simulation.

The low gradient may however not be unrealistic when comparing to the knowledge of the geology. From the geological conceptual model formulated in chapter 4 the groundwater deeper in the aquifer might be almost stagnant and the estimated gradient from the measured water levels may only influence the upper part of the aquifer around B19. This possible explanation is sketched in figure 6.15.

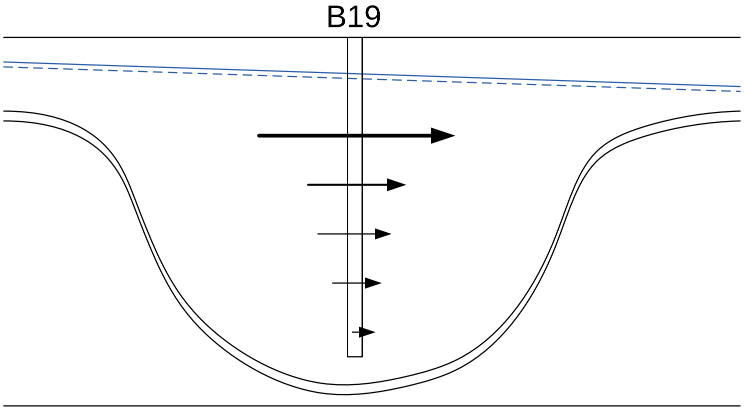


Figure 6.15: Based on the conceptual geological model discussed in chapter 4 may the groundwater flow in the top of the aquifer be much higher than in the bottom. This gives a high gradient even though the water in the bottom of the aquifer is almost stagnant.

This would explain why either the gradient or the hydraulic conductivity have to be very low i order to achieve a good fit to the observed data.

6.4 The overall results of the full scale experiments

Three different full scale experiments has all given new important informations about the pollution at Varbro well field.

In the first experiment, the pumping rates were changed for a prolonged period of time in order to investigate any possible effect on the concentration of chlorinated compounds. The lowest expected response time on approximately 25 days, found by a time series analysis described in chapter 5, was proven wrong by the field experiment. Minor changes has been observed which indicates that short-termed high intensity pumping is affecting the concentrations as well. No general and precise effect has been identified after 45 days, but by the time series analysis were significant correlations between concentrations of TCE and the rates with a lag time of 90 days as well. The water sampling should be continued until an effect is documented.

In the second experiment, level specific water samples were extracted from the polluted well two times with different intervals in depth. The results showed, that the influx of the pollution occurred in the screen section 58 m b.s. On the bore logging from 2005, a small change on the natural gamma log in 60-65 m b.s. is observed [Andersen et al., Januar 2006]. This indicates a change in the geology, which might be a thin low permeable layer. In the same interval, the water influx through the screen section is low, which could be caused by blocking of the filter or by a less permeable layer in that interval. This gives reason to believe that the pollution has stopped and formed a pool of DNAPL on this possible thin low permeable layer, which correlates with the fact, that the highest concentrations in the inflowing water was found 58 m b.s.

The third field experiment was a "Push, drift and pump back" experiment. This experiment gave more than one possible result, and the pore water velocity is therefore calculated from each of them. From the calculated pore water velocities and the distances to each of the possible sources of the pollution, a rough calculation is made of the transport time from the source to the polluted well, and thereby a guess on the year of the spill. The result is listed in table 6.2.

Table 6.2: *Three different results were achieved by the "Push, drift and pump back" experiment. The pore water velocity has been calculated from each of them. Assuming that the pollution does not reach B19 before 2003 is the transport times from the different possible sources and the year of the spill estimated.*

Fitting attempt	Possible source	Pore water velocity, v_p [m/s]	Transport time [years]	Year of spill
Fixed Gradient	Dry cleaner site Pond Military area	$2.7 \cdot 10^{-7}$	29 41 93	1974 1962 1910
Fixed hydraulic conductivity	Dry cleaner site Pond Military area	$5.3 \cdot 10^{-8}$ - $1.6 \cdot 10^{-7}$	50 - 150 70 - 210 160 - 480	1853 - 1953 1793 - 1933 1522 - 1843
No fixed parameters	Dry cleaner site Pond Military area	$7.1 \cdot 10^{-9}$	1117 1563 3573	886 440 1571 B.C.

Chlorinated compounds was first imported to Denmark in the 1930s. This eliminate the area of the vehicle wash ramp in Skibsbylejren as a possible source, as the pollution by the estimated values should have been spilled latest around 1910 to be able to show concentration in the polluted well in 1993. Both the lake and the dry cleaner site is in two of the cases possible. The dry cleaner was operating only in the 1960s, which is in good correlation with two of the cases. This makes the dry cleaner site very possible as the source of the pollution.

The calculated transport times and year of the spill is however just a result of a rough calculation, and should only be used as indicative values.

An influence area has been created from the results listed in table 6.2 by using the two pore water velocities that gave the most realistic result: $v_p = 2.7 \cdot 10^{-7}$ m/s and $v_p = 1.6 \cdot 10^{-7}$ m/s. As chlorinated compounds first was imported in the 1930s will this be the outer limit. It is assumed that the pollution did not happen after 1990 which thereby account for the inner limit. This output of these rough estimations appear from figure 6.16. The dotted line marks 1970 as the import of the compounds peaked in the 1960s and 1970s.

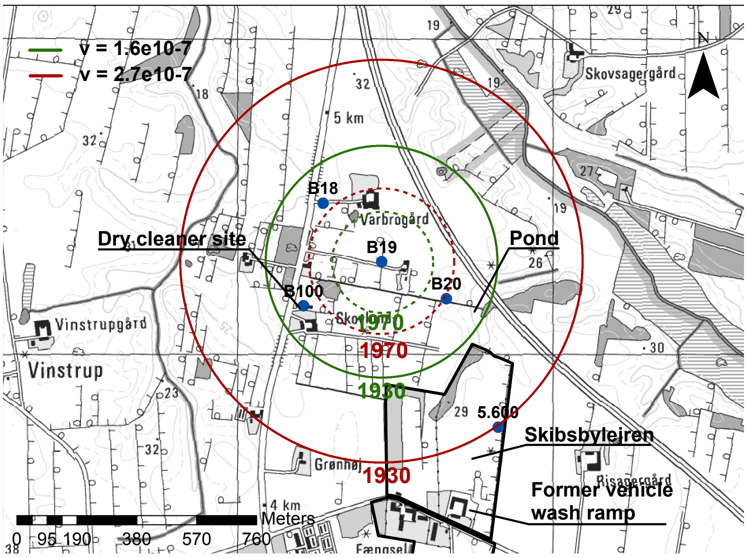


Figure 6.16: *Influence area estimated, calculated from 2 different pore water velocity and historical limitations connected to chlorinated compounds. The different pore water velocities gives quite different results.*

The two different pore water velocities used in figure 6.16 gives quite different results and illustrated that the sensitivity of these rough calculations are high. In both cases is the vehicle wash ramp in Skibsbylejren, however, excluded as a sources but the northern area of Skibsbylejren is still in the influence area.

7

Development of a solute transport model for estimation of the pollutant influence area by particle tracking

A simple numerical model has been set up by the use of the GMS, groundwater model system, software package. The purpose of this model is to narrow down a influence area, in which the pollution should be located, on the basis of the results from the full scale field experiments and the achieved knowledge about the geology and water flow direction of Varbro well field.

The model will focus on the area around the polluted well, B19, and the locations of the possible sources of the pollution. The model area will therefore cover a relatively small area. The grid is refined around the polluted well down to a cell size on 5 x 5 m. From the polluted well is the cell size increased by 5 % to a maximum cell size of 50 x 50 m.

Most of the model will be limited by a no flow boundary which is drawn from the potential contour lines. A no flow boundary does not allow the water to flow out of the model. Figure 7.1 shows the modelarea and the different types of boundaries used in the model.

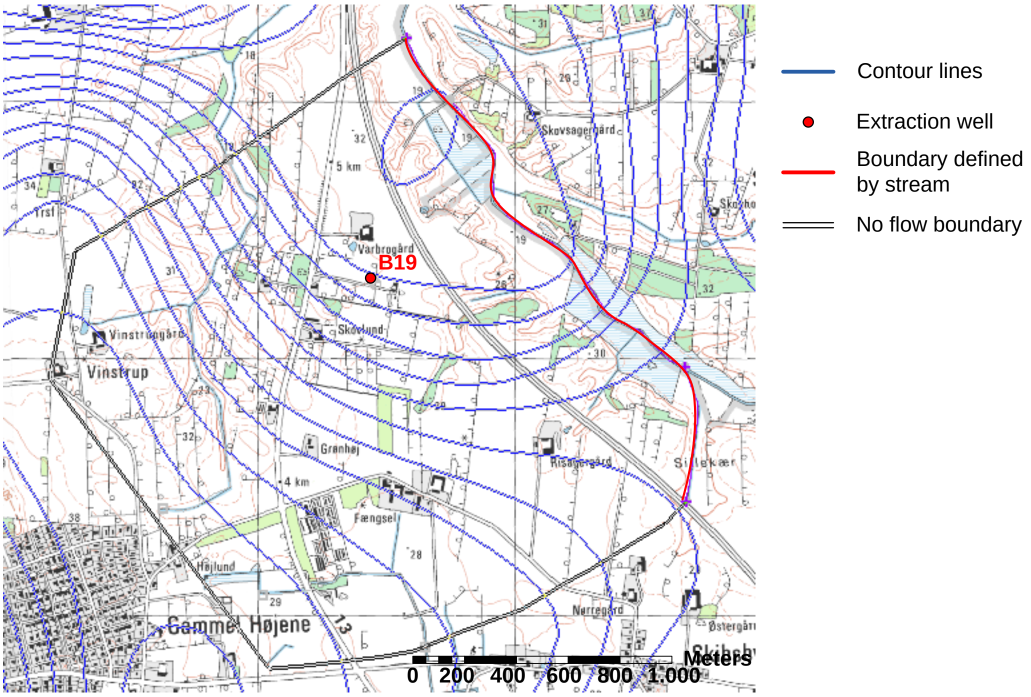


Figure 7.1: The model area and the boundary conditions used in the solute transport model.

On the northeast side of the model the boundary is defined by a stream (Varbro Å). Two different kind of boundaries can be used here: Specified head boundary or drains. The specified head boundary allows all water to flow through the model boundary without any limitations. The drain has the same effect but is limited by a drain conductivity. In the calibration of the model both of these boundary types will be used.

Hjørring Municipality has made a larger groundwater model covering the entire municipality. This model will be referred to at the Hjørring model. The Hjørring model will be used as an offset for this solute transport model where specific values will be used as starting values. The geological layers from the Hjørring model will also be used in this model. These consist in general of 5 geological layers where only 4 of them covers the area around Varbro well field. Layer 3 is mostly the broadest layer and covers the depth of the screen section of the polluted well. This is the depth of most interest because the pollution according to the level specific water samples is located 58 m b.s. Layer 3 is therefore refined by splitting it into 17 thinner layers. All together the model consists of 20 layers. A vertical cross section of the model is showed in figure 7.2.

7.1 Calibration of the model

The model is calibrated according to observation data from synchronous measurements of the water level in a non pumping situation. Every observation well used in the calibration of the model is located in central parts of the model. The allowed deviation between observation and model simulations is set to 1.5 m. The model is calibrated by primarily changing the hydraulic conductivity of the layers. Even though the 4 original layers has been divided into 20, the old layers will be used to define the different zones. The hydraulic conductivity will therefore be defined by 4 different materials in the GMS which means that material 3 will cover 17 layers. This is illustrated in figure 7.2. The forth zone is very thin and only present in a small part of the model. The material zone covering this layer does not appear from figure 7.2.

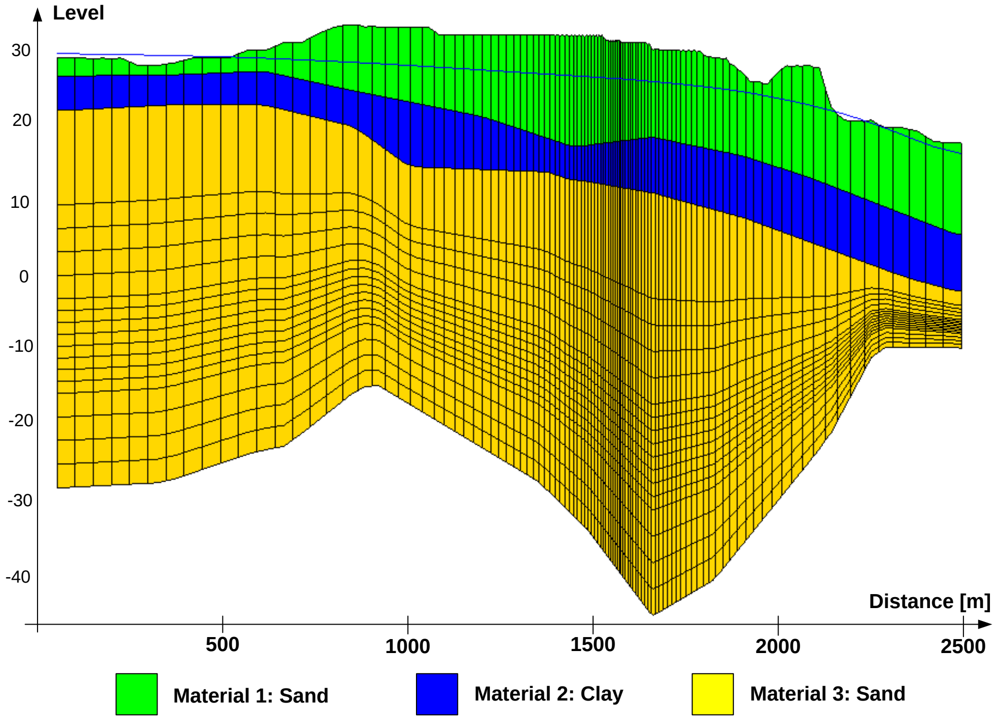


Figure 7.2: *The different zones which defines the hydraulic properties in the model. Material 3 covers 17 layers while the others only cover one layer.*

The boundaries of the model is of great importance to achieve a correct water flow. Three different attempts on calibration by using three different options for the boundaries has therefore been made.

By letting the northeast boundary be a specified head boundary, one calibration of the model was performed. By the calibration, most of the observation points was within the accepted interval. The points in the area of the pond was calibrated higher than the measured water levels. The model does however not take any consideration to the pond as it is assumed not to have a greater impact on the groundwater flow. The calibrated model and the deviations is seen in figure 7.3 where the green bars shows observation point in the allowed interval. If a bar is yellow is the error larger than allowed but less than 200% while the red bars are erros larger than 200%.

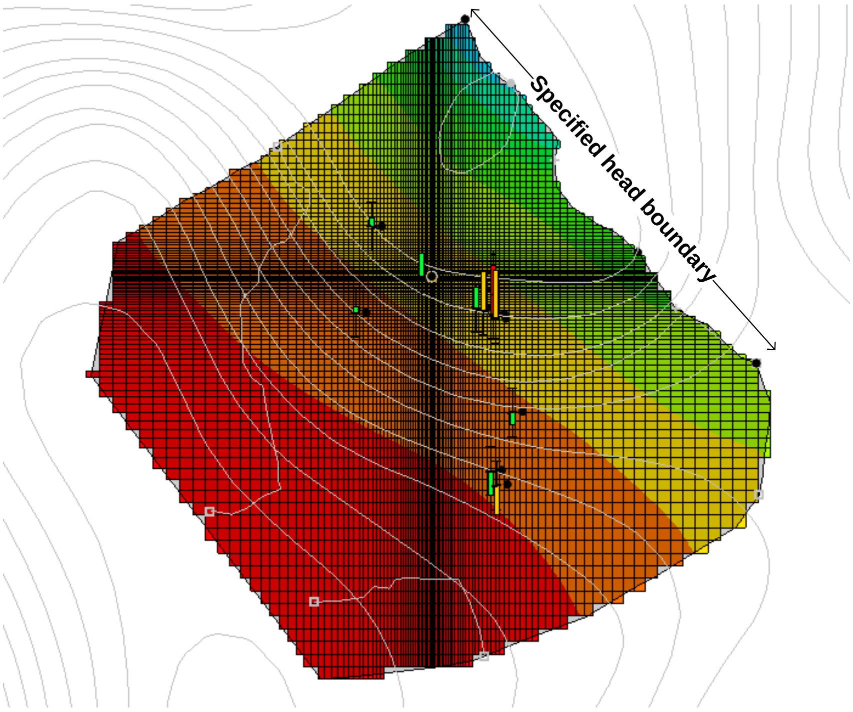


Figure 7.3: *Calibration 1: The stream is used as a specified head boundary.*

The general calibration is acceptable due to the observation points but by comparison with the contour lines the water does not seem to have the desired flow direction. The geology is thereby not itself leading the water in the expected direction. The expected direction might however not necessarily be the right one. This calibration will be referred to as calibration 1. Selected parameters used in the model is listed in table 7.1.

The stream used as the northeast boundary branch into two smaller streams at the upper part. The lower part of the stream might, because of the reduction, have a limited or lower contact to the groundwater. This part is therefore changed to a drain with a drain conductance of $1 \cdot 10^{-6}$ m^2/h and a new calibration is made. As for the other calibration the points by the pond is calibrated higher than the observation but the calibration in general is acceptable. This calibration attempt will be referred to as calibration 2. The result appear from figure 7.4 whereas the parameters used in the calibration appear from table 7.1.

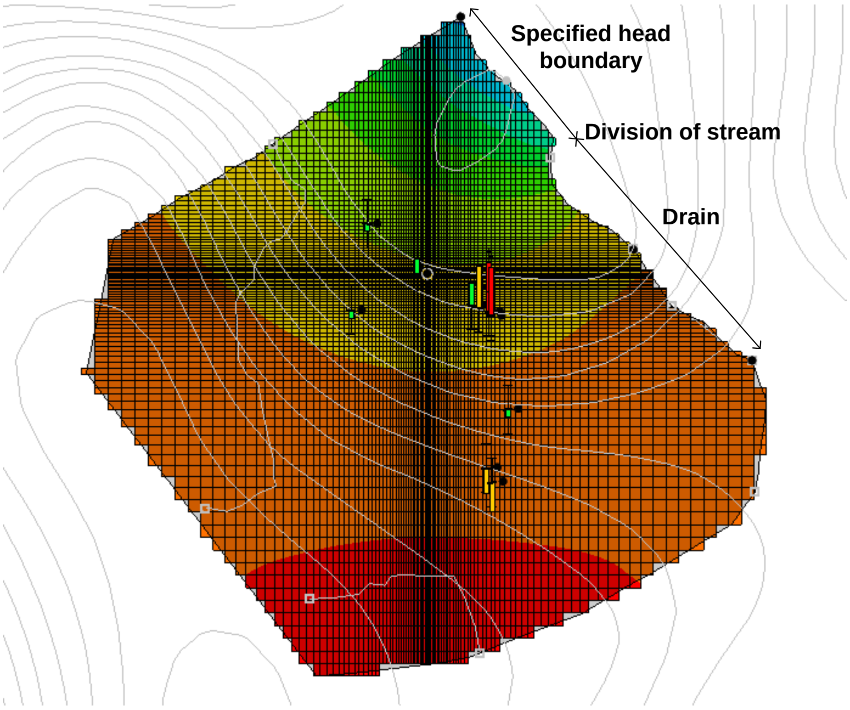


Figure 7.4: *Calibration 2: A specified head boundary is used down to the point the stream split into two smaller streams. From there, the flow out through the boundary is limited by a drain conductance.*

The division of the stream into two smaller streams does not seem to lead the water in the exact expected direction either but might be a better option than the before mentioned. By making the specified head boundary longer and the drain shorter the model will be forced to match the counter lines. A calibration of the model under these boundary conditions has therefore also been made for comparison. There is however no justification of this choice of boundary conditions, but if the flow direction of the water is not right, a solute transport model based on it will be misleading. This calibration will be referred to as calibration 3. The result is shown in figure 7.5 and table 7.1, respectively.

By using three different possibilities of defining the northeast boundary of the model three acceptable calibrations are achieved. The first attempt by letting the entire boundary be a specified head boundary is the most common and reliable way of defining the boundaries whereas the other two attempts are marked by expectations to the direction of the water flow. The fact that the stream divides into two smaller streams at the upper part of the boundary might though be of importance whereas there is no geological justification of the boundary used in the calibration 3. The hydraulic conductivities used in every material zone in the different calibrations is summarised in table 7.1, where the hydraulic conductivities used in the Model from Hjørring Municipality is listed as well.

Table 7.1: *The hydraulic conductivities in the 4 material zones used in the model in the three different calibrations. For comparison is the hydraulic conductivities used in the Hjørring model for the same layer showed. All values are given in m/s.*

Material zone	Soil type	Calibration 1	Calibration 2	Calibration 3	Hjørring Municipality
1	Sand	$5.5 \cdot 10^{-5}$	$1.2 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	$6.7 \cdot 10^{-6}$
2	Clay	$1.7 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$1.7 \cdot 10^{-6}$	$1.6 \cdot 10^{-7}$
3	Sand	$2.7 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$	$3.1 \cdot 10^{-5}$	$5.0 \cdot 10^{-4}$
4	Clay	$5.0 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$

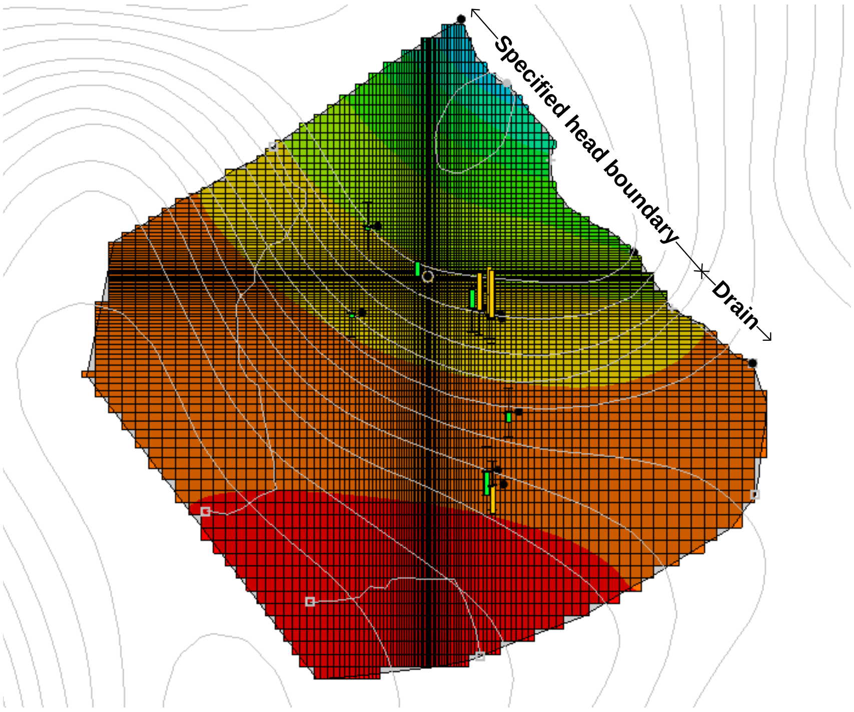


Figure 7.5: *Calibration 3: Most of the boundary is classified as a specified head boundary while the south end of the boundary has the properties as a drain. There is no justification of this way of splitting the boundary but the result match the counter lines better than in the 2 other calibrations.*

The values of the hydraulic conductivities used in the different calibrations is in the approximate magnitude as the values used by Hjørring Municipality. Also, they correspond well with the saturated hydraulic conductivities found by laboratory analysis of soil samples from the area of Varbro well field and the “Push, drift and pump back” experiment. For comparison, these values are summarised i table 7.2.

Table 7.2: *The hydraulic conductivities found by laboratory and field measurements respectively.*

Analysis of soil samples		
Depth [m b.s.]	Soil type	Hydraulic conductivity [m/s]
5	Sand	$3.8 \cdot 10^{-6}$
12	Silt	$2.2 \cdot 10^{-7}$
19	Clay	$2.7 \cdot 10^{-8}$
27	Sand	$1.6 \cdot 10^{-5}$
36	Sand	$7.6 \cdot 10^{-6}$
39	Clay	$1.2 \cdot 10^{-8}$
50	Clay	$3.4 \cdot 10^{-8}$

“Push, drift and pump back” experiment		
Depth [m b.s.]	Soil type	Hydraulic conductivity [m/s]
0-80	Sand	$2.7 \cdot 10^{-5}$

Assumable, the analysed sand sample from 27 m b.s. represents the primary aquifer in the area of Varbro well field as it is collected between an upper and a lower clay layer where the lower clay layer is expected to define the bottom of the aquifer. The hydraulic conductivity measured from that sample is very similar to both the value found by the “Push, drift and pump back” experiment and the values found by calibration of the model by GMS in material zone 3. This correlation support the model calibrations and makes it more reliable. Still, the general flow direction of the three calibrations is clearly different but the effect it will have on the solute transport modeling is uncertain. This will be investigated by backward and forward particle tracking.

7.1.1 Particle tracking for valuation of the calibrated model

Particles has been added on the water table surface at the locations of the possible sources for a tracking forward in time to clarify whether or not they will be drawn to the polluted well in any of the three calibrations. Average values of yearly extraction rates has been used on the three wells in the particle tracking. As the rates has been changing over time 3 different pumping situations has been used. These are listed in table 7.3.

Table 7.3: *Three different average values of the yearly extraction rates in 5.5631, B19 and B20. All rates are in [m^3/h].*

	B18	B19	B20
Average extraction rates from 1996 to 2011 [m^3/h]	10.3	7.5	4.8
Average extraction rates in 1996 [m^3/h]	11.2	7.4	5.3
Average extraction rates in 2011 [m^3/h]	8.4	5.3	3.5

The three calibrations showed quite different particle pathways from the locations of the possible pollution sources. The wells the particles appear in is showed in table 7.4.

Table 7.4: *Appearance of particles in any of the three extraction wells at Varbro well field by addition of particles to the top of the water surface at the locations of the three suspected sources of the pollution. In cases where the particles appear in a well at high extraction rates only in used: (Yes).*

Starting location	Calibration	Appearence of particles		
		B18	B19	B20
Dry cleaner site	1	No	Yes	No
	2	Yes	No	No
	3	Yes	(Yes)	No
Pond	1	No	No	(Yes)
	2	No	No	Yes
	3	No	No	Yes
Skibsbylejren	1	No	No	No
	2	No	No	Yes
	3	No	No	(Yes)

Of all three calibrations, only one showed a flow of particles from the location of the dry cleaner site to the polluted well, B19, no matter what pumping situation was used. This was calibration 1. Particles from the location of the dry cleaner site does, however, also appear in the polluted well in calibration 3, but only when high flow rates are used on this well.

The particles added at the location of the pond and Skibsbylejren does in non of the cases appear in the polluted well, but is mostly flowing towards B20. In chapter 4 it was discovered that the polluted well most likely not was in hydraulic contact with the two other extraction wells at Varbro well field. The geological layers used in the model does, however, not take this into account. The extraction flow at B18 and B20 was therefore set to zero in order to investigate whether or not particles from the three possible sources then would appear in the polluted well. The result appear from figure 7.6, 7.7, and 7.8.

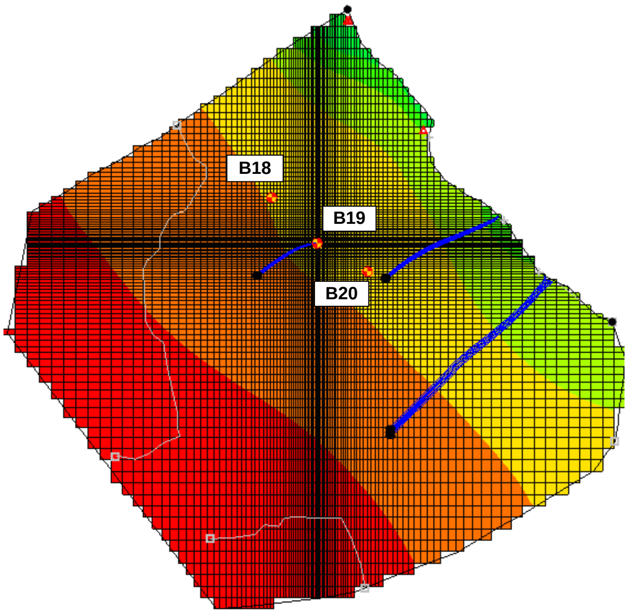


Figure 7.6: *Calibration 1: Particle tracking when only B19 is pumping. The situation has not changed from when all pumps where pumping.*

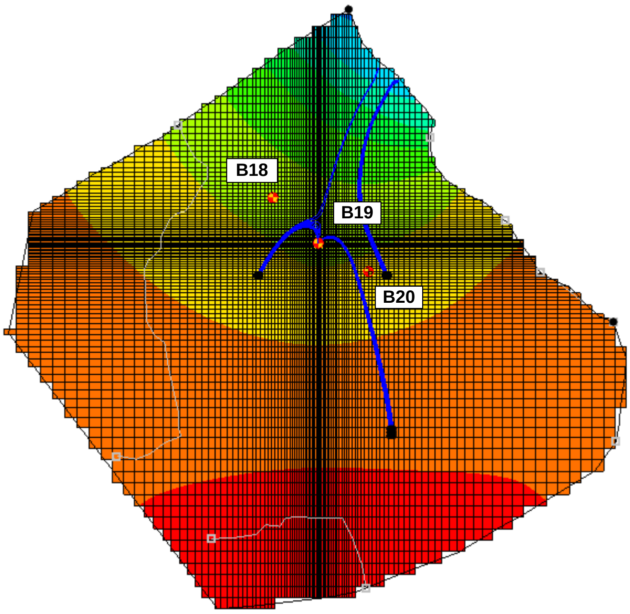


Figure 7.7: *Calibration 2: A part of the particles from the dry cleaner site appear in B19 depending on the extraction rate when this is the on active well. Also particles from Skibsbylejren appear in B19. This is the only calibration where this happens.*

The particles from the location of the dry cleaner did in all calibrations appear in the polluted well, but it is only possible to drag particles from Skibsbylejren to the polluted well with calibration 2. The particles added at the pond will in all cases flow out of the model.

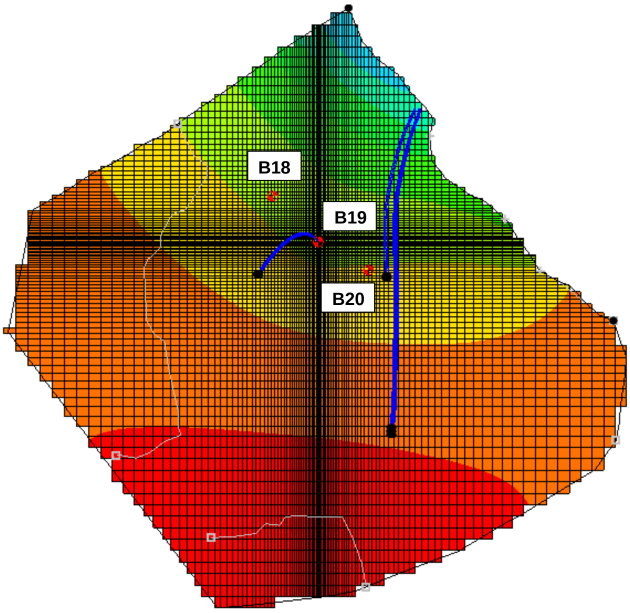


Figure 7.8: *Calibration 3: The particles from the dry cleaner site reaches B19 whereas the particles from the other two locations flow out of the model. Only B19 is pumping in this situation.*

Non of the the possible sources could be completely eliminated on the basis of the three full scale field experiments discussed in chapter 6, even though, the dry cleaner site and the pond seems more likely than the Skibsbylejren according to table 6.2 and the influence area sketched in figure 6.16. Both calibration 1 and calibration 2 is therefore used in further investigations with the purpose of decreasing the influence area. Calibration 1 is chosen because it is the only calibration where particles from one of the possible sources appear in the polluted well when pumping on all the extraction wells. Calibration 2 is on the other hand chosen because it is the only calibration which is able to drag particles from both the dry cleaner site and Skibsbylejren towards the polluted well when only the polluted well is active.

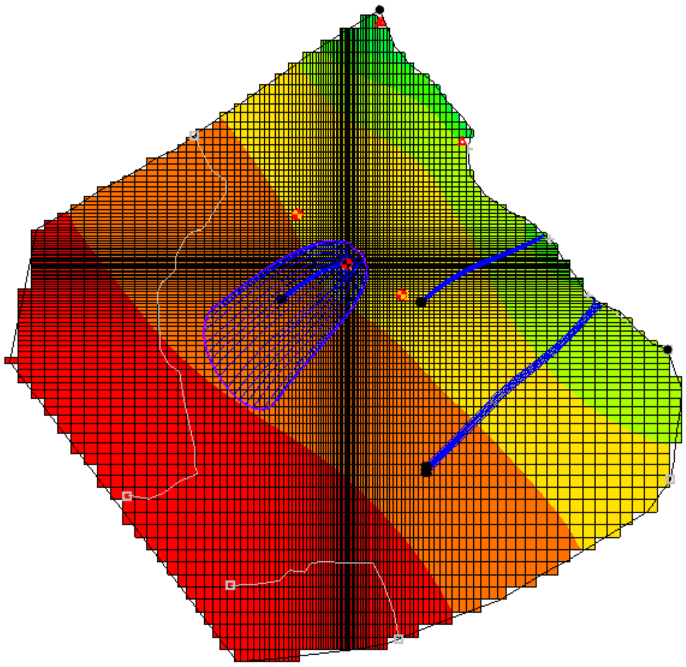
7.2 Estimation of influence area by model particle tracking

From the particle tracking forward in time from the possible pollution sources to the polluted well, the transport time of these particles can be used to make an estimate of the year of the spill. It is assumed that the particles does not reach the polluted well before 2003 where it was detected for the first time. Using calibration 2 the following years of the spill was calculated:

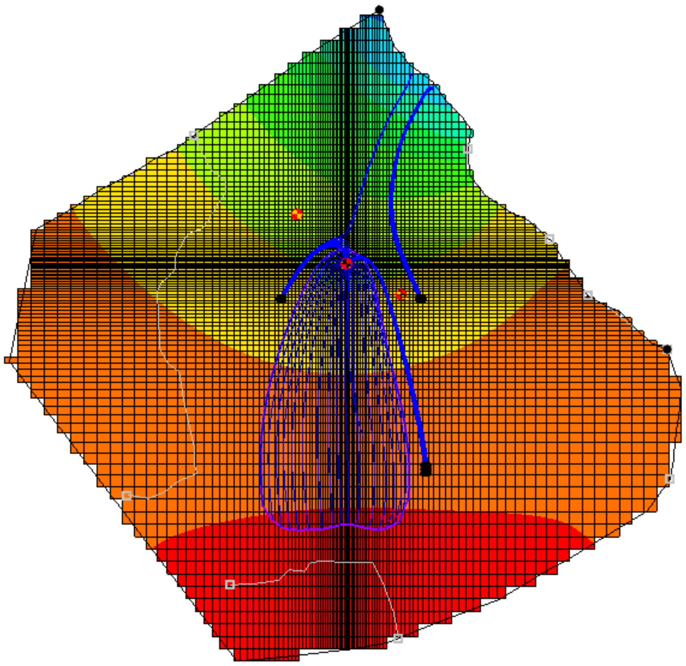
- Dry cleaner site: 1984
- Skibsbylejren: 1961

The pond has not been taken into considerations as no particles by model calculations would flow from that location to the polluted well. According to historical records, the dry cleaner was closed in the late 1960s. The year of the spill calculated from the particle tracking is much later in time and does not correlate with the historical records. It is however possible that the pollution has reached the well earlier than 2003. The year of the spill estimated for Skibsbylejren seems, though, realistic according to the historical use of chlorinated compounds, where the import peaked around the 1960s and 1970s.

In the same manner that particles were tracked forward in time from the different possible locations of the pollutant source, particles can be traced backward in time from an extraction well by the GMS. To investigate the catchment area of the polluted well particles were therefore tracked backward in time. The 1930s is used as the maximum time limit of particle tracking as this was the decade the import of chlorinated solvents began. The catchment area of the polluted well is shown in figure 7.9 using both calibration 1 with 3 active wells (7.9(a)) and calibration 2 with only 1 active well (7.9(b)).



(a) Catchment area of the polluted well using calibration 1 with 3 active wells.



(b) Catchment area of the polluted well using calibration 2 with 1 active well.

Figure 7.9: *Particle tracking back in time from the polluted well. This defines the catchment area. The time limit of the back tracking of the particles is 1930 where the import of chlorinated solvents began in Denmark.*

The two calibrations shows quite different catchment areas but together they will still account for a smaller area than the influence area sketched in figure 6.16. The influence area has thereby been decreased, but two possible sources does still remain: the dry cleaner site and Skibsbylejren.

Suggested method for source tracking of dense chlorinated compounds

8

The ideal source tracking is fast, exact and has a minimal cost. But quality and cost is often closely connected, and the choice of cheaper alternatives will often instead result in prolonged and expensive investigations. At Varbro well field several investigations were performed at possible pollution sources and at the polluted well, but not interconnected and not at the same time. I believe that a structured pollutant investigation is the best tool for pollution source tracking. This tool should start out with simple methods and mappings of the geology and flow direction of the groundwater. Models by the GMS is proven useful in source tracking on the foundation of a solid data basis, and should be used both in the preparation of the investigations, and as a part of it. Furthermore the tool should be specific to the compounds of investigation, as chlorinated compounds and oil products has quite different physical and chemical properties and thereby different transport properties. It might however be enough to distinguish between DNAPL and LNAPL.

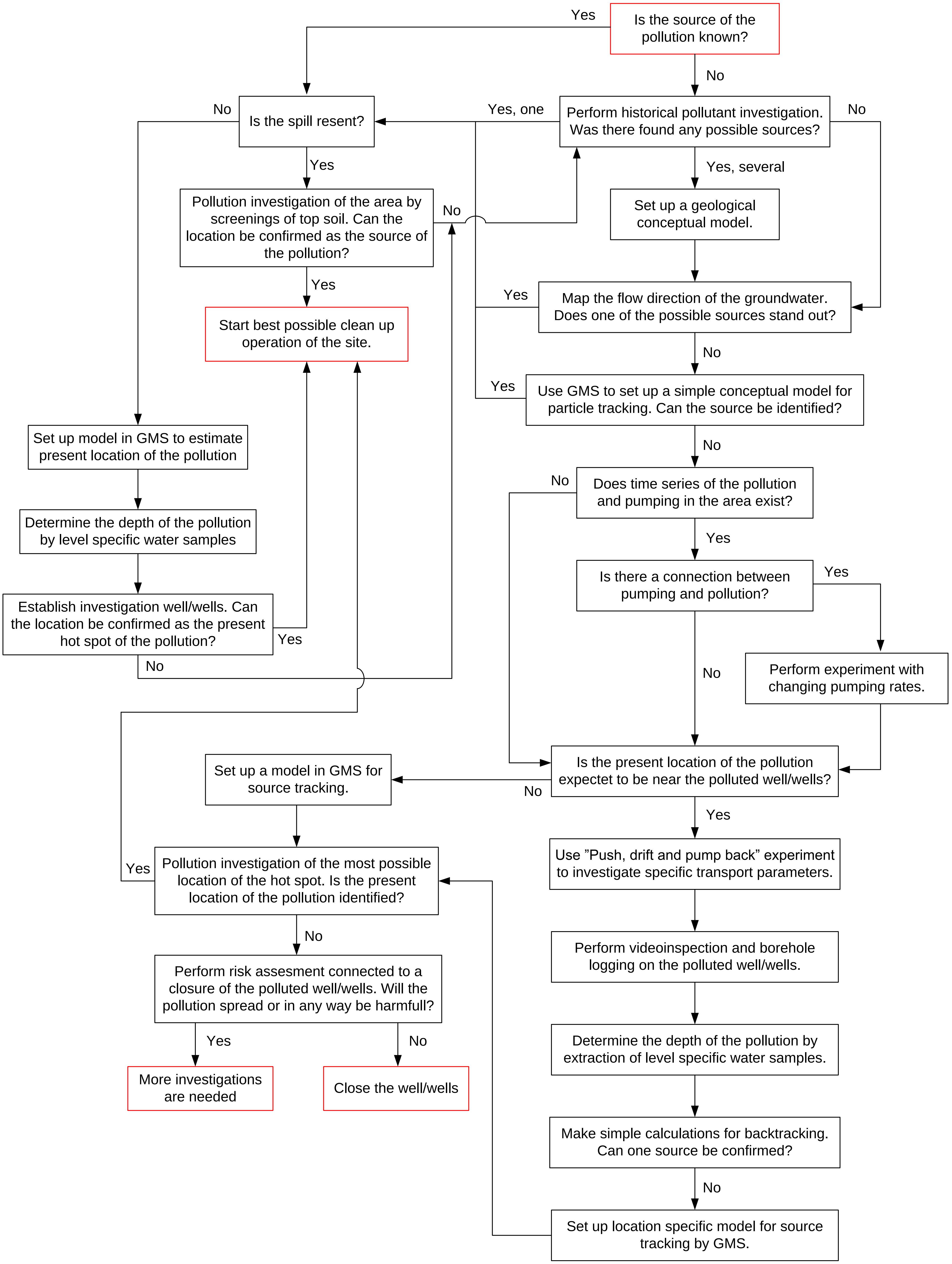
A structured source tracking should start with a general screening of the polluted area by investigating the pollutant history, the geology and the water dynamics. This should be followed up by field experiments and new direct measurements, and finally by more extensive investigations and complex model studies. In some cases the general screening will be enough to identify the source of the pollution, and then track the present position and spreading of the pollution by simple calculations and modeling by GMS. In other cases more investigations are necessary, and the general screening of the area will then form the foundation of the following investigation strategy for a more efficient source tracking.

The three full scale field experiments applied in this work will also form an important part of a source tracking tool. They are all three simple, fast conducted experiments with a low cost, and gives useful results that might be crucial in the investigation of the pollution source. The experiments should be supported by other direct measurements and modeling in order to achieve the best result.

When the original source is identified, it should be taken into consideration whether or not the spill is resent. There may not be many traces of the pollution left at the original polluted soil site after a drifting time of maybe 50 years.

These different investigations and considerations connected to a source tracking has been gathered in an investigation strategy consisting of several steps of different investigations, direct measurements and modeling, all based on of a solid background knowledge. The suggested investigation strategy appears from a flow chart of decision-making in source tracking on the following page. The flow chart is focused on chlorinated compounds, where the geology among others are an important part, as the transport of a DNAPL to a great extend will be controlled by the geological layers and variations.

Flow chart – Decision-making in source tracking of chlorinated compounds



The flow chart is constructed in such a way that the complexity of the polluted site is reflected in the complexity of the investigations. The flow chart seeks to find the most simple method for a successful source tracking by starting with basic investigations and then build on these by adding more and more investigations with an increasing complexity. The simple investigations and calculations functions thereby itself as a source tracking tool in cases where the pollution source is easily identified but also as the foundation of decision-making regarding which extensive investigations should be chosen in a given situation. The flow chart connects thereby the simple and the comprehensive investigations in a complete strategic plan.

Modeling of different levels of complexities can with advantages be used in source tracking and is therefore implicated several times in the flow chart and could be used even more. The flow chart prepare the ground for a repeatedly interaction between direct measurements and model calculation.

9

The future of Varbro well field - closure or continued use?

A final attempt of tracking the pollution at Varbro well field has been carried put. Possible sources has been pointed out on the basis of historical records and has been investigated by several different methods. A geological conceptual model has been set up and the flow direction of the groundwater has been mapped. Time series has been analysed, full scale field experiment has been conducted, and finally a model by the GMS software package has been set up with the purpose of pollution source tracking.

From the results of the different investigations an influence area has been created. That area should contain the location of the original spill of the pollution. The influence area is based on simple calculations by hand and narrowed down by particle tracking using GMS. Figure 9.1 gather the the influence area found on the basis of the field experiments and the influence area found by particle tracking. Notice that two different pore water velocities has been used in the calculation of the influence area from the field experiments. These are marked by different colors (red and green). The pollution source should be located in the area limited by both influence areas or very close to the limit as the particle tracking showed that particles located slightly outside the catchment area would be reach the well at certain pumping situations.

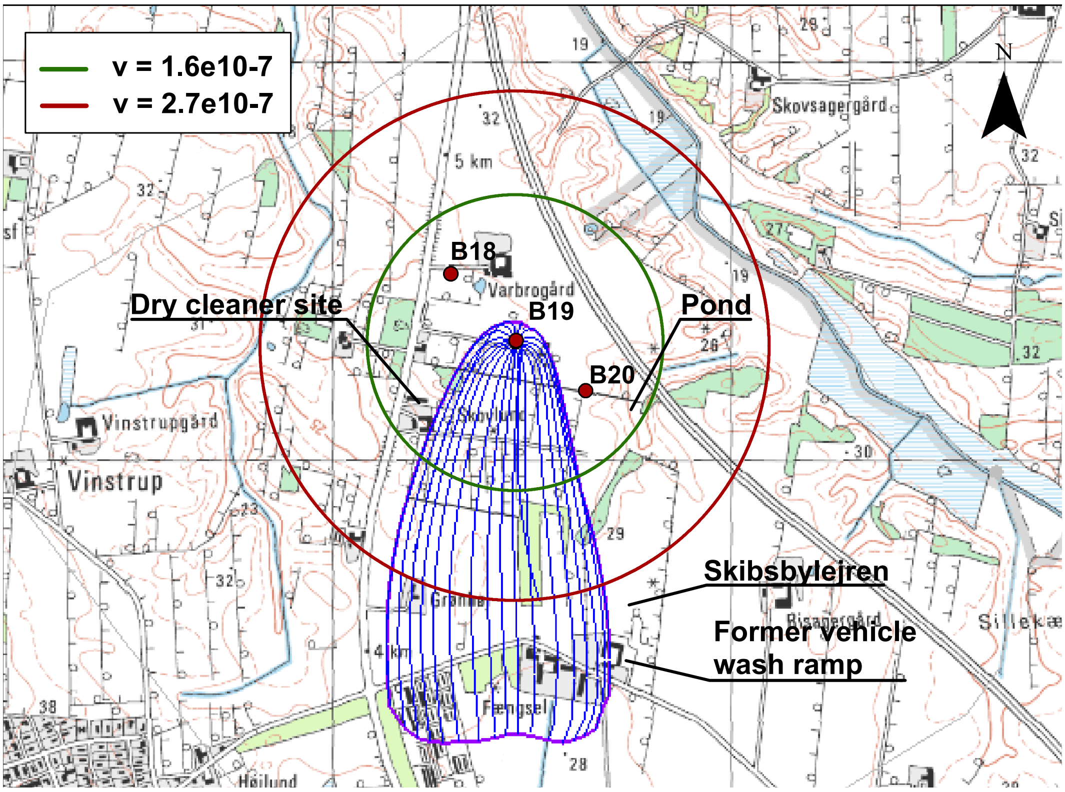


Figure 9.1: *Gathering of the influence areas found on the basis of field experiments and particle tracking the the GMS. The pollution souce should be located in the area covered by both influence zones. Notice that two different pore water velocities has been used in the calculation of the influence area from the field experiments.*

At this point, two of the possible sources are covered by the influence area. From the results of the different investigations discussed throughout this report there is some points that makes the possible sources more or less likely as the source of the pollution. These are all summerised in table 9.1.

Table 9.1: *Summery of the different proves and disproves of each of the suspected pollution sources, found by analysis, experiments and model calculations throughout this report.*

Dry cleaner		
	Proves	Disproves
Pollutant history	Pollutions are often observed at dry cleaner sites	TCE most commonly used before the 1950s
Former investigations	Analysis of the unsaturated pore space gaseous phase showed traces of chlorinated compounds	Chlorinated compounds were not proven by water samples
Geology and water flow direction	Located almost directly upstream of the polluted well	
Model simulations	The catchment area of the polluted well covers the location	The calculated years of the spill does not correlate with the history

Skibsbylejren		
	Proves	Disproves
Pollutant history	Pollutions are often observed in military areas	
Former investigations	Analysis of the unsaturated pore space gaseous phase showed traces of chlorinated compounds	Chlorinated compounds were not proven by establishment of boreholes
Geology and water flow direction	The area seems to be a part of the catchment area Could be an explanation of why the pond is polluted	B20 has to be completely shut off to avoid pollution of that well
Model simulations	The catchment area of the polluted well covers the location but only if there is no hydraulic contact to B20	

Pond		
	Proves	Disproves
Former investigations	Chlorinated compounds has been detected in the sediment of the pond	Only low concentrations has been measured in the pond and the area surrounding it
Model simulations		The location is not covered by the model-simulated catchment area

The pond is eliminated as a suspect of the pollution. It was not possible by any model calculations to simulate a flow of the pollution from the pond to the polluted well, not even if B20 was taken out of operation. The concentrations found in the sediment of the pond is furthermore not in a magnitude that could cause the pollution observed in B19. The pollution of the pond might be a separate smaller pollution that is not coupled to the pollution of B19. If the pollution has its origin in Skibsbylejren, different particle pathway could, however, also explain the pollution of the pond.

On the contrary, several results indicates that the original source of the pollution could be either the dry cleaner site or Skibsbylejren. It is possible that B19 is influenced by two different pollutions; one with its origin at the location of the dry cleaner site and one with its origin in Skibsbylejren. This would, however, be an unusual coincidence, especially since only one well is affected by the pollution. In both cases the spill must be assumed to have occurred several years ago. The locations are due to dissolution an solute transport likely not any longer the present location of the pollution pool influencing B19. several results of the different investigations and experiments indicated that the present location of the hot spot is relatively close to the well. These indications are listed here:

- There is a remarkably correlation between the changes in concentrations and the changes in pumping rates. The delay between the time series of these was by analysis estimated to about either 25 days or 90 days. With a response time that short, the source should be located very close to the well. The response time has, however, not been proven experimentally.
- The retention of VC in soil is slightly different than the retention on TCE. With a long travel distance VC will be expected to reach the well faster than TCE but by analysis of the time series of these two compounds was no lag discovered. This indicates a short travel distance between hot spot and the well.

9.1 Suggestion of a future investigation strategy

Further model calculations by the GMS should be conducted by using time series of the pumping rates and then investigate whether or not changes in concentrations in the polluted well matches the observations. This could possible exclude either the dry cleaner site or Skibsbylejren as the suspected sources.

It is also recommended to continue the experiment with changing pumping rates to clarify if a more significant tendency appear after 90 days of an increased pumping rate. It should, however, be taken into consideration whether or not spot checks once a week is the best monitoring method. A passive sampling method may show a more significant effect. SorbiCells by SorbiSense could for instance be used. Sampling by SorbiCells is described in appendix G.

The geology is in this case very important to the solute transport. It is therefore suggested to investigate the geology further at the distance between the polluted well and the dry cleaner site and Skibsbylejren respectively, e.g. by geophysical methods. Also, pumping experiments in combination with synchronous measurements of the water table should be conducted. These further investigations would clarify the geological differences and give a very solid foundation of the investigation of the suspected source of the pollution. The pumping experiments will prove or disprove the theory of a missing hydraulic contact between different wells at the area of Varbro well field. This simple and inexpensive experiment could possible exclude one of the suspected sources.

A suggestion of a future investigation strategy is thereby:

1. Use time series in modeling to evaluate the possible sources
2. Continuing the experiment with changing pumping rates up until Juli 2012
3. Investigate the hydraulic contact between well at Varbro well field
4. Geophysical investigation of the distance between the sources and the well

9.2 Possible solutions for continued use of Varbro well field

The suggested further investigations should exclude either Skibsbylejren or the dry cleaner site as a suspect of the pollution. In any case is the possibilities as illustrated in figure 9.2.

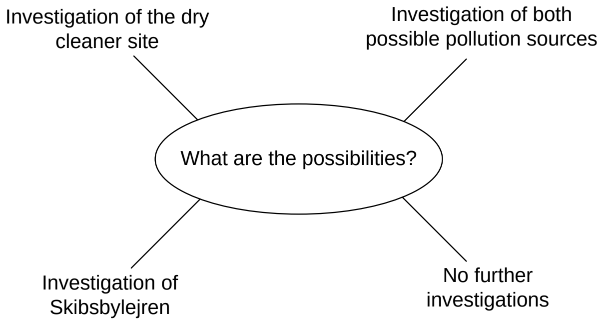


Figure 9.2: *The possibilities for at continued use of Varbro well field.*

The possible pollution sources can be investigated further depending on which seems most likely as the source or it can be chosen not to make any further investigations. In that case should the pumping on B19 be continued as previously to avoid spreading of the pollution. The pollution may be delimited from the other extraction wells right now but no layers are impermeable and the pollution will most likely penetrate these layers and spread to the other wells if B19 is closed. This is therefore not recommended.

Depending on what a more detailed solute transport model will show, both or just one of the possible sources can be investigated further. It is however important to get a deeper understanding of the geology before initiating these investigations. This could be by geophysical methods or by establishment of geotechnical boreholes in the area of the investigation. For the actual investigation of the pollution can a number of boreholes be established at the distance between the investigated location and the polluted well, as a wide range to cover the pollution in the best possible way.

Conclusion

10

The main objective of this report was to make a suggestion how to improve the existing procedures for source tracking of chlorinated compounds on the basis of a case story: Varbro well field, north of Hjørring. The outcome was a flow chart for decision-making in source tracking (chapter 8). This flow chart focus on the simple model calculations and experiments as a basis which gradually becomes more advanced by more complicated cases. Through the case story has several different investigations been proven efficient in source tracking and has therefore been included in the flow chart. The following conclusions were made:

Geological conceptual model of Varbro well field

- The geology at Varbro well field is complex and highly influenced by a buried valley. A geological conceptual model has been made and appear from figure 4.10.
- Laboratory analysis of soil samples gave important hydraulic parameters such as the effective porosity and hydraulic conductivities.

Determination of the groundwater flow direction at Varbro well field

- Measurements of the groundwater potential confirms that the catchment area of the polluted well include both Skibsbylejren and a dry cleaner site which are both suspected pollution sources.
- There is no hydraulic contact between the polluted well, B19, and the other extractions wells at Varbro well field.

Time series analysis

- There is a degradation potential at the site. Time series shows an accumulation of the breakdown product Vinyle Chloride which is highly toxic and carcinogenic.
- Regardless of different retentions there is no delay time between the concentration of Trichloroehylene and the concentration of Vinyle Chloride, which indicates that the pollution is located close to the polluted well.
- There is a remarkably connection between the concentration and the pumping rates. When increasing the pumping rate the concentration of chlorinated compounds will also increase with a response time on 25 to 90 days.

Full scale field experiments

- A response time on changes of the pumping rates can after 45 days of experiment not be confirmed as a uniform tendency. It is believed that a change in the concentration will occur latest about 90 days from the start of the experiment.
- Level specific water samples showed that the pollution is located approximately 58 m b.s. A flow log and a natural gamma log suggests the presence of a low permeable layer about 60 m b.s. The pollution might be located on the top of that layer.
- The "Push, drift and pumpback" experiment showed very small pore water velocities indicating that the water surrounding the screen section of the polluted well, B19, is almost stagnant. This is illustrated in figure 6.15.

Solute transport models by particle tracking

- If it is assumed that there is no hydraulic contact between B19 and the other extraction wells at Varbro well field, particles added at the dry cleaner site and in Skibsbylejren will both appear in the polluted well. Particles added at the pond will not.

In a combination of field experiments, laboratory analysis and model calculations, an influence area has been created in which the location of the pollution should be placed. The area appear from figure 9.1. Two possible sources at Varbro well field remains. The dry cleaner site and Skibsbylejren. Both of them are possible according to both model calculations and historical records.

Bibliography

Andersen, H., Petersen, A. and Mossin, L.: Januar 2006, *Hirtshals Vandværk. Boringsundersøgelser i B19 DGU nr. 5.594, B20 DGU nr. 5.596 og B18 DGU nr. 5.631*.

Atmadja, J. and Bagtzoglou, A. C.: 2001, State of the art report on mathematical methods for groundwater pollution source identification, *Environmental Forensics* **nr. 2**, 205–214.

AVJ: 2001, Håndbog om undersøgelser af chlorerede stoffer i jord og grundvand, *Teknik og Administration* **nr. 5**. Amternes Videncenter for Jordforurening.

Bjerg, P. L., Broholm, M. M., Lange, I. V., Troldborg, M., Janniche, G. S., Lemming, G., Santos, M. and Binning, P. J.: 2011, *Forekomst af fri fase og kvantificering af forureningsflux for chlorerede opløsningsmidler*.

Dansk Geofysik A/S: Januar 1999, *Hirtshals Kommune. Geofysisk kortlægning ved Vinstrup Kildeplads. Multielektrode Profilering (MEP)*.

FBE: December 2011, *Etablissement 533 Skibsbylejren. Supplerende undersøgelse af grundvandsforurening med chlorerede opløsningsmidler*.

GEUS: 2012, *Jupiter - Danmarks geologiske og hydrologiske database*, De Nationale Geologiske Undersøgelser for Danmark og Grønland.

Grontmij - Carl Bro A/S: 2011, *Multilevel Sampler til 3D måling af grundvandsforurening*.

Hjørring Kommune, L. M.: 24. november 2009, *Notat. Supplerende historiske oplysninger vedr. renseri og opfyld af udgravning på Ringvejen 666 og 672, Hjørring*.

Jensen, J. B., Mortensen, L. B. and Blicher, B. W.: 2008, Anvendelse af grundvandmodel til kildesporing, risikovurdering og design af afværgetiltag, *ATV jord og grundvand* **4. - 5. marts 2008**. Vintermøde om jord- og grundvandsforurening.

Jørgensen, F. and Sandersen, P.: September 2009, *Kortlægning af begravede dale i Danmark. Opdatering 2007 - 2009*.

Loll, P. and Moldrup, P.: 2000, *Soil Characterization and Polluted Soil Assessment*.

Miljøstyrelsen: 2008, *Branchevejledning for forurenede renserigrunde*, Vol. nr. 1.

NIRAS: December 2010, *Notat. Forurening med chlorerede opløsningsmidler - Varbro Kildeplads. Lokalisering og afgrænsning af grundvandsforurening*.

Orbicon A/S: 23. oktober 2006, *Hirtshals Kommune, Varbro Kildeplads. Notat, Undersøgelsesboring*.

Region Nordjylland: 2010, *Tidligere renseri Ringvejen 672, Hjørring - Supplerende undersøgelse*.

Schmidt, H.: 2012, *Mailkorrespondance*,
Niras.

SorbiSense: 2. maj 2012, Sorbicellen.

Spitz, K. and Moreno, J.: 1996, *A practical guide to groundwater and solute transport modeling*.

Chlorinated compounds

A

Chlorinated compounds has mostly been used as solvents for textile cleansing and degreasing of metals, but they may also be included in eg. preservatives and in the production of dyestuff. The use is different according to the specific compound and its properties. In table A.1 is the industrial use of three different chlorinated compounds shown [AVJ, 2001].

Table A.1: *Some industrial uses of three different types of chlorinated compounds [AVJ, 2001]*

Compound	**Industrial use**
Tetrachloroethylene	Textile cleansing. Degreasing of metals and skin before tanning. Production of medicaments. Impregnating agent
Trichloroethylene	Textile cleansing. Degreasing of metals and skin before tanning. Production of paint, varnish, glue and PVC.
Vinyle chloride	Production of PVC

For textile cleansing has especially Tetrachloroethylene (PCE) and Trichloroethylene (TCE) been widely used but not equally. Which of these compound that have been used the most, is strongly attached to the mechanisation of the dry cleaner industry. The history of the dry cleaner industry is illustrated as a time line in figure A.1.

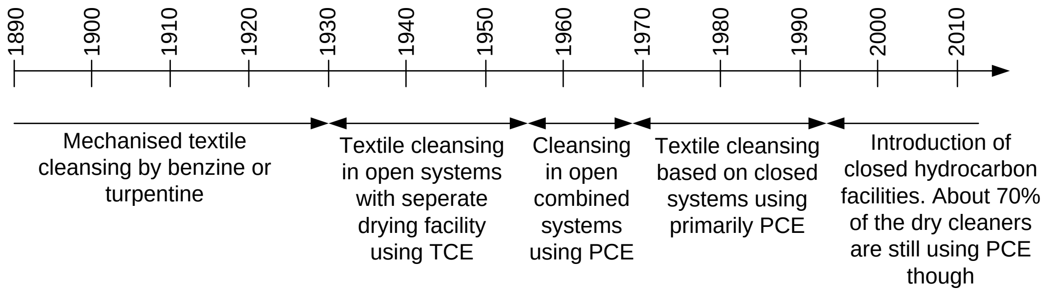


Figure A.1: *The mechanisation of the danish dry cleaner industry and the changes of cleaning fluids by time [Miljøstyrelsen, 2008].*

The import of chlorinated compounds in Denmark started in the 1930ies and peaked in the 1960ies and 1970ies. Today is the import dropped to about one tenth of the highest level. The main part of the imported chlorinated compounds consists of PCE and TCE.

A.1 Physical and chemical properties

Chlorinated compounds can be divided into two major groups, the aliphatic and the aromatic compounds. For industrial purposes are the aliphatic compounds the most used chlorinated solvents because of their distinctive degreasing properties. TCE, PCE and VC are all examples of aliphatic compounds.

Aliphatic compounds are in general characterized by their volatility and for having a density higher than water. Though, VC and cloromethane differ from the other aliphatic chlorinated compounds by having a density lower than water and an higher volatility than the rest of the chlorinated compounds. The aliphatic compounds have also a relatively low water solubility. This solubility can be further reduced if a free phase consist of more than one chlorinated compound referring to Raoults law. The solubility of each compound will then be reduced with a factor corresponding to the mole based part of the compound in the free phase. This can result in significant changes and is important to keep in mind as a pollution often contains more than one kind of chlorinated compounds [AVJ, 2001].

The aliphatic compounds all have a poor sorption to soil particles as they are non-polar. The retention of the chlorinated compounds is therefore dependent on the content of organic matter.

Table A.2 shows some physical and chemical properties of three of the most mentioned chlorinated compounds in environmental correlation: PCE, TCE and VC. For comparison is the same properties for benzene shown in the table. Benzene is found in oil pollutions.

Table A.2: *Physical and chemical properties of some chlorinated compounds and benzene [AVJ, 2001] [Spitz and Moreno, 1996].*

Compound	**Chemical formula**	**Density [g/ml]**	**Water solubility [mg/l]**	**Henry's law constant [-]**	**log K_{ow} [-]**
Tetrachloroethylene	C_2Cl_4	1.62	240	0.67	2.88
Trichloroethylene	C_2HCl_3	1.46	1400	0.38	2.53
Vinyle chloride	C_2H_3Cl	0.91	2763	3.24	1.38
Benzene	C6H6	0.88	1760	0.23	2.10

The properties listed in table A.2 are significant to the mobility and spreading of each compound in the soil matrix. Because of the specific properties of the chlorinated compounds are they referred to as DNAPL (dense non-aqueous phase liquids) contrary to benzene. As the values in table A.2 indicates, is benzene also a volatile compound with poor sorption properties and low water solubility. The mobility of this compound is though quite different from the mobility of chlorinated compounds, as benzene is not quite as volatile, slightly more water soluble and has at density lower than water. Benzene is then referred to as a LNAPL (Light Non-Aqueous Phase Liquid). VC is again an exception and is also a LNAPL but as Henry's law constant indicates is VC much more volatile and have even lower sorptions qualities than the rest of the chlorinated compounds. Table A.3 shows the distribution of chlorinated compounds between air, water, and soil particles in sandy soil for PCE, TCE, VC, and benzene [AVJ, 2001].

Table A.3: *The Distribution of three chlorinated compounds and benzene in the unsaturated and the saturated zone using standard values for soil parameters from JAGG 1.5 [AVJ, 2001].*

Compound	**Distribution in % (mass) in air/water/soil in sand**	
	Saturated zone	**Unsaturated zone**
Tetrachloroethylene	- / 68 / 32	36 / 27 /37
Trichloroethylene	- / 83 / 17	32 / 43 / 26
Vinyle chloride	- / 99 / 1	86 / 13 / 1
Benzene	- / 93 / 7	27 / 60 / 13

The values in table A.3 are standard values from JAGG 1.5. The distribution of chlorinated compounds in the saturated zone is shown for a water content at field capacity.

A.2 Degradation

The degradation of chlorinated compounds is primarily biological and is strongly dependent on the redox potential. Besides that is it often incomplete and very slow. There are different types of biological degradation. Roughly these comprise anaerobic reductive dechlorination, oxidation and co-metabolism. Oxidation can appear both under aerobic and anaerobic conditions [AVJ, 2001].

A.2.1 Anaerobic reductive dechlorination

This is the most frequently observed natural degradation mechanism and will only appear under anaerobic conditions. By this degradation is one chlorine-atom split off at a time with the possibility of a complete degradation to ethene. Chlorine is used as an electron acceptor, where hydrogen often will be the electron donor. The anaerobic reductive dechlorination from PCE to ethene appear from figure A.2. By dechlorination of TCE will cis-1,2-dichloroehtene (cis-DCE) be the main product, whereas less than 1 % of the product will be trans-1,2-dichloriethene (trans-DCE) and 1,1-dichloroethene (1,1-DCE).

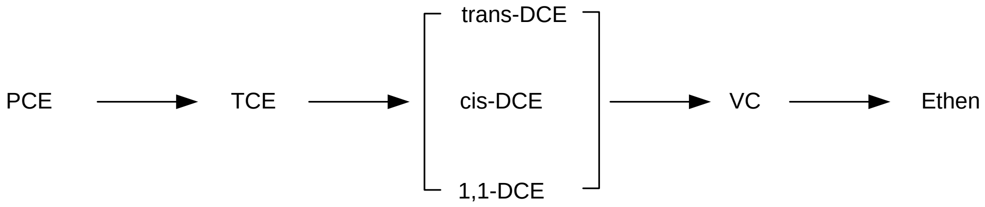


Figure A.2: *Anaerobic reductive dechlorination of PCE to ethene [Bjerg et al., 2011].*

The highly chlorinated compounds are the most unstable, which naturally result in a higher rate of degradation of PCE and TCE than VC. This can cause to accumulation of VC as the dechlorination of VC is very slow and only appear under strongly reduced conditions [Bjerg et al., 2011].

A.2.2 Aerobic and anaerobic oxidation

Oxidation is possible for the less chlorinated ethenes as VC, where the chlorine-atoms acts as donors, and the acceptor is a oxidizing agent as oxygen, nitrate, manganese, iron and sulfate. By accumulation of VC is biological degradation by oxidation an important factor. But it is however uncertain to what extent anaerobic oxidation appear naturally, and since PCE and TCE is dechlorinated to VC under anaerobic conditions is aerobic oxidation rarely an option in nature [Bjerg et al., 2011].

A.2.3 Co-metabolism

Aerobic co-metabolism is theoretically possible for most chlorinated compounds. It is an enzymatic process, where chlorinated ethenes are degradated by using another compound at the primary substrate. The primary substrate should be present in relatively high concentrations compared to the chlorinated compound, and that will often cause anaerobic conditions. Aerobic co-metabolism does therefore rarely exist naturally [Bjerg et al., 2011].

A.3 Transport and dilution mechanism

Chlorinated solvents are non-aqueous liquids with a higher density than water and are referred to as Dense Non-Aqueous Phase Liquids (DNAPL). By a spill the DNAPL will suppress the water in the pore space and spread as a separate liquid deep down in the aquifer. The spreading and transport of the DNAPL is thereby only limited by the permeability of the geological layers at the site whereas the dilution of the DNAPL is dependent on the contact between water and DNAPL and the groundwater flow direction [Bjerg et al., 2011]. In this text is distinguished between two types of DNAPL's: Residual DNAPL and Mobile DNAPL.

- **Residual DNAPL**: Appear at the transport in depth as immobile DNAPL in the pore space.
- **Mobile DNAPL**: Accumulation of DNAPL on the top of a low permeable layer in a mobile DNAPL pool.

The transport of a DNAPL is simplest described by a conceptual model of a hypothetical example with different soil types. Figure A.3 shows an simple conceptual model of the Spreading and dilution of DNAPL in sand and clay [Bjerg et al., 2011].

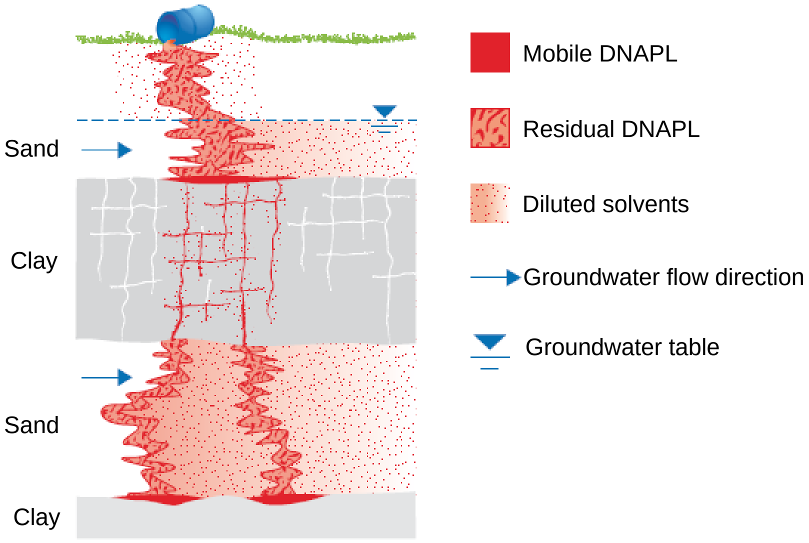


Figure A.3: Conceptual model of spreading and dilution of DNAPL in a sand aquifer with clay layers [Bjerg et al., 2011].

In the unsaturated zone a part of the DNAPL of volatile chlorinated compounds will evaporate and spread in the pore space volume by diffusion. The rest will spread downward to the saturated zone as residual DNAPL. In sand aquifers will the residual DNAPL spread downward till it reach a less permeable layer of e.g. clay. Diluted solvents will spread from both the residual and mobile DNAPL by the groundwater flow direction in the sand aquifer [Bjerg et al., 2011].

At the top of the low permeable layer the DNAPL will gather in a pool of mobile DNAPL. The DNAPL is mobalised by pumping or penetration of the low permeable layer as branched “fingers”. The branched “fingers” are illustrated in figure A.3.

In sand aquifers are, however, rarely homogeneous. There will often be layered formations of finer or coarser particles. Formations of finer particles will result in accumulations and retention of a part of the DNAPL. This is illustrated by a conceptual model of the distribution of DNAPL in a sand aquifer in figure A.4. Also, the figure illustrates the distribution of the DNAPL over time [Bjerg et al., 2011].

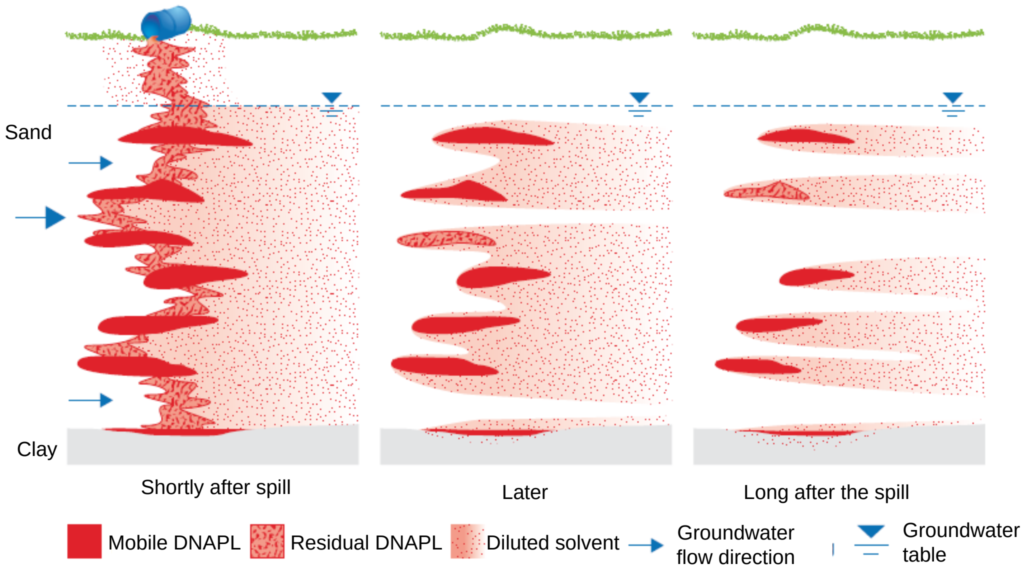


Figure A.4: *Conceptual model of the transport and spreading of DNAPL over time in a layered sand aquifer [Bjerg et al., 2011].*

By time, the DNAPL will be diluted. The residual DNAPL will be diluted first as it will have the highest surface area and thereby a higher contact with the water surrounding it. After a longer period of time the DNAPL may be separated into several smaller DNAPL's as illustrated in figure A.4. By time, the pollution plume will thereby be limited to a smaller vertical interval [Bjerg et al., 2011].

Locations of environmental historical elements of Varbro well field

B

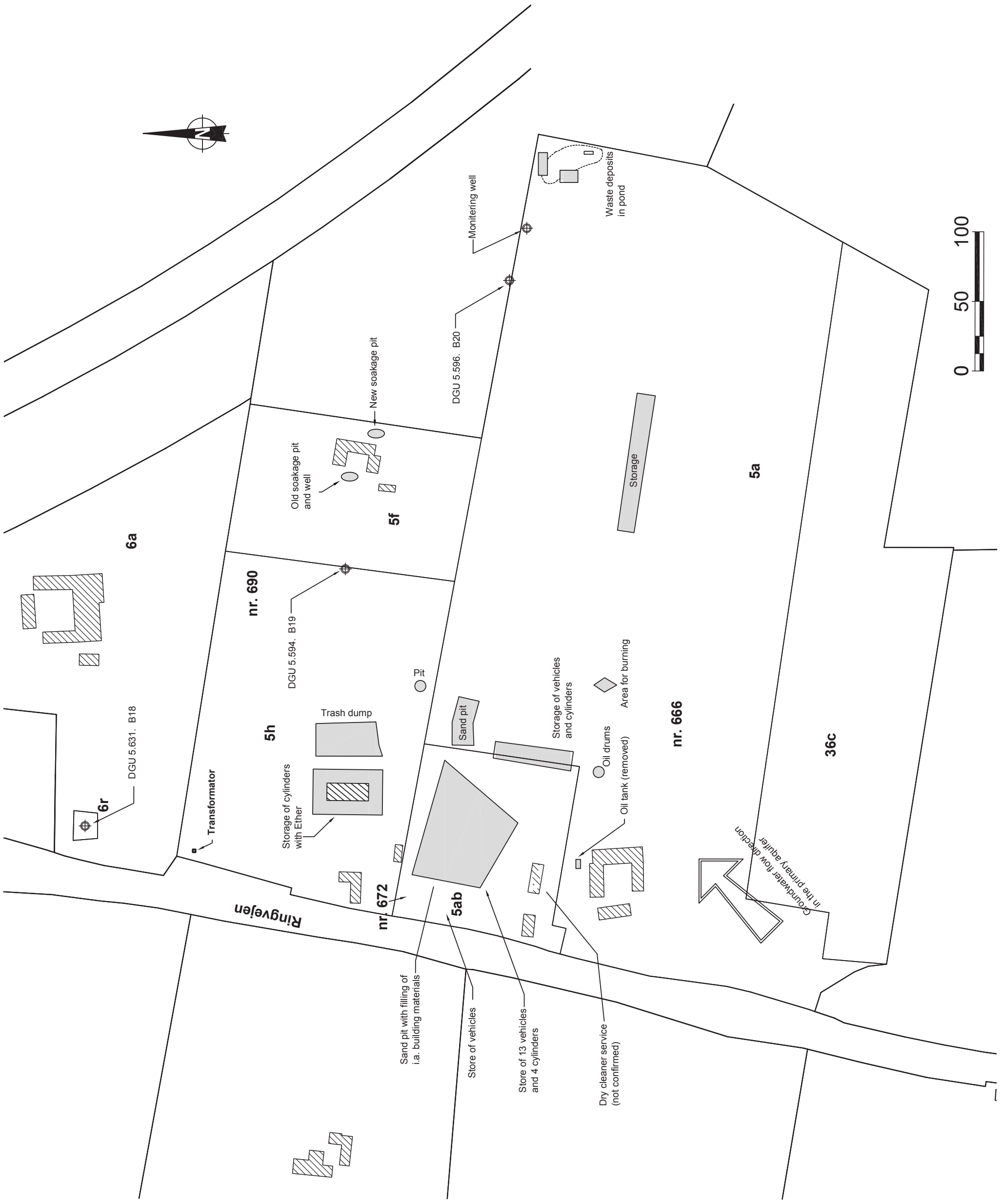
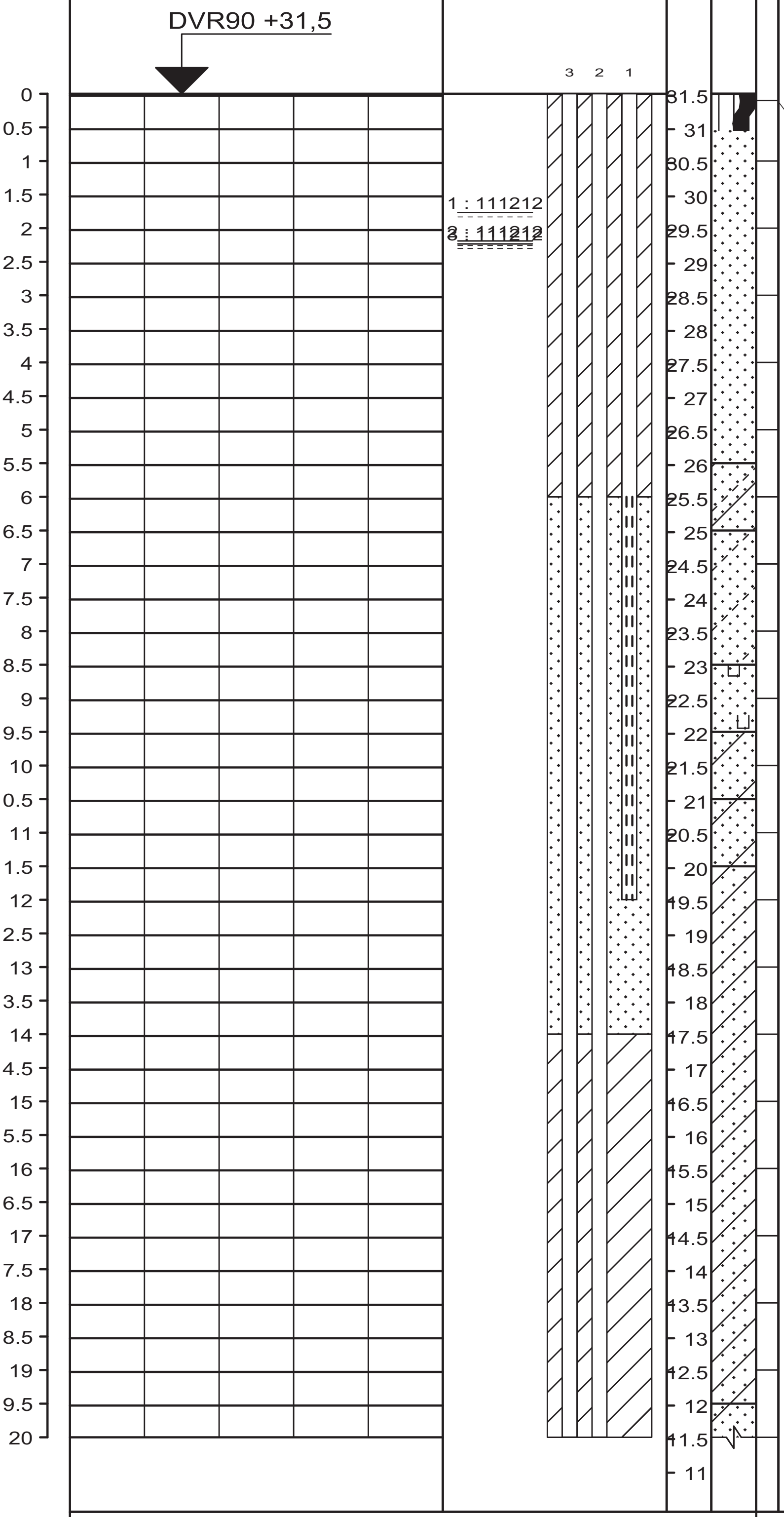


Figure B.1: *Different activities over time that might have had some environmental effects [Region Nordjylland, 2010]*

Borehole journals - F1 and F2

C

Dybde	Forsøgsresultater	Filtersætning	Kote (m)	Geologi	Prøve	Nr.	Jordart Karakterisering	Aflejring	Alder	Lugt	Misfarv.



Nr.	Jordart Karakterisering
01	FYLD: MULD, græsdækket, mørk brun
10	SAND, fint - mellem, velsorteret, gul brun
20	SAND - " -
30	SAND - " -
40	SAND - " -
50	SAND - " -
60	SAND, fint, siltet, sv. leret, (klumper af ler), sorteret, gul brun
70	SAND, fint, sv. siltet, (klumper af silt), organisk materiale, velsorteret, gul brun
80	SAND, fint, siltet, organisk materiale, velsorteret, gul brun
90	SAND, fint, glimmer, organisk materiale, m. skalfragmenter, velsorteret, gul brun
100	SAND, fint, sv. leret, (klumper af grå ler med sorte indslag), organisk materiale, sorteret, grå brun
110	SAND, fint, sv. leret, sorte striber, organisk materiale, sorteret, grå brun
120	LER, sandet, sorte striber, okker udfældninger, klumper, sorteret, grå
130	LER - " -
140	LER - " -
150	LER, fed, mørke partier, klumper med okkerudfældning, sv. sandet, sorteret, grå
160	LER - " -
170	LER - " -
180	LER - " -
190	LER, st. sandet, fint, sorteret, grå
200	SAND, st. leret, fint, klumper med okkerudfældninger, sorteret, grå

Fortsættes

: Ingen mislugt
* : Svag mislugt
** : Middel mislugt
***: Kraftig mislugt

Boremetode : Luftskylleboring

Sag : 205350 533 Skibsbylejren - suppl undersøgelser

Dato : 20111121 Boret af : K. SØRENSEN & SØN DGU-nr.: 5.1814 Boring : F1
Udarb. af : SGA/TINE Kontrol : DAHL Godkendt : DAHL Dato :

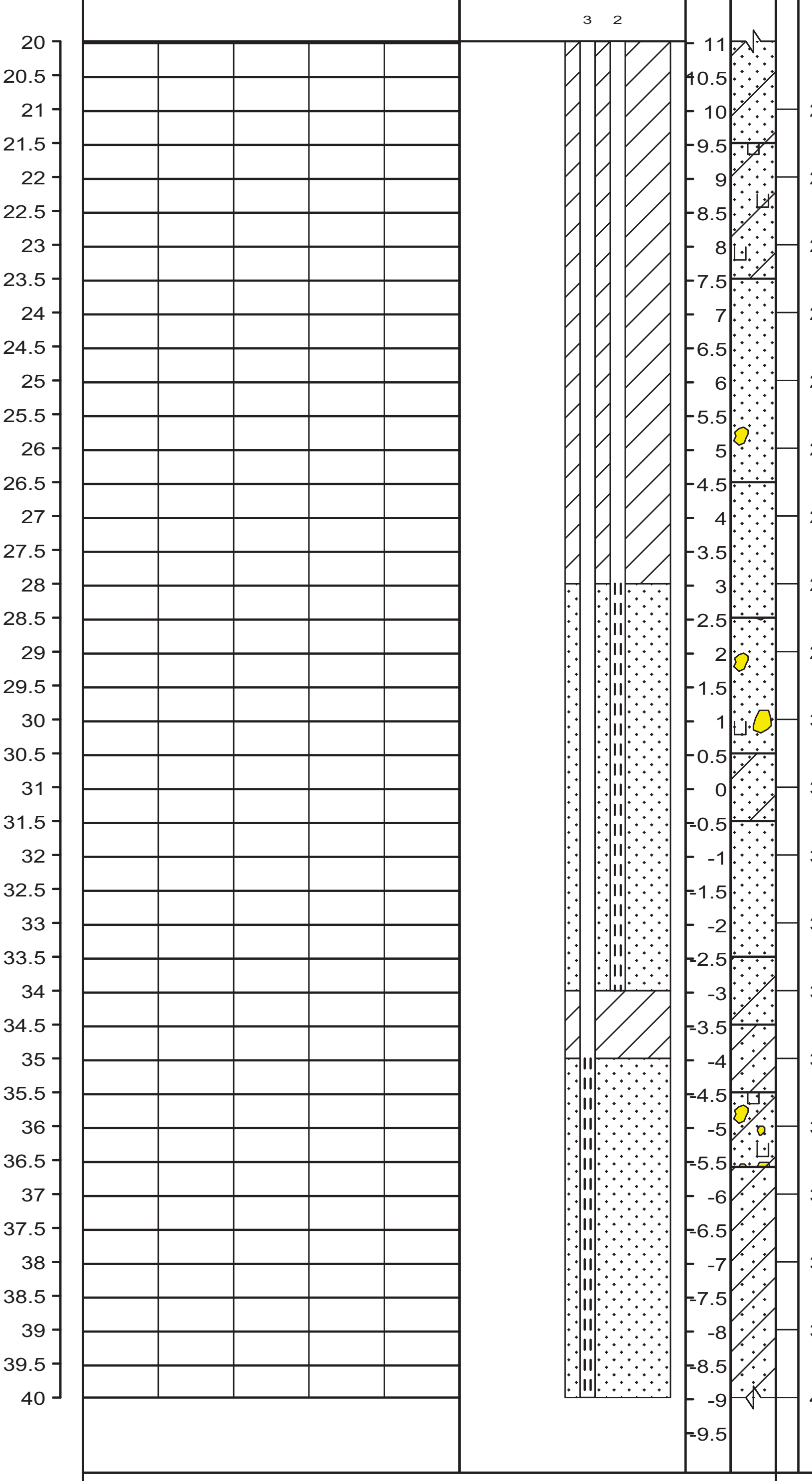
NIRAS Rådgivende ingeniører og planlæggere A/S

Borejournal

BRegister - PSTMDK 2.0 - 14/12/2011 11:05:55

Dybde	Forsøgsresultater	Filtersætning	Kote (m)	Geologi	Prøve	Nr.	Jordart Karakterisering	Aflejring	Alder	Lugt	Misfarv.

Fortsat



Nr.	Jordart Karakterisering
210	SAND, st. leret, mørke sorte partier, sorteret, grå
220	SAND, fint - mellem, sv. leret, (klumper af ler), enkelte stenet, skalfragmenter, sorte partier, usorteret, grå
230	SAND, fint - mellem, sv. leret, enkelse sten, gruskorn, skalfragmenter, usorteret, lys grå
240	SAND, mellem, velsorteret, lys grå
250	SAND, fint - mellem, velsorteret, lys grå brun
260	SAND, fint - mellem, enkelte sten, bryozoer, velsorteret, lys grå brun
270	SAND, fint - mellem, bryozoer, velsorteret, lys grå brun
280	SAND, fint - mellem, bryozoer, enkelte gruskorn, velsorteret, lys grå brun
290	SAND, fint - mellem, bryozoer, enkelte sten, få gruskorn, velsorteret, gråbrun
300	SAND, fint - mellem, m. skalfragmenter, bryozoer, enkelte sten, få græskorn, sorteret, grå brun
310	SAND, fint - mellem, bryozoer, sv. leret, (enkelte klumper af ler), få gruskorn, velsorteret, grå brun
320	SAND, fint - mellem, velsorteret, grå brun
330	SAND, fint - mellem, få gruskorn, velsorteret, grå brun
340	SAND, mellem, bryozoer, sv. leret, (klumper af ler), enkelte gruskorn, sorteret, grå
350	LER, sandet, få gruskorn, sorteret, grå
360	SAND, mellem, gruset, enkelte sten, sv. leret, m. skalfragmenter, usorteret, gråbrun
370	LER, sandet, enkelte gruskorn, sorte partier, mangan, usorteret, grå
380	LER - " -
390	LER, sandet, enkelte gruskorn, sorte partier, okkerklumper, usorteret, grå
400	LER, sandet, okkerklumper, sorte partier, mangan, grå

Fortsættes

: Ingen mislugt
* : Svag mislugt
** : Middel mislugt
***: Kraftig mislugt

Boremetode : Luftskylleboring

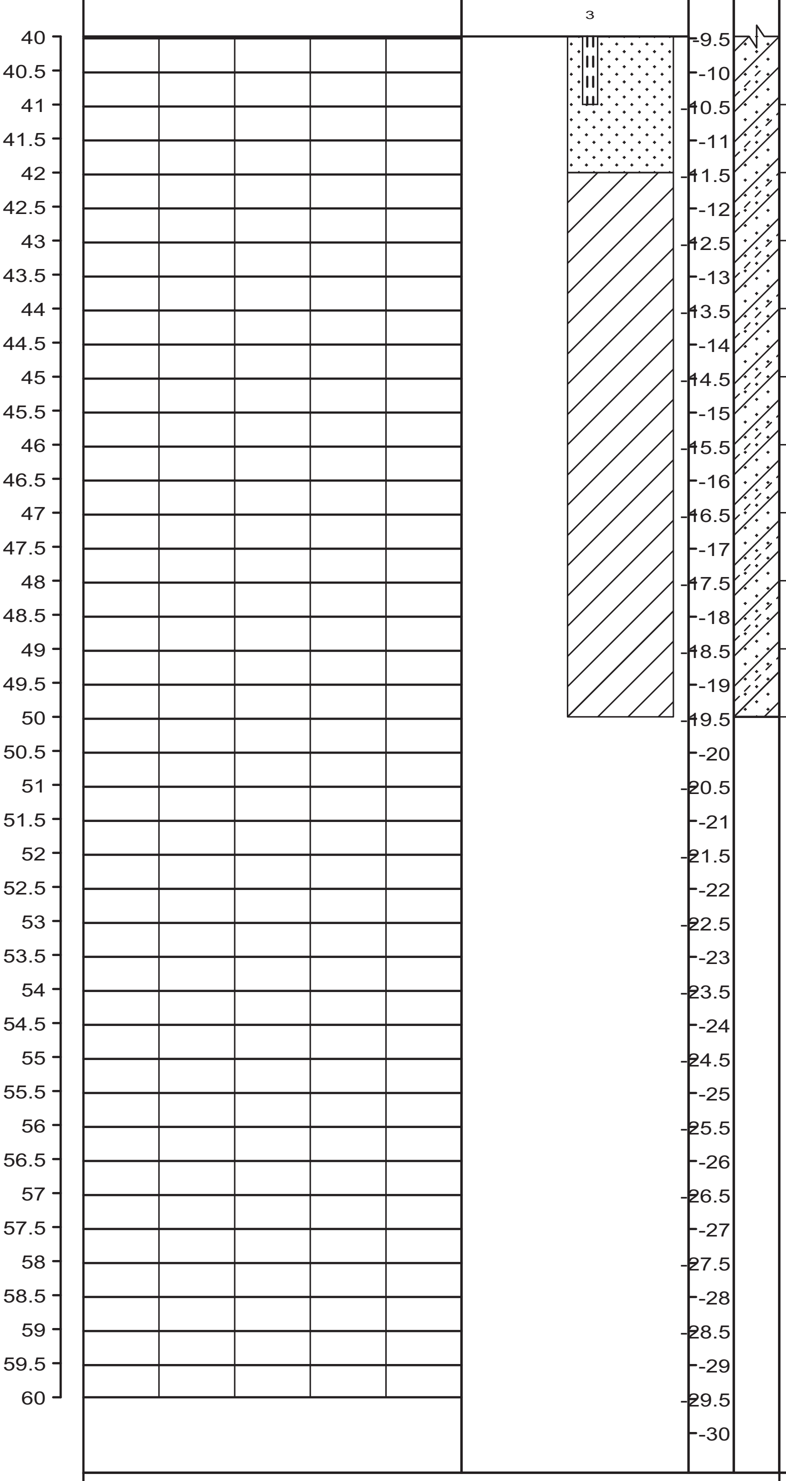
Sag : 205350 533 Skibsbylejren - suppl undersøgelser

Dato : 20111121 Boret af : K. SØRENSEN & SØN DGU-nr.: 5.1814 **Boring : F1**
Udarb. af : SGA/TINE Kontrol : DAHL Godkendt : DAHL Dato :

NIRAS Rådgivende ingeniører
og planlæggere A/S

Borejournal

Dybde	Forsøgsresultater	Filtersætning	Kote (m)	Geologi	Prøve	Nr.	Jordart Karakterisering	Aflejring	Alder	Lugt	Misfarv.
							Fortsat				
41			-10.5			410	LER, sandet, siltet, okkerudfældninger, sorte partier, grå				
42			-11.5			420	LER, sandet, okkerudfældninger, sorte partier, siltet, grå				
43			-12.5			430	LER - " -				
44			-13.5			440	LER - " -				
45			-14.5			450	LER - " -				
46			-15.5			460	LER - " -				
47			-16.5			470	LER - " -				
48			-17.5			480	LER - " -				
49			-18.5			490	LER - " -				
50			-19.5			500	LER - " -				



: Ingen mislugt
* : Svag mislugt
** : Middel mislugt
***: Kraftig mislugt

Boremetode : Luftskylleboring

Sag : 205350 533 Skibsbylejren - suppl undersøgelser

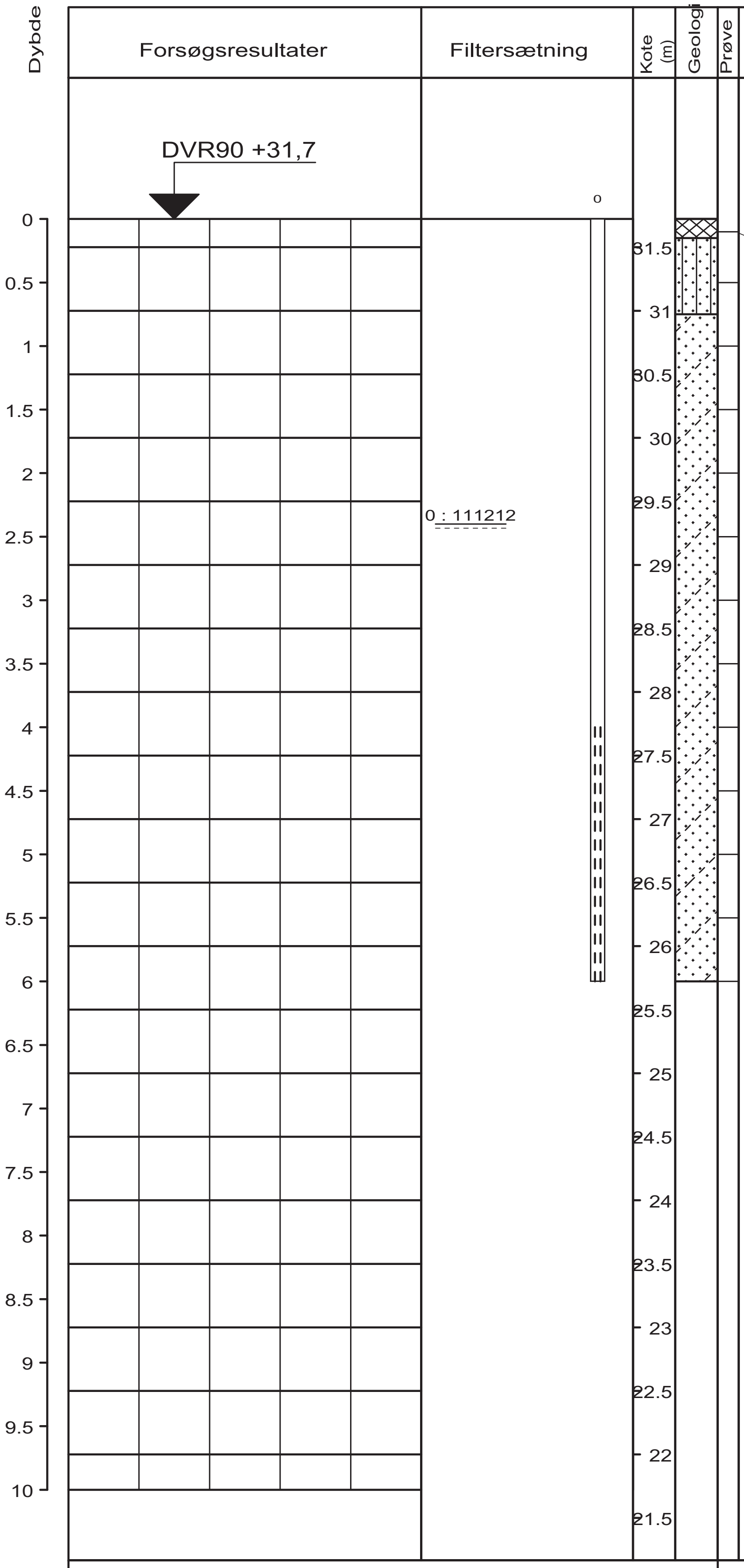
Dato : 20111121 Boret af : K. SØRENSEN & SØN DGU-nr.: 5.1814 **Boring :F1**

Udarb. af : SGA/TINE Kontrol : DAHL Godkendt : DAHL Dato :

NIRAS Rådgivende ingeniører og planlæggere A/S

Borejournal

BRegister - PSTMDK 2.0 - 14/12/2011 11:05:55



Nr.	Jordart Karakterisering	Aflejring	Alder	Lugt	Misfarv.
01	ASFALT				
05	FYLD: SAND, fint, lys brun				
10	SAND, fint, sv. siltet, gul brun				
15	SAND - " -				
20	SAND, fint, siltet, gul brun				
25	SAND, fint, siltet, slirer af rødt sand, mellem, gul brun				
30	SAND, fint, siltet, grå brun				
35	SAND - " -				
40	SAND - " -				
45	SAND - " -				
50	SAND, fint, siltet, slirer af rødt sand, mellem, grå brun				
55	SAND - " -				
60	SAND - " -				

: Ingen mislugt
* : Svag mislugt
** : Middel mislugt
***: Kraftig mislugt

Boremetode : Snegleboring 6"

Sag : 205350 533 Skibsbylejren - suppl undersøgelser

Dato : 20111118
Udarb. af : SGA/TINE
Boret af : K. SØRENSEN & SØN
Kontrol : DAHL
Godkendt : DAHL
DGU-nr.:
Dato :

Boring : F2

S. 1 / 1

NIRAS Rådgivende ingeniører og planlæggere A/S

Borejournal

BRegister - PSTMDK 2.0 - 14/12/2011 11:07:41

Bore hole logging

D

Water samples

E

To confirm that only borehole B19 is affected by the pollution of chlorinated compounds at Varbro well field were water samples extracted from several boreholes in the area for analysis of TCE and PCE.

As expected was TCE and PCE only detected in water samples from B19 and further samples were therefor extracted in the polluted well to keep track of the pollution. Samples were extracted with a two week interval for approximately half a year after which the sampling was intensified to a one week interval. Furthermore were samples extracted from the two closest located boreholes, B18 and 5.596, for the first half year.

E.1 Sampling procedure

Fundamentally all water samples were extracted in the same way, but different pumping systems were used as some well liners were so narrow that a pump could not pass through. For these were a hose with a closing mechanism used, and the water were pumped up by hand. This method is possible more unstable as the water might be oxidised in the process, but is estimated not to have a greater impact on the results for this project, as the search was only for traces of chlorinated compounds, in the boreholes this method was used for. No exact concentration was therefore necessary.

All boreholes were, so far it was possible, pumped clean before extraction. The borehole at the dry cleaner site, B100, had a poor return flow, and could therefore not be pumped clear before the sampling.

(a) (b)

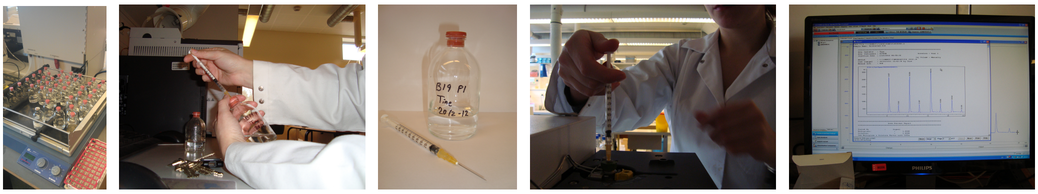
Figure E.1: *Water sampling procedure and the final result of the sampling from different boreholes. All bottles were filled completely to avoid loss of chlorinated compounds before analysis.*

For the sampling was a bottle with a tight-fitting stopper used. As Chlorinated compounds are extremely volatile, the water was supplied through a hose to the bottom of the sampling bottle, such that the water was supplied under the water surface to reduce stirring and oxygenation. Furthermore was the sampling bottle filled completely. For this purpose was a needle used to let surplus water and air out of the sampling bottle, when the stopper was inserted. Different hoses were used for different bore holes, as a small part of water and pollution may stay in the pose after use. Use of the same pose will induce pollution of a potentially clean water sample.

E.2 Pollutant analysis

All water samples are analyzed by gas chromatography with an electron capture detector (ECD). Before the analysis are 30 ml of the water from the sampling bottle transferred to a 120 ml bottle to attain a relative big gasphase and attain a state of equilibrium of the chlorinated compounds between the water- and gasphase. The relative big gasphase in the 120 ml bottle is chosen as we are working with low concentrations of chlorinated compounds, and therefore wants to drag as much compounds to the gasphase as possible to get a clear effect by the detector in the gas chromatograph.

To make sure that the sample is in equilibrium before a gas sample is extracted for analysis on the gas chromatograph, is the 120 ml bottle placed on a shaking table for at least 3 hours. The time of equilibrium was found by analysing the same sample at different times after the preparation of the sample. The raw data from this analysis is attached on the enclosure CD.



(a) Shaking table (b) Sample extraction (c) Sample (d) Injection well (e) Output

Figure E.2: *Different states of the analysis of the water samples for chlorinated compounds by gas chromatograph.*

For TCE is an injection volume of 0.1 ml used, whereas there for PCE is used an injection volume of 0.3 ml as there are considerable less PCE present in the samples than TCE. Injection volumes larger than 0.3 ml will damage the column of the gas chromatograph and give misleading results. It was not possible to analyse the samples for VC as it was present in small concentration and because VC shows smaller effects on the detector than e.g. PCE as VC only contains one chlorine atom.

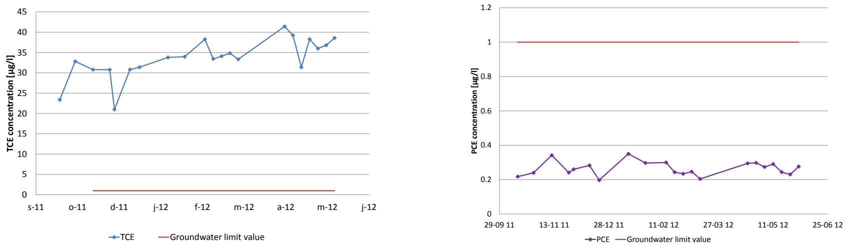
There have been extracted one sample from 11 different boreholes in the area of the polluted well 5.594 to confirm, that the pollution is still limited to that well. The result from the analysis of the samples appear from table E.1.

Table E.1: Results from water samples in the area of the pollution at Varbro well field.

Borehole no.	**Filter interval [m u.t.]**	**Trichloroethylene (TCE) [µg/l]**	**Tetrachloroethylene (PCE) [µg/l]**	**Total chlorinated compounds [µg/l]**
Groundwater standard		1	1	1
5.631	53-73	0	0	0
5.594	54-74	14.74	0.22	14.95
by 5.594		0	0	0
5.596	29.5-33.5	0	0	0
by 5.596		0	0	0
5.600	34.5-35.5	0	0	0
F1	6-12	0	0	0
F1	28.5-34.5	0	0	0
F1	35.5-42	0	0	0
F2	4-6	0	0	0
B3	1.5-3.5	0	0	0
B4	1.5-3.5	0	0	0
B100	10-11.5	0	0	0

As expected was 5.594 the only borehole which was polluted. There was October the 12th, 2011, found TCE above the groundwater standard and a smaller amount of PCE.

The water sampling in 5.594 and the two nearest boreholes (5.631 and 5.596) was continued for several months. Still no concentrations of either TCE or PCE were detected in 5.631 and 5.596, whereas both constantly were detected in 5.594. The concentrations of TCE and PCE measured from October the 12th 2011 to June the 1st 2012 appear from figure E.3.

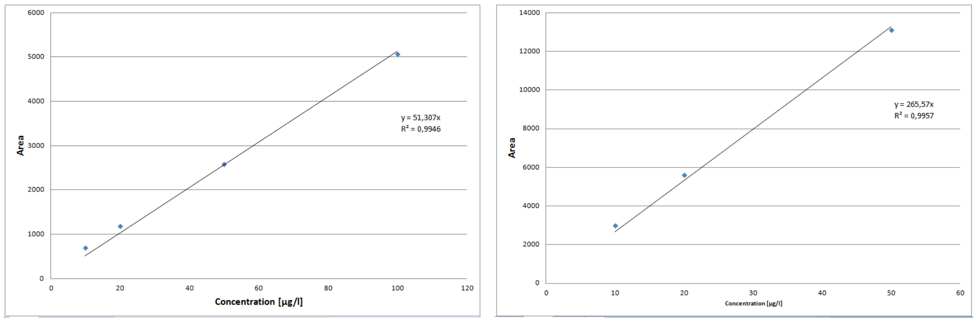


(a) Measured concentrations of TCE in 5.594 (b) Measured concentrations of PCE in 5.594

Figure E.3

E.2.1 Standard curve

To convert the output from the gas chromatograph was a standard curve produced for both TCE and PCE. The result appear from figure E.4.



(a) Standard curve for TCE

(b) Standardcurve for PCE

Figure E.4

As it appear from figure E.4 is there a linear correlation between the output area and the concentration from which the concentrations in the samples will be calculated.

ECD detectors are more sensitive than e.g. FID, and by repeatedly sample analysis within a short period of time might the detector show different effects for the same concentration at the start and the end of an operation. Therefore was a standard sample analyses before and after a series of samples were analysed. This has however not been a problem for any samples in this report.

E.2.2 Sensitivity and uncertainty test

The sensitivity of the procedure of analysis on the gas chromatograph was tested by injecting the same sample repeatedly. Here was found a standard deviation of 1.4 μg/l for TCE and only 0.009 μg/l for PCE which both are considered permissible. The raw data from the test is attached on the enclosure CD.

The uncertainties about the sampling procedure were tested as well, to investigate if the time of the sampling have an impact on the result. Three samples from 5.594 extracted with a 30 minutes interval was therefore analysed. Each sample was analysed in duplicate. The result gave a standard deviation on the three samples on 0.65 μg/l for TCE and 0.01 μg/l for PCE, which is assumed just the uncertainty from the analysis procedure.

F

Soil samples

Two boreholes, F1 and F2, were established in November 2011 within Skibsbylejren - a warehouse and auction area. Skibsylejren is one of the possible sources of the pollution at Varbro well field. The location of the boreholes appear from figure 2.7 in chapter 2.2. F1 is a 50 m deep borehole with three screen sections in different depth while F2 is a 6 m deep borehole with one screen section.

(a) (b) (c)

Figure F.1: *Establishment of borehole F1 and collection of soil samples in November 2011.*

Soil samples were collected from both of the boreholes. Partly to investigate the possible soil pollution in the area and partly as an investigation of the geology and the specific hydraulic parameters at different geological layers. The samples were therefore taken in three different manners, all evenly distributed by the depth.

In the investigation of the pollution samples were collected in bags for PID measurement on the headspace within the bags. The result from the PID measurement serves as an indicator of which samples might be polluted and is therefore used in the decision of which samples should be analyzed further. For a further analysis has soil been sampled in glass jars for later analysis by gas chromatography.

Regarding the investigation of the geology and the hydraulic parameters has larger samples been collected for different experiments. These were sampled in 5 L buckets.

Each of the analyzes and their results will be presented in the following subsections.

F.1 PID measurement

A PID detector shows a fluctuation if a volatile compound is present in the sample. A fluctuation on the soil samples may therefore not necessarily be a sign of chlorinated compounds as the detector measures the total amount of volatile compounds in the sample. This method is however often used to decide which samples should be analyzed further as it is fast and inexpensive.

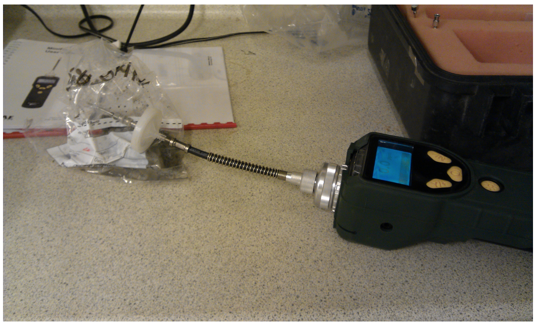


Figure F.2: *PID measurement of one of the soil samples from F1.*

The soil samples stays in the closed bags placed dark and cold for about 24 hours to ensure that the equilibrium is reached and to avoid unwanted bacterial activity. The PID measurement of the soil samples showed minor fluctuations in samples taken from 6, 8, and 10 m u.t., which is in approximately the same area as fluctuation by PID measurements on soil samples from The bore hole on the dry cleaner site. In both cases are the fluctuation low but in the approximately same amount.

The PID measurements of the soil samples is shown in the bore hole journal of F1 in enclosure C.

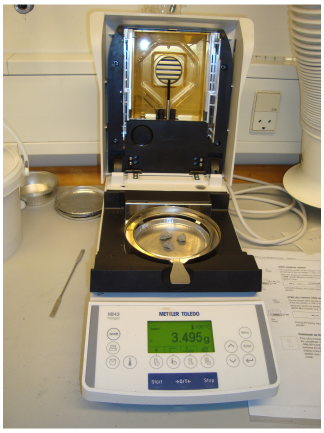
F.2 Pollutant analysis

On the basis of the PID measurements, were 8 soil samples in glass jars selected for further analyses by gas chromatography. The 100 ml glass jars were filled with approximately 30 ml soil sample and stored cold for at least 24 hours to ensure equilibrium between the sample an the gaseous phase. The soil samples are analysed with reference to the same procedure as used in the analysis of the water samples. Even though fluctuations were observed by the PID measurement, non of the samples showed any trace of chlorinated compounds by analysis by gas chromatography. The fluctuations may be caused by small amounts of oil products which previously has been detected within Skibsbylejren or it could simply just be a disorder as the fluctuating samples were very wet.

F.3 Gravimetric water content

The water content in a soil sample tells a lot about the type of the main part of the particles in the sample. The gravimetric water content is measured on every soil sample collected from borehole F1 and F2. The purpose of this analysis is mainly to create a foundation for a selection of samples which should be analyzed further to achieve a geological understanding of the location. The analysis of the gravimetric water content along with the visual description and the bore hole log will all be used in this selection to ensure that every layer is represented in the further investigations.

The gravimetric water content is measured on the samples collected in buckets. It is measured by heating approximately 3 g of sample at 105°C and continuously measuring the weight. When the weight has not changed for a certain period of time the analysis stops. The gravimetric water content is calculated on the wet weight basis. On the basis of the gravimetric water content are 7 samples picked out and analyzed further.



F.4 Grain size analysis

The purpose of the grain size analysis is to identify the main fraction of the 7 samples which were picked out on the basis of the measurement of the gravimetric water content. The main fraction in the sample will in all probability be dominant in preparation for the hydraulic properties. There may, however, be samples consisting of almost equally parts of two different fractions.

Figure F.3: *The result of one of the grain size analysis.*

The grain size were determined by an analysis of dry sample material. If more more than 10 % of the samples is smaller than the finest sieve they are assumed to be clay samples. This was the case for the samples collected in 12, 19, 39 and 50 m b.s. The sample from 36 m b.s. also had a very high amount smaller than the finest sieve. This sample did however also contain both fine, medium and coarce grainde sand and gravel. The specific data is attached on the enclosure CD.

F.5 Effective porosity

The effective porosity is one of the most important parameters when modeling the transport of water and pollutants. The Effective porosity can be determined from intact soil samples. In this case we wish to determine the effective porosity of every geological layer found by the establishment of the 50 m deep borehole, F1. It was however not possible to get intact samples at these depths. Therefore has the intact samples been made by packing the soil samples.

The packed samples has been wetted to saturation and afterward drained to pF = 2 in a "retention box" illustrated in figure **??**. The mass of the sample was determined before and after and from these informations can the effective porosity be calculated. The calculations and results are attached on the enclosure CD.

Figure F.4: *The retention box*

F.6 Hydraulic conductivity

As the effective porosity is the hydraulic conductivity a important parameter when modeling transport mechanism. The hydraulic conductivity is found by experiments on the packed soil samples used to determine the effective porosity. The laboratory experiment is based on a conversion of Darcys law as constant pressure is presumed doing the experiment. The Darcy flow is described in equation F.1.

$$Q = K\frac{dh}{dl}A\left[\frac{m^3}{s}\right] \tag{F.1}$$

The experimental set up is illustrated in figure F.5. Water is sent through a soil sample with a given pressure. The amount of water penetrating the sample over time is used in the calculation of the hydraulic conductivity. The calculations and results are attached on the enclosure CD.

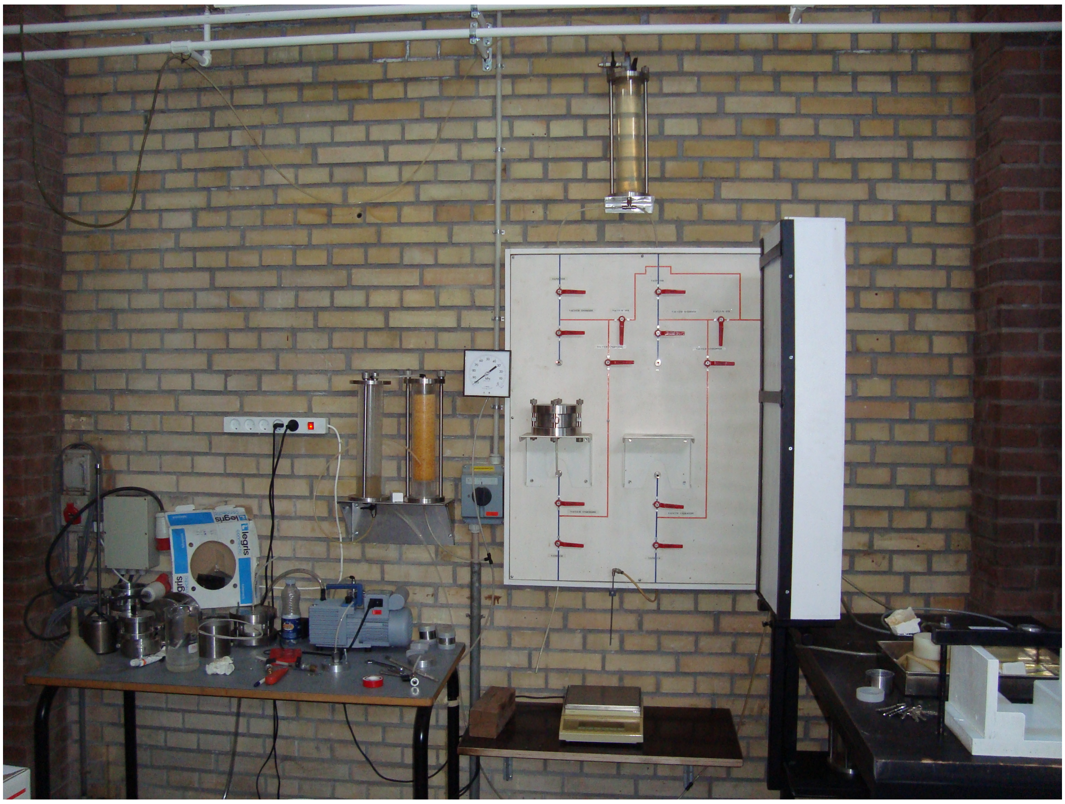


Figure F.5: *The set up used to measure the hydraulic conductivity of the different soil samples. The set up is based on Darcy's law.*

Methods for level specific water sampling

G

Several factors come into play in the case of choosing the optimal method for level specific water sampling. If the water dynamics is approximately stationary, might random samples be enough to value the state of the pollution, whereas random samples in area with shifting pumping rates often will be misleading, because the transient water dynamic might affect the concentration of the pollutant. This phenomenon is sketched in figure G.1.

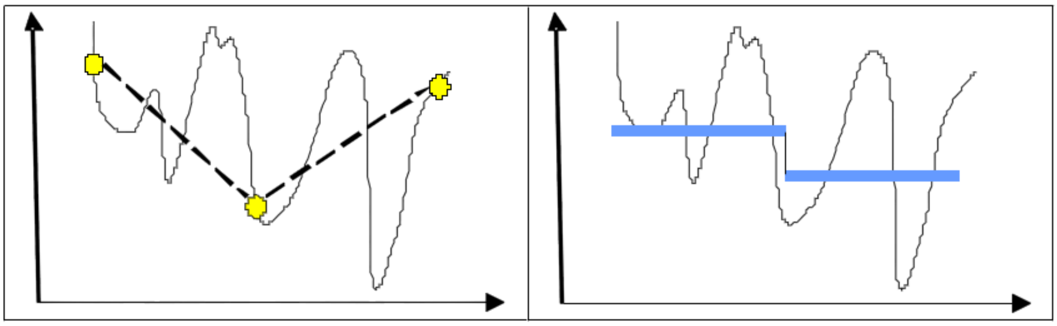


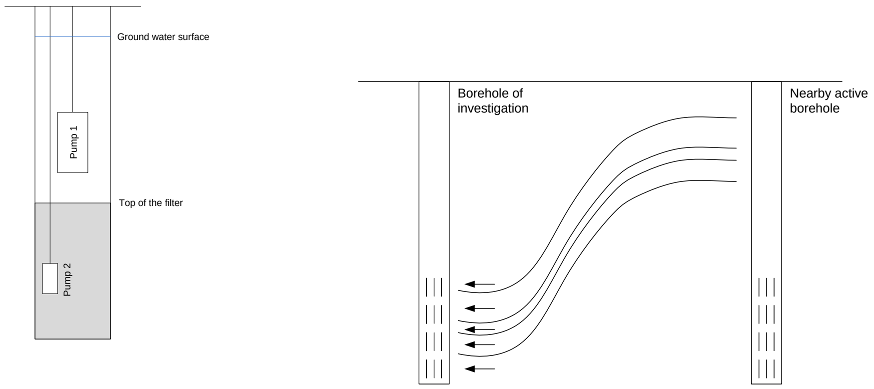
Figure G.1: *Random samples (left) gives a snapshot of the pollution while average values (right) shows the general tendency [Grontmij - Carl Bro A/S, 2011].*

If the pumping is varying in time might passive sampling for an average measurement or continuous measurements be a better option. An example of passive sampling is also sketched in figure G.1 [Grontmij - Carl Bro A/S, 2011]. Another factor is the financial aspect; Is the output of the method sufficient compared to the expenses of it?

Examples of methods, for level specific water sampling, are: a two pump separation system and packers, which are both active sampling methods, plus the passive sampler: SorbiCell from SorbiSense. SorbiCells as a multilevel sampler and the two pump system have been the most relevant subjects regarding the pollution of Varbro well field, and will be discussed further in the next sections.

G.1 The two pumping system

The two pumping system is one of the most common methods for level specific water sampling for analysis of xenobiotics. This method involves pumping in two separate levels, usually above the filter and within the filter. A master pump with a high performance is places in the top of the filter to provide a constant stationary flow through the filter and well liner. A smaller pump will be used for the water sampling in the filter. The sample is in this way a mixed sample of the water underneath the small pump. The pricip of the method is sketched in figure G.2 [Schmidt, 2012].



(a) Princip of the two pumping system method.
(b) Possible influence of nearby active boreholes on the water influx to the borehole of investigation.

Figure G.2: *[Schmidt, 2012]*

If there is active boreholes near to the borehole of investigations, might it be necessary to take these out of operation in the period of the sampling, as the active boreholes else will create a downward gradient towards the investigation borehole, as illustrated in figure G.2(b). This will give misleading results, as the samples might show considerable concentrations in the bottom of the filter, which will actually represent water from a higher level.

The water influx through the filter is rarely uniform at every level of the filter because of deposits of the filter and changing geology. Therefore is a flowlog often needed to calculate the exact concentrations in the samples [Schmidt, 2012].

The pros and cons of the two pumping system is summarized in table G.1.

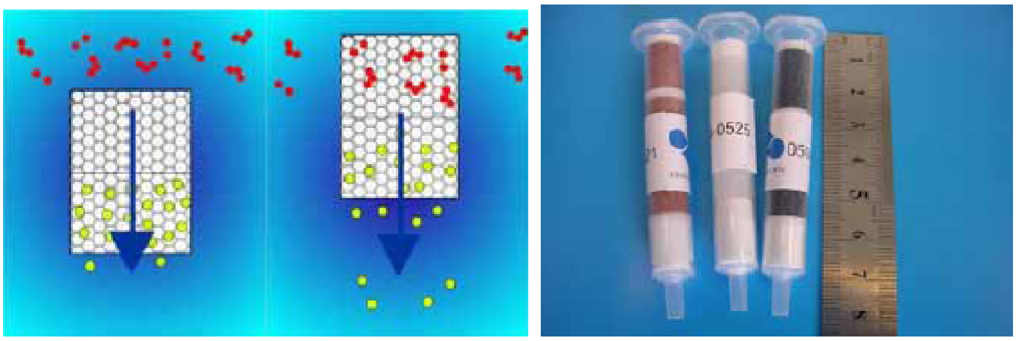
Table G.1: *Different pros and cons of the two pumping system.*

Pros	**Cons**
- Often the most inexpensive method	- Requires energy
- Very simple setup	- Discharge of a larger amount of water to terrain
- Samples from several levels in a short period of time	- Pumping before sampling is required
	- A flowlog is often needed for calculation of the concentrations

The two pump method is one of the most inexpensive methods, as the only expenses are the pumps, which are a sunk cost, and the analysis of the samples [Schmidt, 2012].

G.2 SorbiSense multilevel sampler

The multilevel sampler from SorbiSense is based on the SorbiCell technology. SorbiCells are passive sampling units consisting of a polymer, in which the pollutant absorbs, and a filter with a tracer salt, that will be washed out proportionally with the water flow through the cell. The polymer is specific according to the specific pollutant one wish to investigate, and is later extracted from the polymer for pollutant analysis. Figure **??** illustrates the SorbiCell technology and shows examples of some of the cells [Grontmij - Carl Bro A/S, 2011].



(a) By the flow through the SorbiCell is the pollutants (red dots) absorbed and the tracer salt (yellow dots) released.

(b) SorbiCells with different polymers.

Figure G.3: *The princip of the SorbiCell technology [Grontmij - Carl Bro A/S, 2011].*

The SorbiCells are installed in a system, that makes it possible to extract 3 level specific water samples at the same time. Between the cells are packers installed to insure that no vertical flow occurs. This princip separates from the original packer system, as the SorbiCells are passive samplers. Inflow of water from other levels will thereby be avoided. The SorbiSense multilevel sampler can be installed in filters from 1 m to 15 m. Beside that, the sampler will fit into most filters as the widest point of the sampler, the packer system, is down to 5.2 cm. This point is expanded according to the filter size. The sampling period will be between 1 week and 3 month depending on the water flux [Grontmij - Carl Bro A/S, 2011].

The pros and cons of the multilevel sampler is summarized in table G.2.

Table G.2: *Different pros and cons of the SorbiSense Multilevel sampler [Grontmij - Carl Bro A/S, 2011] [SorbiSense, 2. maj 2012].*

Pros	**Cons**
- The sampling is passive - Sampling in more than one level at the same time - There is no requirement for energy - Pumping before sampling is not necessary - Fits into filters with a diameter as small as 63 mm	- One sampling may take up to 3 month - The sampling is restricted to 3 levels - The cell might be effected by colloidal material

The expense of the equipment is about 13,000 danish kroner for the sampler and 3 SorbiCells. In addition to that comes the expenses to the extraction and analysis of the cells. The sampler can be reused but the cells, which per se costs 2250 danish kroner for a 3-pack, are only for a one time use [SorbiSense, 2. maj 2012].