CityChlor Think-Tank

Conceptual Site Model
Bio-washing machine

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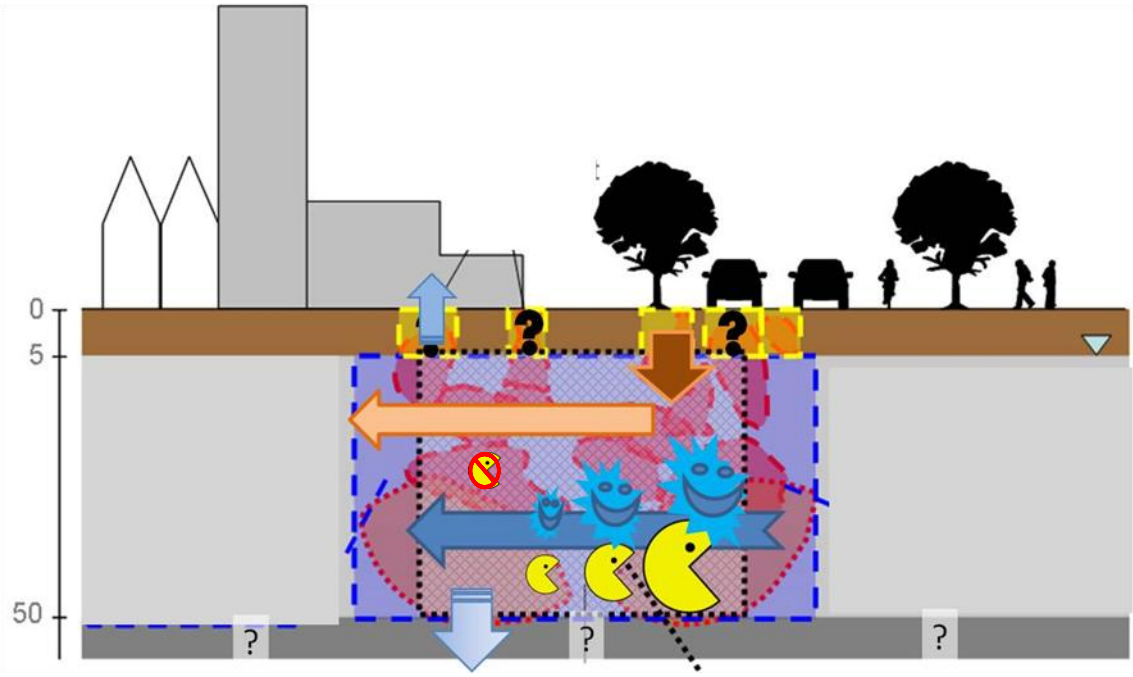

area oriented approach

Investing in Opportunities
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1. Introduction

1.1 CityChlor and the integrated approach

Space is scarce in Europe. Even in the subsurface it is getting busier. Large-scale soil and groundwater contamination with chlorinated solvents are often an obstruction for urban developments. The traditional way of dealing with polluted soil and groundwater does not work in all cases and is not economically and sustainable feasible. In urban environments multiple contaminations with chlorinated solvents are often mixed with each other and spread underneath buildings. This not only leads to technical problems for remediation, but also to liability and financial discussions and hence has an impact on society. An integrated approach and area-oriented approach is needed to tackle the problems. The CityChlor project has demonstrated that remediation and sustainable development can evolve on a parallel timescale.

An integrated approach combines all aspects that are relevant to tackle the problems that pollution with VOC in urban environment causes. Depending on area, site and context different aspects together or parallel to each other can be used. Not only technical solutions are included, but also socio-economical aspects as urban development, communication, financial and legal aspects, time, space, environment and actors (active & passive) have to be handled.

CityChlor did not remain at single case remediation, but looked at the area as a whole in a bigger context: the area-oriented approach. A technical approach that makes it possible to remediate, monitor and control multiple groundwater sources and plumes within a fixed area.

1.2 CityChlor and technical innovations

The managing of knowledge and technical innovations are one of the key to achieve a sustainable city development. A development project has to cope with loads of information coming from different disciplines in different (technical) languages and with different uncertainties. With chlorinated solvents, the knowledge about the pollution will always have a certain uncertainty that can have an impact on the course and the costs of the remediation. An efficient 'managing of knowledge' will try to decrease this degree of uncertainty.

CityChlor therefore also worked on the technical aspects of characterization and remediation. The conventional techniques that are applied for investigation and remediation have their limitations dealing with chlorinated solvents. Promising innovative techniques exist, but do not easily find their way to current application. This barrier is often caused by lack of knowledge on different levels. Experts and contractors do not always have the means to invest in experiments with new techniques, authorities are reluctant to accept techniques of which the results may be uncertain and clients aren't eager to pay for experimental techniques.

Dissemination of knowledge can break this deadlock. CityChlor therefore collected experiences from field application of innovative techniques and implemented itself a number of techniques in pilot projects. For the detailed outcomes, the reader is referred to the specific reports.

CityChlor - “new solutions for complex pollutions” **http://www.citychlor.eu/**

2. Introduction

A CityChlor Think-Tank has been formed for the CityChlor Interreg project consisting of Bioclear, Deltares, Utrecht University (UU), MWH and Wageningen University (WUR). The goal of this Think-Tank is to arrive at a consistent and coherent study set-up for the different core activities within the station area of the municipality of Utrecht. This will ensure that the Think-Tank can supervise and advise the municipality of Utrecht and NL Agency within the CityChlor research project. The aim is to identify activities, give direction to the required study, list contemplated end results and assist in defining who can fulfil a role to achieve this goal.

Aquifer Thermal energy storage (ATES) is being employed as a decontamination technique, i.e. the "Bio-washing Machine", within the Utrecht station area. On the one hand, it is being determined how (bio)monitoring can be optimised; on the other hand, the effect of ATES is being examined on the degradation of VOCl (volatile chlorinated hydrocarbons) contaminants in the subsurface in the station area within the context of the CityChlor project.

Ultimately, CityChlor must arrive at recommendations for smart and effective monitoring within the area-focused approach of the "Biowashing Machine" (how to monitor in a proper and practical manner?) and at responsible area-focused groundwater management (how to control risks?). Advice will also be provided about the operation, steering and monitoring of the "Bio-washing Machine".

This study set-up is a growing document that will be adjusted in due course depending on study results and recommendations from the Think-Tank.

2.1 Plan-do-check-adjust cycle

The technical basis of an area-oriented remediation plan is a “Conceptual Site Model” (CSM). The aim of the CSM is to understand the dynamics in the subsoil. The CSM approach is based on the plan-do-check-adjust cycle (figure 3). The outcome of the plan-do-check-adjust cycle is integrated and used to fine tune and up-scale the area oriented approach. Based on this the CSM is adapated (see chapter 4).

Figure 1: Plan-Do-Check-Adjust cycle

The principles of the area-oriented approach in general can be summarized as follows:

- PLAN: establish goals, areas and processes;
- DO: implement area-oriented approach by a combination of source remediation and groundwater plume management;
- CHECK: implement the monitoring program of the area;
- ADJUST: analyse the results, take actions when necessary according to the plan and adjust the area-oriented approach.

The results of the CSM are a distinct contribution to the CHECK part of this approach

2.2 Revisited CSM

The CSM approach is part of the plan-do-check-adjust cycle. The outcomes of the plan-do-check-adjust cycle were integrated to fine tune and up-scale the area oriented approach. The results from the different research lines have resulted in a adapted conceptual site model. The three important aspects that have resulted in an altered view of the situation are: (see report: "Integration of CSM Biowashing machine Utrecht')

- Clean groundwater layer enormously reduces the risk for vapour intrusion;
- The confining layer (aquitard) between the 1st and 2nd aquifer is locally absent;
- Two degradation processes are important in the subsurface of Utrecht: reductive dechlorination and micro-aerophilic degradation The biodegradation capacity is heterogeneously distributed and locally is absent.

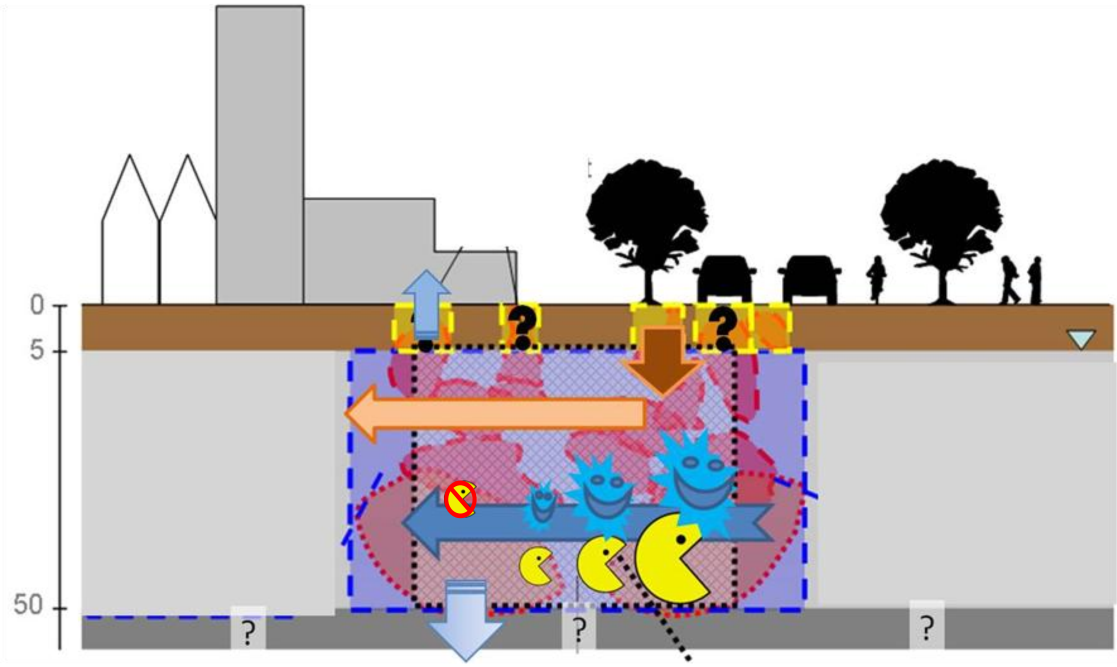


Figure 2: CSM Biowashing machine revisited

3. Study set-up

3.1 Background

The CityChlor project aims to develop knowledge about and gain experience on the realization of an area-focused approach to soil remediation. Within this context, the utilization of sustainable energy with ATES can play an important role. Essential elements of this plan are monitoring and optimization. That is, how can you optimally monitor area-focused groundwater management effectively and efficiently. The choice has been made in Utrecht to deploy ATES as a decontamination tool: the "Bio-washing Machine".

Large-scale contamination of the deeper subsurface aquifers is also present in the studied area. Contaminants mainly consist of chlorinated hydrocarbons and the (intermediary) degradation products thereof. The contamination found in the subsoil cannot always be retraced to the original physical source and/or the responsible party. Additionally, it has emerged that 'plumes' from different sources run into each other at depth. As a case-focused approach is thus illogical and unmanageable, an area-focused approach is the preferable option.

It is also necessary to have clear objectives with regards to an area-focused approach in terms of the expected and required groundwater quality. Processes such as biological degradation, dilution, evaporation and, large-scale ATES systems impact the concentration and physical distribution of groundwater components. It is thus important to understand which processes are relevant in general, and specifically, which yield contaminant concentration reduction.
Therefore, a substantial area demarcation (the system limit) must be identified within which contamination may be present. However, at the same time, within the demarcated area, system limits, in terms of specific concentrations, may not be exceeded.

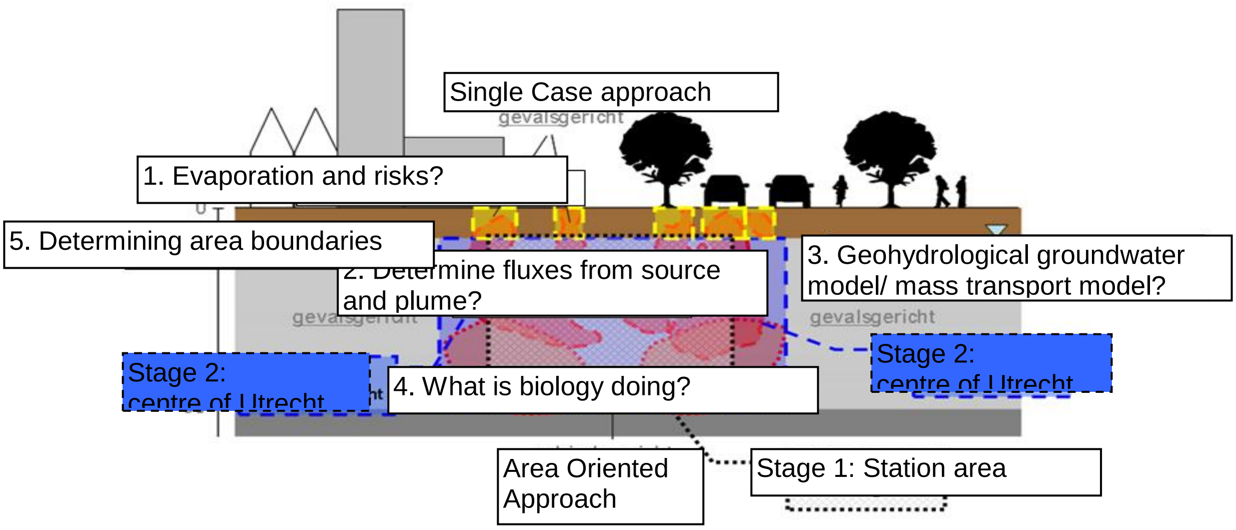


Figure 3: Schematic representation of the items to be addressed in the Utrecht CityChlor project

3.2 Relationship between the different aspects

A number of factors must be considered (see figure 1) when determining the demarcated area and identifying controllable (= 'sustainable') elements to manage risk. Contamination will be mobilized into the (deeper) groundwater from the different source areas that are still present and have not been decontaminated. This means that these groundwater deposits will be fed and, therefore, will have an impact on the total mass of contamination that is released per unit time. Degradation of the contamination reduces the total mass. Therefore, contaminant degradation must be examined fully in a manner that allows proper measurement rather than relying on numerical modelling. Such measurements contribute to the estimation of both the risks as a result of the contamination (do contaminants reach critical objects?) and to the determination of the system limit. Another process that can possibly remove contamination from the system is volatilisation into the vadose zone. The contamination will be transported from both the unsaturated layer and the groundwater to the vadose zone. It is important to map and monitor volatilisation in particular due to the risks associated with this process.

Final contamination boundaries and concentrations must be properly determined through a modelling approach which integrates results from measured degradation potential. Area boundaries can be defined based on these calculations.

Another aspect to be kept in mind is the impact of the (multiple) ATES systems in the area on the contamination present. It is important that the following factors be determined: (i) where will these systems have an impact on the spread of contamination, (ii) where will the impact be on degradation, and (iii) where could they lead to risk increase. Increased risks occur, for example, when highly contaminated groundwater ends up in shallow groundwater layers, which in turn increases volatilisation. Similarly, when ATES is applied to DNAPL (dense non-aqueous phase liquid) sensitive areas the contaminant concentrations increase, especially when there is a limited degradation capacity. In other areas, dilution may occur due to the mixing of large volumes of contaminated groundwater with non-contaminated groundwater causing risks to, in fact, be reduced. Additionally, ATES may stimulate underground biology and the related degradation process due changes in parameters such as flow and temperature. Conversely, it could disrupt or slow down biological degradation, depending on the tolerance of subsurface microbial populations and increases in the aforementioned parameters.

We propose that attention be paid to these aspects in sub-studies.

Based on current monitoring and newly gained knowledge, ultimately, a smart monitoring programme can be designed where the focus will be on indicator parameters that are important for the operation of the system as a whole. Moreover, an indication will be given on the deployment of several ATES systems in an effective manner.

3.3 Sub-studies

Study questions:

Essentially, the following elements are involved:

1. Does evaporation of contamination from source areas take place? If so, to what extent and what are the related risks? (Section 3.1)
2. Does additional volatilisation take place when (multiple) ATES systems are employed yielding increased risk with respect to ATES implementation? (Sections 3.1, 3.4, and 3.5)
3. What portion of the contamination is leached to the plume? Here, an inventory of source locations and a determination of the fluxes from the source and plume are necessary. (Section 3.2)
4. Where is the contamination flowing towards and can it be found in the subsurface in Utrecht? This involves geohydrological groundwater model and substance transport model (Sections 3.2 and 3.5)
5. Does the soil have degradation capacity? If it does, how large is this expected to be? Which biological processes play a role? Where is this capacity active in terms of time and space? (Section 3.3)
6. What changes in the macrochemistry (redox potential and mineral composition) of the groundwater due to pumping and heating associated with a large-scale ATES system? What is the net impact of groundwater being pumped around on the degradation and spread of the contamination, including the possible impact of DNAPLs? (Sections 3.4 and 3.5)

Different subprojects, as described below, will be set up in order to obtain answers to these studied questions.

Based on the questions above, the specifics can be determined for:

- Identifying the area boundaries;
- The smart monitoring of the contaminated area;
- Setting up a smart monitoring plan with innovative measuring techniques.

4. Elaboration on the different components

4.1 Volatilisation risks:

1. Selection of locations with comparable characteristics;
   Pertinent sites are selected based on available information (field characterisation) and analysis results of previously measured data in crawl spaces and inside air analyses, for example:
   - Type and concentration of contaminants
   - Soil type
   - Soil humidity/air permeability of the soil
   - Groundwater level and fluctuation
   - Built-upon or not, type of buildings and quality of foundation and floors
   - Degradation potential of the unsaturated zone
   - Evaporation from above ground ATES systems

   Air permeability of the soil and the groundwater level have the greatest impact on evaporation. Ideally locations are both representative of typical conditions at the station area of Utrecht and have been well characterized yielding a dataset of measurements. An alternative would entail two locations: one site that falls into the Emergency Locations category according to Sanscrit based on real measurements and a second location that falls under the Emergency Locations in accordance to Sanscrit where actual measurements do not demonstrate the necessity of this categorization. Preferably, a ATES system is near these locations or one can be positioned there during the project.

2. Efficient and effective field characterisation to obtain insight into the concentrations and process that may play a role with regard to evaporation at a location;
   Monitoring tools that can determine the concentration of contaminants for demonstrating evaporation risks are essential. This refers to both the contamination of sources in the groundwater as well as the concentration in the soil air and indoor air. Subtopics that are important within this context include:
   - Setting up a measurement network in which the subsoil and top soil are included (groundwater, soil air, indoor air).
   - Proper sampling and analyses using existing validated measuring methods for the determination of soil humidity, organic carbon content, concentration of contaminants (top groundwater, pore water in the unsaturated zone, soil gas and inside air), oxygen (dissolved and unsaturated zone) and the groundwater temperature (due to the presence of the ATES system). In addition, recently developed measuring methods will be used and validated to map the situation on location. Examples of this are “passive sampling” (soil and air samples), stable isotope analyses, the presence of bacteria or specific conversion enzymes, radon, and methods that provide insight into the spatial spread of the source zone such as the Enhanced in-situ Soil Analysis (EnISSA) Membrane Interface Probe (MIP) method.

Choices on specific sampling and analysis techniques and the number of and types of samples per location depend upon the location selected. In addition, this will also take place in relationship with the work in the Flux sub-study.

3. Insight into the processes that determine the behaviour of the contaminants including flux and degradation in the unsaturated zone. (see sections 3.2 and 3.3)
4. Predicting the spread and degradation of the contaminants;

   Through comparing different models with and without degradation parameters, validation of the models with measured values is possible.

   1. SANSCRIT: instrument to determine the urgency or non-urgency of a seriously contaminated location (based on CSOIL).
   2. VOLASOIL (RIVM): a more extensive analytical model that takes into account diffusion and advection by the soil and flow through "cracks" in the floor. It is also possible to calculate the concentrations in air inside buildings with basements and/or concrete with this.
   3. STOMP (Deltares/WU): 1D numerical model for the saturated and unsaturated zone and crawl spaces. The processes that are included in the model are spatial diffusion, gas advection and degradation.

   When determining the urgency of a situation, SANSCRIT and VOLASOIL often overestimate inside air concentrations as compared to measurements for specific substances. The absence of degradation in these models is probably part of the reason for this. The STOMP model does take degradation as well as heterogeneity of the soil into account. Proper parameterisation of the different processes, especially degradation, is essential to ensure that the evaporation risks can be assessed.

5. Risk estimation;

   Result from modelling of the selected locations indicates which combination of parameters pose the highest potential risk. A map of risk estimation is made for the location(s) using these results. Finally, criteria for preventing evaporation are drawn up and prioritised.

6. The impact of ATES;

   The impact of ATES on evaporation is unknown. In principle, higher groundwater temperature and increased mixing will mobilise contaminants and this may lead to higher concentrations shallow groundwater and in soil air. Modelling is based on groundwater temperature in an operating ATES system and will provide insight into this. Measured depth concentration profiles can be compared with the calculated concentrations.

4.2 Flux determination

Flux from source areas must be determined within a range and/or reliability interval in order to ensure that a connection can be made between the degradation capacity and system limits and/or decontamination objectives. Using a flux approach, the extent to which the deeper groundwater is being fed with contaminants can be estimated. This estimate can be compared against the contribution of various removal mechanisms for contaminants that play a role in deeper groundwater (for example, degradation and evaporation).

Multiple parameters are essential to the determination of flux, which is mass per unit time: concentrations in the groundwater, the flow rate and the lateral flowing surface (surface through which contaminants flow).

A combination of time-averaged concentration measurements as well as determination of both the flow rate and direction is required for flow through a specific plane.

Different options are available to measure concentrations:

1. Regular sampling in observation wells.
2. Solid phase extraction (Sorbisense and sorbiflux).
3. Passive Diffusion Bag Samplers (PDSB) (diffusion sampler).
4. Low Density Polyethylene (LDPE) bag with adsorbents.
5. Silicone rubber hose.
6. PMF

Option 1: Regular sampling in observation wells has the disadvantage that sampling can be unreliable, especially in the case of volatile compounds and that natural fluctuations in groundwater concentrations lead to time variations in measured concentrations.

Option 2: Solid phase samplers (such as the Sorbinsense) measure a time-average concentration, meaning that natural fluctuation in concentrations are averaged out. However, adsorbents may not sufficiently adsorb the compounds present in Utrecht (in particular, cDCE and VC). Insufficient absorption of VC is noted in the literature; inquiries are being made at Sorbisense for current references/information regarding this.

Option 3: The Passive Diffusion Bag Samplers are often used in the USA and are commercially available. An LDPE bag with water is placed in the observation well. Groundwater compounds diffuse through the membrane with time ensuring that the water in the bag has the same concentration as the surrounding water. As time is required to reach equilibrium, diffusion out of the bag is also not instantaneous, allowing retrieval of the sampler and transfer of the water to sampling bottles. Additionally, the equilibration period means that the sample and measured results are also time-averaged to a certain degree over probably a few days. This sampling method is more robust than the regular method. The most critical step is filling the bottles from the sampler, as evaporation can occur during this action.

Option 4. Through modifying the PDBS by filling the LDPE bag itself with an adsorbent, a much longer time of equilibrium is achieved and, therefore, the concentration is integrated over a longer period of time. The robustness is also further improved because the probability of loss or contamination decreases. Reverse calculation of the observed uptake to groundwater concentrations does, however, require calibration of the method.

Option 5. If sorption or absorption methods are used, , as alternative is silicone rubber. The Log K_{OW} of VC is around 1.5, which means that a section of silicone rubber placed in an observation well will have a concentration of VC that is 30 times higher than that in water. This is a factor of 100-200 for DCE. Uptake can further be improved by integrating an adsorption agent into the silicone rubber. This provides more options for measuring time-averaged concentrations. Once again, a calibration investigation is required to determine the relationship between water concentrations and absorption. Silicone rubber is very thermostable, allowing compounds to be thermally desorbed for analysis purposes. Silicone rubber samplers are often used in surface water to determine the concentration of hydrophobic substances at a ng/l level. To the best of our knowledge, applications with VOCl in groundwater have not yet been performed.

Choice:
Preferably, validated techniques are used for which experience with VOCl (in particular cDCE and VC) is available and for which additional calibrations are not required due to the limited investigation time available. Therefore, solid phase samplers and passive sampling bags are the preferred options. The specificity of the sampling for VC and cDCE must, however, be verified in consultation with suppliers.

Direction and rate:
In addition to the (time-averaged) concentration, groundwater direction and flow rate are important. Positioning filters in which samplers can be installed is crucial for the success of this component. This limitation determines where observation wells containing the solid phase and/or passive samplers will be positioned.

In-situ measuring probes are available to determine direction and flow rate (Phrealog) that have also been tested within an SKB relationship (PT6423: "Demonstratie van een methode voor het vaststellen van snelheid en richting van grondwaterstroming met behulp van de Phrealog-sonde" (Demonstration of a method for determining the rate and direction of groundwater flow using the Phrealog probe). It was concluded that the Phrealog does provide usable information, however the result strongly depends on the geometry of the observation well. For a good result, observation wells of at least 50 mm must be used, the probe must be centred in the observation well, and the perforation of the well must be adjusted to the Phrealog structure (bottom part of the observation well, 0.5 m, blind model). In order to obtain an adequate understanding of subsurface flow, measurements should be taken over a long period of time and at different points. The measuring range of the Phrealog is 1×10^{-3} to 1×10^{-6} m/s (approximately 30,000 m/year to 30 m/year) and is probably not reliable in slower flowing water layers. The flow rate in Utrecht is probably lower than 30 m/year.

It is thus currently proposed that conventional measuring methods be employed to estimate direction and rate based on head measurements, soil structure/characteristics and, for example, MIP cone penetration tests. Within this context, an existing, reasonably well investigated contaminated location should be used where, for example, MIP cone penetration test results and contamination plume location(s) are available. Multiple observation wells are probably already available at such a location, however they may not be suitable for the samplers.

Direction and rate may also be verified through a more conservative tracer test.

MIP cone penetration tests are proposed in order to obtain a picture of which layers are most relevant. This ensures immediate mapping of the permeable layers downstream of the source contamination and gives an indication of which layers are contaminated.

Location selection:
A location must be selected that continuously fed by an upstream source. Prerequisites with regard to the location are:

- Study data available about soil and groundwater contamination present in the source;
- Preferably a documented location;
- Location is accessible to allow the positioning of filters downstream of the source;
- Preferably, all measurements have been taken based on flow direction, for example, based on contamination level measurements in the plume area;
- Preferably the MIP cone penetration tests have already been performed.

The Netherlands contribution to the process:
Multiple observation wells are added in a relatively small grid. Subsequently, samplers are positioned to obtain an indication of the extent of the contamination outflow in both the horizontal and vertical plane. Based on measurements of the (probably) flow direction and MIP cone penetration test, he grid's direction with respect to the source and the depth of the filtered section in observation wells will be determined . We propose carrying out downstream sampling at a short distances from the source, both horizontally and vertically in the groundwater column. By positioning different samplers (see the diagram in Figure 2), a good indication of the contamination flux from the source can be derived. Additionally, head measurements can be measured and a grain size distribution can be determined using sampling material collected either during observation well installation and/or during MIP tests.

Prior to contaminant sampling, a tracer test can be performed to verify the direction and rate of groundwater flow. A pump test on newly positioned filters can be performed to verify this calculated permeability.

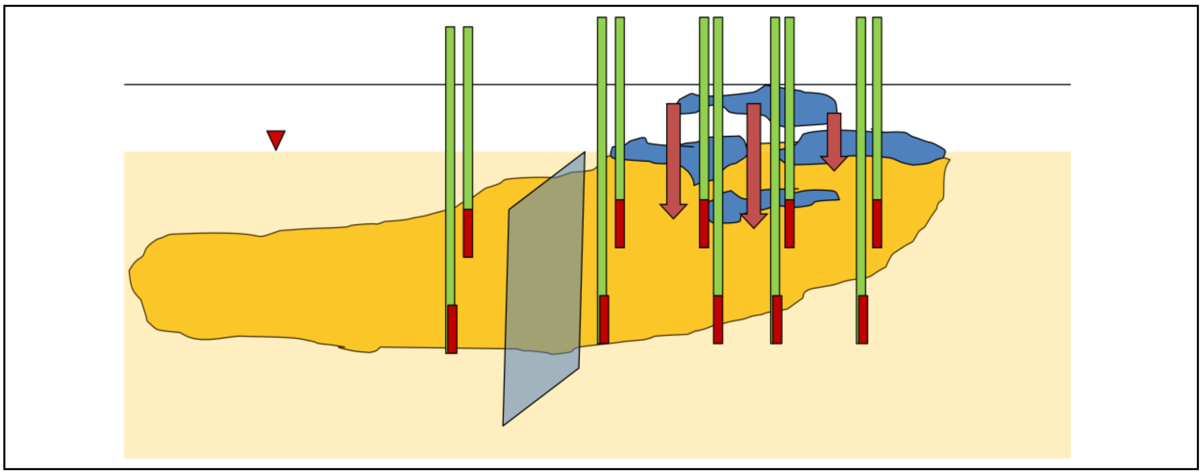


Figure 4: Schematic representation of the positioning of samplers to determine the flux.

Activities:

Step 1: Verification of the different solid phase and passive samplers (month 1).

Step 2: Parallel to step 1; select a location in Utrecht with regard to which many soil and groundwater analyses are available from both the source and plume (month 1).

Step 3: Performance of a MIP cone penetration test, provided this has not yet been performed, to identify permeable layers and the extent of the contamination in the different layers for positioning filters. Head measurements for groundwater flow determination (month 2).

Step 4: Tracer tests to validate the direction and rate (month 3); possibly an additional pump test for determining permeability.

Step 5: Inserting passive samplers (round 1) for the determination of contaminant concentrations released from a source area that has not yet been decontaminated (months 4-5). Steps 5 and 6 can also be interchanged.

Step 6: Inserting solid phase samplers (round 2) for the determination of contaminant concentrations released from a source area that has not yet been decontaminated (months 5-6).

Step 7: In parallel to taking the contaminant measurements: Head measurements for monitoring the fluctuation in groundwater levels (important with regard to interpretation).

Step 8: Data interpretation and extrapolation to the full plane around the relevant location. Comparison with the expected discharge.

Step 9: Extrapolation to multiple locations in Utrecht (based on geo(hydro)logy) and estimation of the total flux.

Number of filters:

For the time being, 8 filters/sampling point are assumed in total under the actual source and 8 filters are assumed in total in the downstream plane (for different depths; the details will depend on the nature and scope/complexity of the selected location in Utrecht).

4.3 Biological degradation capacity

4.4 Background information on the degradation capacity in the subsoil of Utrecht

The degradation capacity of the soil must be determined in order to determine the amount of contaminant that may leach from the source zones (flux); and/or how much contamination is allowed to remain in the plume; and/or to understand the functioning of the system. This is shown in Figure 5.

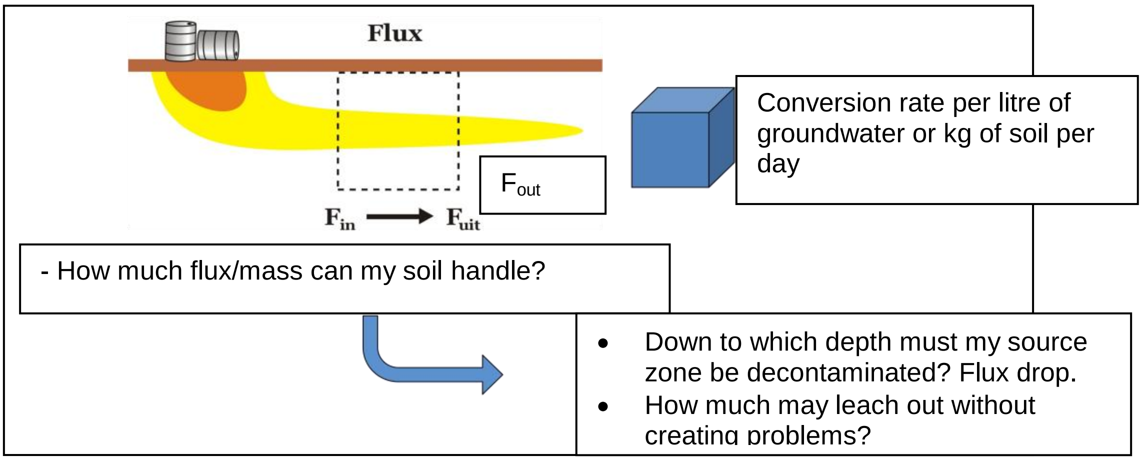


Figure 5: Relationship between the capacity and flux when compared to the decontamination objective for the source.

In this part of the project we investigate whether degradation of VOCl occurs in the saturated zone in Utrecht and, if so, through which degradation processes. Currently, most research into the degradation of VOCl has focused on degradation through reductive dechlorination. For anaerobic degradation of CIS and VC, strongly reducing methanogenic conditions are optimal and the presence of specific *Dehalococcoides* bacterial strains is required. In addition to reductive dechlorination, oxidation by micro-aerophillic bacteria may play a role in the degradation of VOCl under less reducing conditions, under very low oxygen pressures, however the degradation rate will be much lower. It is, therefore, important to determine which degradation processes currently occur in the subsoil of Utrecht.

Bioclear and Deltares have already taken groundwater samples in the past within the scope of different projects in Utrecht to obtain insight in biological degradation processes of VOCl. The conclusion is that reductive dechlorination, one of the most well-known and researched processes in which PCE and TCE are ultimately converted into ethane/ethane, does not, occur on a large scale in the deeper subsurface in Utrecht. Proper conditions and suitable bacteria (*Dehalococcoides* spp.) are found at a number of places in Utrecht, implying that if the microbes are active, contaminant concentrations can be reduced. Locally therefore this process may play a role. Bioclear has already been able to link numbers of *Dehalococcoides* bacteria to the capacity for reductive dechlorination (gram of VOCl/m^3 soil/year). This information can be utilized directly within the CityChlor project.

4.5 Possible activities to determine biodegradation capacity.

The possible activities that can be performed in order to determine the biodegradation capacity in Utrecht are stated below:

- Degradation tests with cDCE and VC from different samples from the deeper subsoil (conducted);
- Degradation tests with ^{13}C-labelled cDCE substrate (conducted);
- BacTRAPs with ^{13}C-labelled substrate placed at different locations in the subsoil (conducted);
- Biodegradation rate determination on location with in-situ mesocosms (in progress);
- Isotope analyses on VOCl in a plume (conducted);
- Isotope analyses (carbon and chloride atom) at different locations in Utrecht;
- Molecular analyses focusing on reductive dechlorination and micro-aerophilic degradation of cDCE and VC (in progress);
- Degradation tests where different water layers are mixed (to determine the effect of variation in redox conditions);
- Tracking the results of reference sites (including from other areas of the Netherlands), with comparable geology/geochemistry, with regard to the degradation capacity found at these locations;
- Make a correlation between the determined degradation capacity and lithographic/geological layer from where the samples originate.

Degradation tests, molecular analyses and stable isotope analyses should be conducted in order to investigate the abovementioned aspects. Part of the degradation tests and molecular analyses, mentioned above, have already been conducted. In the following paragraphs a number of the abovementioned activities are (briefly) described.

4.6 Groundwatersampling and molecular analyses

<u>Groundwater sampling</u>

To determine the overall degradation capacity in the city centre of Utrecht it is important to sample a number of monitoring wells. For this the following sampling methods can be applied:

- Standard monitoring method
- Dialyser method (sampling of large volume with 'kunstnier')
- Bactrap sampling (sampling units containing activated carbon)

On these samples molecular analyses will be/were performed.

<u>Molecular analyses</u>

Molecular analyses are carried out to detect reductive dechlorination and/or micro-aerophillic degradation of cDCE and VC in the city centre of Utrecht. Similar molecular analyses will also be used in the degradation tests. Once the indicator organism/enzyme is known (that is responsible for VOCl degradation in Utrecht), samples for molecular analysis can be taken at a large number of locations in Utrecht. It should be noted, that additional samples must be taken to supplement molecular data, such as (geo)chemical parameters. Correlations between molecular data and geochemical conditions can be determined by using multivariate statistical analysis.

Geochemistry

Specific (geochemical) analyses are required to gain insight in the relationship between geochemistry/lithology and the degradation potential. The concentration of dissolved electron donors and acceptors must be determined. These include nitrate, sulphate, iron, methane and hydrogen (H_2). The quantity of hydrogen is a measure for the redox condition; furthermore hydrogen is the most important substrate for dechlorination. For example, in order to determine the effect of ATES on redox conditions, the hydrogen pressure prior to and during operation of an ATES system must be determined.

Isotope fractionation

An estimate can be made of the degree and rate of degradation in the past by determining the concentrations and isotope fractionation of CIS and VC. The effect of ATES on the aforementioned parameters can also be determined through regular sampling and analysis. It can be demonstrated whether ATES can actually lead to accelerated degradation of contaminants. In stead of measurements in a clear flow path, samples can also be taken from the same monitoring well over time, for example before and during ATES operation. We would like to propose that stable isotope analysis is carried out both with regard to the carbon atom (C) and chloride atom (Cl). This provides insight in which degradation process takes place; beit reductive dechlorination, micro-aerophilic degradation or a combination of different processes. Isotope analysis on the carbon atom is also conducted on the degradation tests.

4.7 Microcosm degradation tests

The assessment whether reductive dechlorination or micro-aerophilic degradation occurs in the deeper subsurface can be done by performing anaerobic degradation microcosm tests. In these tests local soil and groundwater is used to determine the biological degradation capacity. In the current project soil and groundwater was used from three locations to which (^{13}C labelled) *cis*-DCE or VC contamination was spiked. The degradation of both contaminants was followed through headspace measurements.

4.8 In-situ mesocosms

In-situ mesocosms will be installed in the field in order to validate the determined biodegradation in the microcosm tests in the lab and investigate the in-situ biodegradation rate of both reductive dechlorination and micro-aerophilic degradation.

It is known from previous molecular analyses that the bacteria carrying the genes responsible for micro-aerophilic degradation are more likely to adhere to soil surface, therefore the use of in-situ mesocosms is preferred. In-situ mesocosms are permeable tubes containing soil from the location, see figure 5. These tubes will be installed at a specific filter depth in a monitoring well over a period of 6 months. The soil in the tubes is continuously in contact with the surrounding groundwater and thus with the contaminant and degrading bacteria. We expect that the bacterial community on the soil will adapt to the circumstances in the groundwater. At certain time intervals, the mesocosm tube will be removed from the site and taken to the lab and the soil will be analysed for the presence of the genes responsible for contaminant degradation (*Dehalococcoides*, vcrA, etnC, etnE, *Polaromonas*).

Set up:
Periodically, every 2 months soil from a permeable mesocosm tube will be sampled and preserved in the lab for molecular analyses.

Before the mesocosm tubes are removed from the monitoring well groundwater samples for chemical and molecular analyses will be collected. Analyses will be conducted on contaminant, redoxparameters, TOC. We also propose to conduct stable isotope analyses (initially and at the end of the monitoring period). Stable isotope analyses give insight in whether the decrease in contaminant concentration was caused by biological processes or not. If isotope analyses on both C and Cl atoms is conducted it is (in theory) even possible to determine which degradation process has occurred (add ref).

The contaminant data (gathered at each sampling time) will be used to determine a decrease in contaminant concentration over a period of time. This information will be used to determine the in-situ degradation rate. This decrease in contaminant concentration will be linked to the number of degrading bacteria present in the mesocosm sample at that specific sampling time.

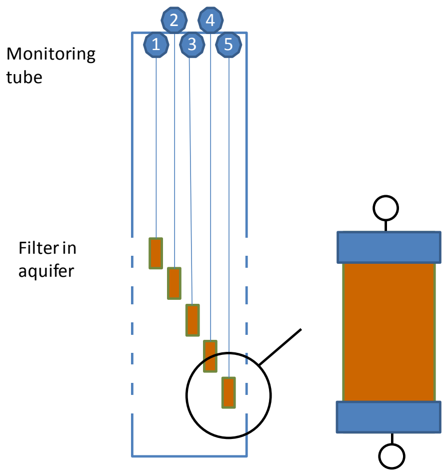


Figure 6. In-situ mesocosm

The in-situ mesocosms will be place in four different monitoring wells:

- Monitoring well 53 and/or monitoring well 67 (micro-aerophilic degradation expected)
- Monitoring well Amsterdamsestraat (in combination with flux measurements)
- Monitoring well Lijsterstraat (in combination with flux measurements)
- Monitoring well ATES proeftuin

4.9 Extrapolation of results to entire city centre area

Once it is established, with molecular analyses, isotope analyses and degradation tests, which degradation processes play a role in Utrecht, it is important to determine the net degradation capacity for the entire city centre area in Utrecht. By determining, for example, that locally no degradation is observed, or isolated reductive dechlorination occurs, or micro-aerophilic degradation occurs, these local measurements can be extrapolated for the central Utrecht area as a whole. If it is possible to link degradation capacity with redox conditions (geochemical data) it would be possible to extrapolate the results from individual monitoring wells to the whole of the city centre area and also determine whether degradation will continue when the contaminant enters a groundwater area with different redox conditions. Thus, the (intrinsic) degradation capacity is translated into time-dependent capacity (will the degradation continue).

It is also important to find out what the impact of an ATES system will be on the degradation capacity because a number of ATES facilities have been/are being installed in the central area of Utrecht. The effects of temperature, changing groundwater flows, and changing redox conditions on the degradation capacity must be taken into account. This can be partially achieved by making a clear link between prevailing redox conditions and specific degradation rates; in the most extreme case, this means determining whether degradation does or does not take place. Subsequently, this information is introduced into a groundwater model, which already models the effect of mixing groundwater on the redox conditions.

4.10 Geohydrology

An appropriate geohydrological model is required to ensure a good prediction of the behaviour of the contaminants in the subsoil. This model will be transparent, flexible, dynamic and efficient with regard to the calculation time and it can also, eventually, be used by other parties.

Transparency is achieved by managed storage of all relevant data and model files in a manner that ensures easy access and allows the information to be readily comprehensible to stakeholders.
A prototype for an Internet portal will be set up for this purpose that will, ultimately, have to be supported, preferably within the municipality of Utrecht. This can also support the transition to the Key Subsurface Register (BRO) for the Municipality of Utrecht.

Flexibility is required, as new data will emerge continuously during the implementation of the project that we must be able to process in the geohydrological model. Also model schematics will have to be refined based on new questions or insights. Deltares already has ample experience with this from setting up the iMOD[1] (Interactive MODelling) user interface. Dynamic developments such as temporary drainage set-ups, ATES, deep underground structures, etc., can also be processed in the model based on the time when they have or will be implemented.

The transport model will be based on a calculation efficient flow path approach that Deltares also applied for the Port of Rotterdam. The contaminants are followed on flow lines in time, taking into account delivering from source zones, retardation, and redox dependent (sequential) degradation. The calculation time of this method was short enough for the Port of Rotterdam that an uncertainty analysis was also performed using a Monte Carlo simulation. This method will be adjusted for the situation in Utrecht so that a non-stationary flow situation, which occurs automatically with regard to an ATES system, as well as the mixing of contaminants and redox conditions in ATES pits are included.

The usefulness of currently existing models will first be assessed and, if required, a new model will be built. Should a new model be built, an inventory of existing models will be complied, such as the "Utrecht Biowashing Machine" model of the Municipality of Utrecht and the Hydromedah model (developed by Deltares for Water Board Hoogheemraadschap De Stichtse Rijnlanden), and this information will be used as much as possible. In addition, a detailed 3D subsoil model will be produced using the borehole logs of the Municipality of Utrecht and the information from DINO (Data en Informatie van de Nederlandse Ondergrond; Data and Information about the Dutch Subsoil) and other data such as pump tests and geophysical data. The TNO GEOTOP method will be used within this context, which will produce a quantification of the heterogeneity within the water-carrying layers.

Estimates of the input parameters such as the initial contamination situation, concentration and size, degradation parameters, initial redox parameters, etc., will be suggested and included in a Monte Carlo analysis to determine uncertainty.

Multiple variables will be calculated for the result of the model, such as the average or median contamination situation and the probability of exceeding a standard at specific times. Concentrations and loads in ATES systems, potential receptors and reduction of mass in source zones can also be modelled. In addition, different scenarios can be calculated by adjusting/expanding the ATES systems.

4.11 Impact of ATES

4.12 Background

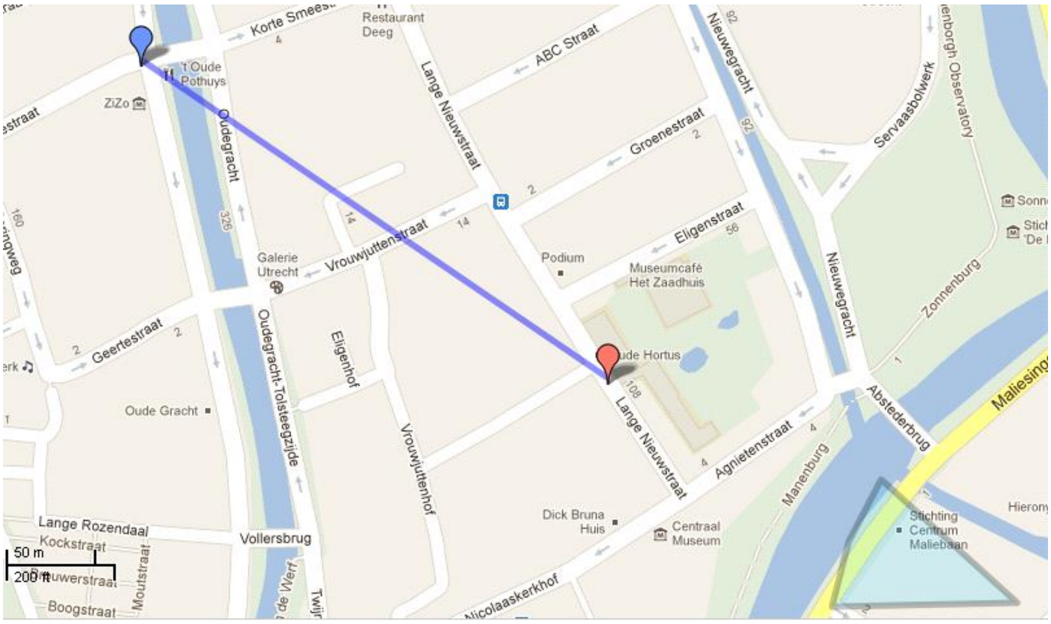
Aquifer Thermal energy storage (ATES) systems are employed as a sustainable energy saving technology for providing indoor climate control within the city centre of Utrecht. As the groundwater in the aquifer below the city centre is extensively contaminated with chlorinated solvents (VOCls) the effects that these ATES systems may have on the degradation of these contaminants, and its potential functioning as a "Bio-washing

[1] iMOD is a user interface that is based on the well-known Modflow software.

Machine" within an area-wide contaminated groundwater management approach is studied within the context of the CityChlor project. Within the CityChlor project a pilot ATES study with a duration of 2 years is proposed.

4.13 Selected location “Museumkwartier”

Museumkwartier, an area in the southern part of the centre of Utrecht has been selected by the Utrecht Municipality as the site to study the impact of ATES on chlorinated solvent contaminated groundwater (Figure 7). Within this area the preferred location of two ATES wells has been determined by the Utrecht



Municipality (REF W+B). Distance between the two wells is approximately 320 m.

Figure 7: Location of the hot (red) and cold (blue) well for the ATES pilot in the Museumkwartier area. Blue triangle indicates groundwaterflow direction range (W-NW)

Tabel 3.1. Geohydrologische schematisatie (bron: Dinoloket; Tauw, 2010)

van (m -mv)	tot (m -mv)	lithologie	formatie	geohydrologische eenheid	doorlaatbaarheid (kD) c.q. weerstand (c)
0	- 4 à -5	leem	Echteld	deklaag	c = 10 - 100 d
- 4 à - 5	- 50	fijn tot grof zand, soms grindig. Lokaal voorkomen kleilenzen	Kreftenheye, Urk, Sterksel	1^e watervoerend pakket	kD = 2100 m^2/d (k= ca. 45 m/d)
- 50	- 70 à - 75	leem	Waalre	1^e scheidende laag	c = 2.000 dagen

Figure 8: Geohydrological conditions for the municipality of Utrecht (W+B).

4.14 VOCl contaminant conditions at “Museumkwartier”

Analysis of contaminant conditions were based on recent characterisation in 2008 for the area (Oranjewoud, 2009):

- Predominantly cis-DCE and vinyl chloride (VC);
- VC concentrations generally higher than cis-DCE;
- Contamination evaluated at 2 depth ranges (below ground surface): 25-35m and 35-45m. Surface levels at +3 - +10 m NAP;
- Concentrations generally higher in 25-35m bgs, but exceptionally high concentrations for cis-DCE (13000 µg/l) and VC (1500 µg/l) recorded at 39-40m (well 409);
- No signs of any significant degradation beyond VC;
- Iron-reducing conditions.
-

4.15 ATES configuration

Recently Witteveen+Bos have determined the required specification for the ATES system at Museumkwartier (REF). An important boundary condition was that the specifications of the ATES installation should allow it to be used by a yet unknown building, after the Citychlor ATES pilot is over. The following key specifications were used:

- Required maximum pumping capacity of 105 m^3/hr, for the final configuration of 2 hot wells and 2 cold wells;
- Initial configuration of 1 hot and 1 cold well is sufficient for pumping rates that do not require permits (<10 m^3/hr);
- In-well pump with capacity of 10-20 m^3/hr;
- Filterlength of 30m, ranging from 20m –NAP to 50m –NAP. Based on the information on vertical contaminant distribution, the top of the filter would start in the shallow contaminated zone, the bottom of the filter would extent into a “clean” part of (uncharacterized?) aquifer;
- Regional groundwaterflow velocity is estimated at 10 m/yr (W+B).

4.16 Boundary conditions for ATES pilot

The ATES configuration provides some important boundary conditions for research set-up:

- The filterlength of 30 m provides the depth across which groundwater will be mixed. Separating this filterlength into 2 separate, consecutive well screens of 15m would allow more flexibility in controlling the degree of mixing;
- Monitoring locations should be within the radius of influence from the well as wel at reference locations. The maximum distance is mainly determined by the pumping rate, pumping duration and well screen length. To get a first impression of the dimensions required the cylindrical radius of influence was calculated, assuming a spatially homogenous permeability field and ignoring background groundwater flow;

- The calculations were performed for 2 yrs of continuous pumping at 10 m^3/hr and 100 m^3/hr (Figure 99). The maximum calculated values for both pumping rate (78m and 248m) remain well below the distance between the two ATES wells (325 m), but are a gross overestimation of actual radius of influence, if pumping is not:
  - Unidirectional;
  - Continuous.

When multiple cycles of injection and extraction are planned within the 2 year period then maximum monitoring distance is further reduced.

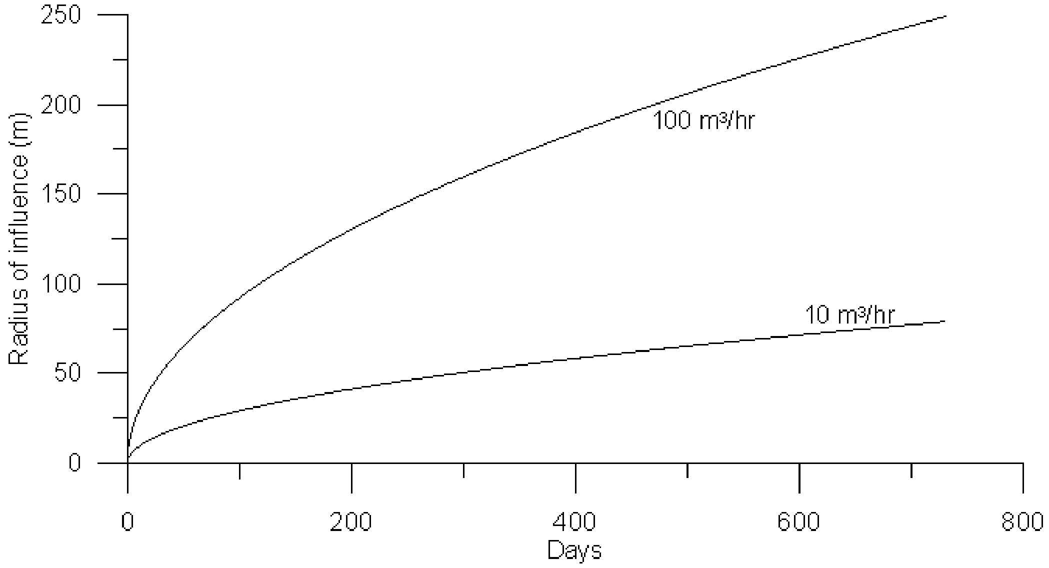


Figure 9: Calculated radius of influence for 2 continuous pumping rates over a 2 year period

If 4 cycles of injection and extraction are considered during a 2 year period than the calculated maximum radius of influence is for continuous pumping at 10 m^3/hr is 28m and at 100 m^3/hr it is 88m. The actual monitoring radius to be considered is dependent on the actual pumping rates used, continuity of pumping and practical considerations, but a maximum monitoring radius of <40m seems likely for a cyclic pumping approach. Monitoring at 1 - 5 - 10 m distance form well.

Putting these maximum monitoring radii in perspective, the indicated regional groundwaterflow velocity of 10m/yr will have an significant impact on the movement of injected ATES water, particularly at lower pumping rates. Monitoring becomes particularly challenging, if the direction of regional groundwaterflow is unknown in advance. This is because for the injection of a relatively small watervolume, the range of direction (W-NW) can result missing the ATES water at an installed monitoring line.

Instead of cyclic pumping phases, we could consider testing conditions sequentially, i.e. continuous injections under alternating conditions. Under higher pumping rates this could force the nett flow direction between the injection and extraction well. Although it would be preferable to measure in a straight line between the two wells, this might be difficult due to finding suitable and accessible spots for installing monitoring wells. As a result contemplating changes in concentrations not location specific but on the basis of changes in the total area affected.

4.17 Research setup

In Januari 2012 two wells were constructed (Geotron). The distance between the wells is approximately 260 m. Each well is equipped with observations wells at various depths. To monitor degradation, observation wells are positioned on a line connecting the ATES wells at six locations. The locations are chosen to achieve uniform sampling of groundwater quality in time. These locations are determined using an analytical solution for groundwater flow between two wells in a homogeneous isotropic confined aquifer. Natural groundwater flow (10 m/y, W+B) is assumed to be negligible with respect to the groundwater velocity resulting from operating the ATES wells.
Assuming continuous operation of the ATES system at 105 m^3/h the sampling wells should be realized at the locations in Table 1 (Figure).

Observation point	Distance from well [m]	Velocity [m/d]	Residence time [d]
1	0.2	304.08	0.00
2	62	1.29	26.60
3	92	1.02	53.21
4	118	0.94	79.90
5	142	0.94	105.50
6	168	1.02	132.19
7	198	1.29	158.80
8	259.8	304.08	185.40

Table 1. locations of sampling wells

Observation points 1 and 8 are located near the injection and production wells and have already been installed (geotron). The locations of the other observation wells are specified as distance from the injection well. At each location, observations wells are installed at four depths. Each well is also equipped with a glasfiber optical cable to be able to monitor temperature changes (see Effect 2 in paragraph 5.1).
At the given flow rate of 105 m^3/h the injected water front takes 26.5 days to travel between each observation well. To be able to monitor the development of degradation as the injected front progresses, sampling should be performed at least at the same rate (once in 30 days).

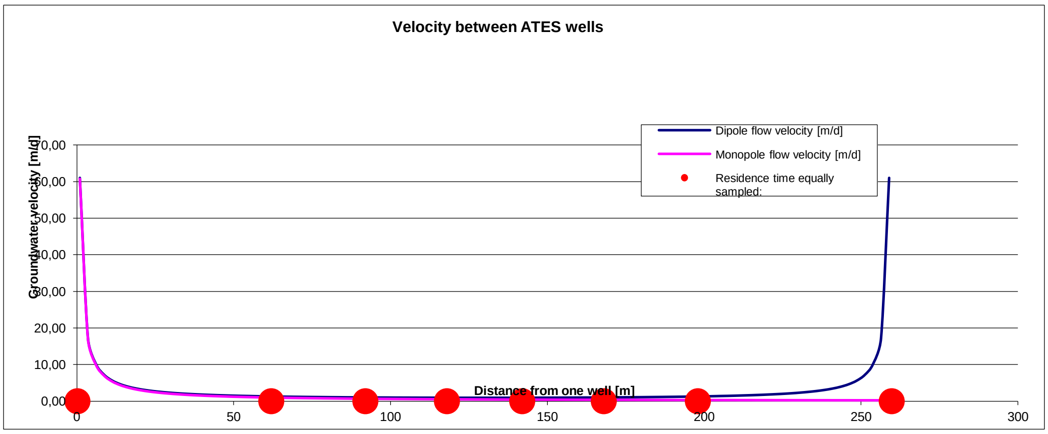


Figure 1: Steady state velocity distribution between the two wells and observation points located at distances separated by equal travel time.

5. Research approach

5.1 Potential effects

In the research approach several factors that may contribute to enhanced degradation are considered. To distinguish the effect of these factors, results will be compared with:

1. Initial starting conditions.
2. Conditions at reference wells outside the influence of the ATES system: 1 upstream and 2 lateral.

The following potential effects will be considered:

Effect 1: Effect of increased flow velocity: may increase release of contaminants?

Effect 2: Effect of spreading and diluting contaminants across a larger aquifer volume: may enhance the use of available natural attenuation capacity.

Effect 3: Effect temperature elevation: may increase degradation rates. Highest achievable temperatures should be considered, preferably 25°C or higher (but prevent density effects to occur that may bias/complicate the monitoring).

Effect 4: Effect of electron donor supply: to overcome substrate-limited conditions. Or only add biomass (see results MMB labtests). Include monitoring for well-plugging as this fear prevents the use of stimulated degradation in ATES systems sofar. Another option is adding low concentrations of oxygen (micro-aerophilic conditions).

5.2 Proposed monitoring

	Groundwater (sources and wells)	**Sediment**
Tracer	Bromide (as NaBr)	
Divers	Pressure, temperature, EC	
Bacteria	- Bacteria that are involved in degradation: On species and genes DNA: DHC, VC reductase, Polaromonas, EtnC en EtnE, Bacteria/genes involved in nutrientcycles total bacteria; McrA (methane formation), DsrA en B (sulphate reduction) On activity RNA: VC reductase, EtnC en EtnE, McrA (methane formation), DsrA en B (sulphate reduction)	←idem
Macro chemical parameters	- Chloride - Iron: (III) and (II) - Nitrate - Ammonia - Sulphate	- Organic carbon - Iron: (III) and (II) - Total

	- Sulphide - Manganese - Calcium - - Metals? - methane	Sulphur, Sulfphate → Sulphide precipitations in the soil
Contaminant + degradation products	VOCl, ethene + ethane	-
….	Redox EC (divers) Temperature (divers) pH alkalinity	-
Mass discharge	Fluxmeter, cumulative concentrations	-
Average concentrations	Sorbisense PFM	-
Isotopes	VOCl	-
Temperature	fibreglass cabels	-

5.3 The result: Determining the area boundaries and the impact on receptors

The preceding components give insight in the degradation processes but, nevertheless, there will still be a degree of uncertainty when predicting contamination concentrations and locations. The following must, therefore, be considered when determining the area boundaries:

- Keeping the monitored/influenced area as small as possible.
- The probability that contamination (at higher concentrations than the limitvalue) escapes the area boundary. A monitoring network must be set up for this and a fall back scenario may have to be enforced.
- Decontaminate a number of plumes/source zones that are expected to reach the area boundary at concentrations higher than the permitted limit in such a way that concentrations decrease sufficiently to stay below the limits at the area boundary.

These choices must, ultimately, be made by the municipality. Indications on the following will be provided by the geohydrological model:

- Where the boundary must be to ensure that this probability is smaller than a determined percentage.
- What the probability is for a number of potential boundaries of the managed area.
- What the post-remediation value is for a number of sources/plumes that form a threat for the area boundary or a receptor within the managed area.

5.4 The result: Smart monitoring programme

Smart monitoring of the contamination in Utrecht

New innovative (smart) monitoring tools are used to, ultimately, apply area-based groundwater management in the municipality of Utrecht. The components mentioned above can be used to define the parameters that are of absolute importance and where the critical boundaries are. A smart monitoring network becomes possible based on this.

A distinction can be made between **process** monitoring and **boundary** monitoring within this context:

1. Process monitoring: monitoring as stated in section 3.3, where sources are monitored, allowing knowledge and data to be obtained from the parameters in the area. This knowledge can be used to improve the model and to obtain a better picture of the system limit.
2. Boundary monitoring: cost effective monitoring based on a cost-benefit analysis; where are the main risk locations at the system boundary that may threaten the receptor? The data obtained at the system limit can be used to improve the model, allowing boundary monitoring to be optimised. This is an iterative optimisation process.

Process monitoring (see section 3.3) will be implemented within the project, and the data will be processed in the model (section 3.4). As the arrival time of the (potential) contamination at the area boundary is expected to be later than the closing date of the project, boundary monitoring is not included in the monitoring plan drafted within the project.

6. Results

It is possible to consider the area-oriented system as a black box in which the degradation capacity is known and total amount of contaminant (flux) is known. The processes occurring in the subsurface are modelled and the outcome provides information on risk prone areas and boundary limits etc. These risk prone areas can be related to various aspects such as vapour intrusion, exceeding the set norms at the boundary of the system, threat to other receptors.

The area-oriented approach only applies if the microbial degradation capacity (amount of contaminant that can be degraded by the microbiology within the system) is greater than the contaminant flux (amount of contaminant entering the system per unit time).

In an area-oriented approach the following procedure is required.

1. First of all (step 1) determine which ‘critical objects’ need to be protected. In Utrecht these are: 2nd aquifer, potable water abstraction well and indoor air concentration (vapour intrusion).
2. Estimate the total amount of contaminant mass present in the area.
3. Develop a groundwater model to determine the fate of the contaminant and follow the pathlines to determine risk prone areas.
4. Determine the degradation capacity within the (dynamic area). It is important to monitor the degradation processes and determine whether sufficient biodegradation capacity is present.
5. Define the system boundaries.
6. Determine which actions are needed/ monitoring program is required.

For more details see report; Integration of results CSM ‘Bio-washing machine’

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