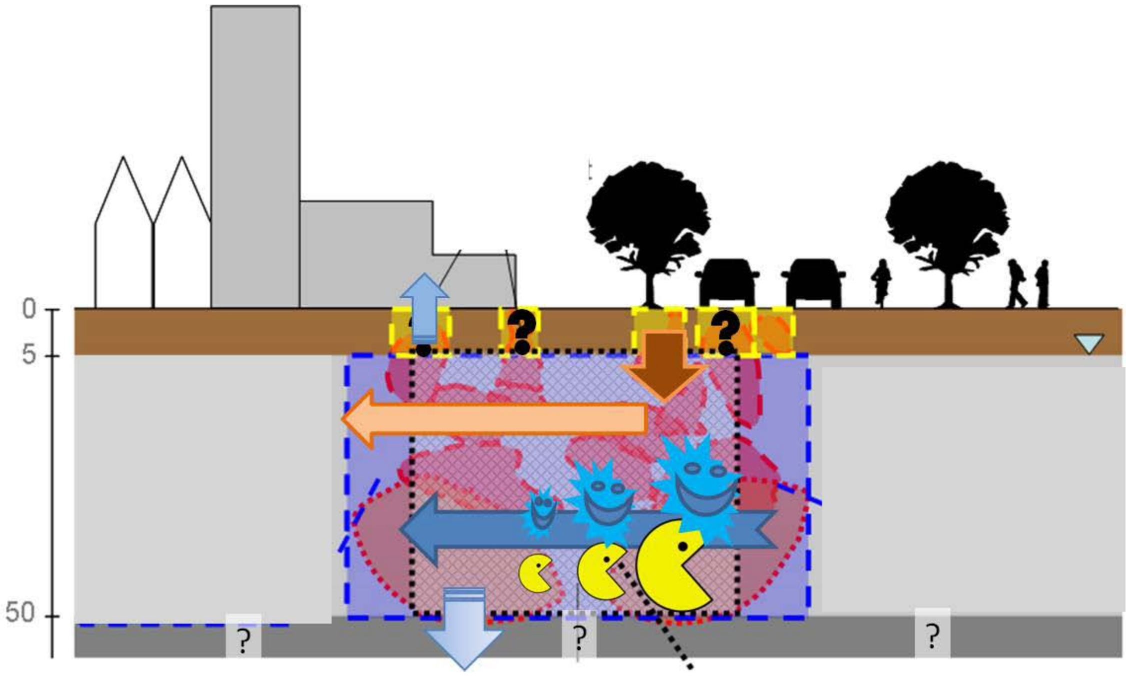
# Integration of results CSM 'Bio-washing machine'

## Different innovative characterization methods and models for optimisation of the area-oriented approach

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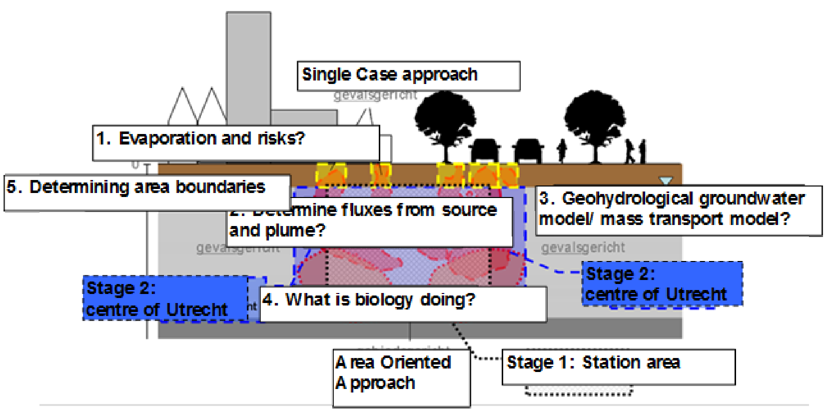
# Summary


The CityChlor project aims to develop knowledge about and gain experience on the realization of an area-oriented approach in urban groundwater remediation. Within this context, the utilization of sustainable energy with ATES (Aquifer Thermal Energy Storage) can play an important role. Utrecht has chosen to deploy ATES as a remediation tool: the "Bio-washing machine". The predominant contaminants in the City centre of Utrecht are chlorinated volatile organic hydrocarbons (VOC). For the city centre of Utrecht a remediation plan was formulated. This remediation plan has been approved by the authorities. This plan is based on an area-oriented approach in which a 40% contaminant mass reduction must take place within 30 years. Essential elements of the area-oriented plan are monitoring and optimisation of the remediation plan.

The main aim of this CityChlor project is to derive recommendations for smart and effective monitoring within the area-oriented approach of the "Bio-washing machine" thereby completing the plan-do-check-adapt cycle. For this purpose the municipality of Utrecht and AgencyNL Soil+ organized a ThinkTank which is an ‘Expert panel meeting’. This ThinkTank consisted of Bioclear, Deltares, MWH, University of Utrecht and Wageningen University. In this ‘ThinkTank’ a conceptual site model (CSM) was proposed. This CSM was used to understand the situation in Utrecht, describe the interactions between the various aspects (vapour intrusion, contaminant flux, contaminant degradation rate, contaminant transport). The CSM is depicted in figure 1. Based on this CSM various aspects of area-oriented approach have been studied within this project. The focus of these research lines has been on site characterisation and degradation processes occurring in the subsurface, possible vapour intrusion from shallow groundwater layers to the surface and expected spread of groundwater contamination related to time and flux measurements from source zones. All these aspects form an important part of the insight needed to come to a reliable area-oriented approach and to come to an optimisation of the area-oriented approach. In the current report the results from individual reports have been integrated in order to draw conclusions with regard to the optimisation of monitoring the area-oriented approach.


**Conceptual Site Model (CSM) area-oriented approach Utrecht**

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 as shown in chapter 4. The three important aspects that have resulted in an altered view of the situation are:

- Clean groundwater layer enormously reduces the risk for vapour intrusion;
- The confining layer (aquitard) between the 1$^{st}$ and 2$^{nd}$ 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.

Within the framework of the CityChlor Utrecht project various different aspects with regard to the area-oriented approach were investigated. These mainly focussed on the development and application of innovative characterisation methods. Processes such as biological degradation, dilution, volatilization and large-scale ATES systems have an impact on the concentration and physical distribution of groundwater contaminants. It is thus important to understand which processes are relevant.

In an area-oriented approach a substantial area boundary must be identified within which contaminants are allowed to spread. However, at the same time, within this demarcated area (system boundary) specific concentration norms apply which may not be exceeded. The integration of the results led to a optimized monitoring program. This program is based on two possibilities for area-oriented approach in Utrecht:

A. Area-oriented approach based on currently implemented remediation plan.
B. Area-oriented approach based on receptor security.

In the area in which the area-oriented approach is applied it is not necessary to precisely determine the contaminant flux from each individual source zone within the area but it is important to know the contaminant flux leaving the system area and the processes that result in concentration reduction. This can be monitored by determining the contaminant flux in monitoring wells placed at the boundary of the system. The perfect place for this is the border between the dynamic and peripheral area. One of the important processes is the degradation within the system. Therefore it is important to determine whether the degradation capacity stays active within the system. Furthermore it is important to determine the contaminant flux from source zones outside the dynamic zone (in the peripheral zone) if it poses a threat to the receptors.

The area in which the area-oriented approach is applied based on receptor security the only important aspect is that the receptors may not be threatened by the contaminant. In this case it is not necessary to precisely determine the contaminant flux from each individual source zone within the area. Focus on measurements at the boundary of the system and only measure contaminant concentration (use passive samplers like the PFM or Sorbiflux). Within the system it is important to know whether the biological degradation capacity is higher than the contaminant flux. The balance between the biodegradation capacity and the contaminant flux is the key control instrument for the area-oriented approach. Furthermore it is important to localise the vapour intrusion prone area.

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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.

# 2 Outline research set up area oriented approach Utrecht

This report describes an integration of the outcomes of the CSM Bio-washing machine. In this programme a number of research lines have been set up in order to develop characterization methods and models to optimize the area-oriented approach in general and specifically the area-oriented approach in the City of Utrecht: “The Bio-washing machine”. The predominant contaminant in the City centre of Utrecht are chlorinated volatile organic hydrocarbons (VOC). For the city centre of Utrecht a remediation plan was formulated. This remediation plan has been approved by the authorities. This plan is based on an area-oriented approach in which a 40% contaminant mass reduction must take place within 30 years. This remediation plan is called the “Bio-washing machine” approach.

Within the framework of the CityChlor Utrecht project various different aspects with regard to area-oriented approach were investigated. These mainly focussed on the development and application of innovative characterisation methods. In the current report the results from individual reports have been integrated in order to draw conclusions with regard to the optimisation of monitoring the area-oriented approach.

The individual reports are:
1. Vapour intrusion.
2. Contaminant flux determination.
3. Biodegradation capacity.
4. Geohydrological modelling.

## 2.1 Project set up

In the city centre area of Utrecht (studied area) large-scale contamination of the deeper subsurface aquifer is present. The contaminants mainly consist of chlorinated hydrocarbons (VOC) and the (intermediate) degradation products. The contaminants in the subsoil cannot always be retraced to the original physical source and/or the responsible party. Additionally, at depth 'plumes' from different sources mix together to form larger plumes. Due to these aspects case-based approaches are not possible, and thus an area-oriented approach is the preferable option. The municipality of Utrecht has opted for this area-oriented approach in the city centre of Utrecht.

The CityChlor project aims to develop knowledge about and gain experience on the realization of an area-oriented approach in urban groundwater remediation. Within this context, the utilization of sustainable energy with ATES (Aquifer Thermal Energy Storage) can play an important role. Utrecht has chosen to deploy ATES as a remediation tool: the "Bio-washing machine". Essential elements of an area-oriented plan are monitoring and optimisation of the remediation plan.

When dealing with an area-oriented approach it is necessary to have clear objectives with regard to for example the expected and required groundwater quality. As stated in the remediation plan in Utrecht a contaminant reduction of 40% is required within 30 years. Processes such as biological degradation, dilution, volatilization and large-scale ATES systems have an impact on the concentration and physical distribution of groundwater contaminants. It is thus important to understand which processes are relevant in general, and specifically, which cause contaminant (concentration) reduction.

In an area-oriented approach a substantial area (system boundary) must be identified within which contaminants are allowed to spread. However, at the same time, within this demarcated area specific concentration norms apply (for example based vapour intrusion risks) which may not be exceeded.

Within the Utrecht CityChlor project research has been conducted on various aspects of the area-oriented approach. The focus has been on site characterisation and degradation processes occurring in the subsurface, possible vapour intrusion from shallow groundwater layers to the surface and expected spread of groundwater contamination related to time and flux measurements from source zones. All these aspects form an important part of the insight needed to come to a reliable area-oriented approach. In §1.3 more information is given on these different research questions.

## 2.2 Goal

The main aim of this CityChlor project is to derive recommendations for smart and effective monitoring within the area-oriented approach of the "Bio-washing machine", thereby completing the plan-do-check-adapt cycle (see §1.3). Furthermore the goal is to optimize the risk-based area-oriented groundwater management.

## 2.3 City centre Utrecht

### 2.3.1 Contamination and remediation plan

The city centre of Utrecht is contaminated with chlorinated hydrocarbons (VOC). For the city centre of Utrecht a remediation plan has been formulated. In this remediation plan the definition of the source zones are areas where contaminant (PCE) is present above a depth of 5 m-gl. In the subsurface below 5 m-gl no DNAPLs are present only residual product is present.

The remediation plan, based on a clustered approach, has been approved by the authorities. This plan is based on an area-oriented approach in which a 40% contaminant mass reduction must take place within 30 years. This remediation plan is called the “Bio-washing machine” approach. In figure 1 the Bio-washing machine area is shown including the location of the sampling wells, the area is approximately 3.2 km$^2$.

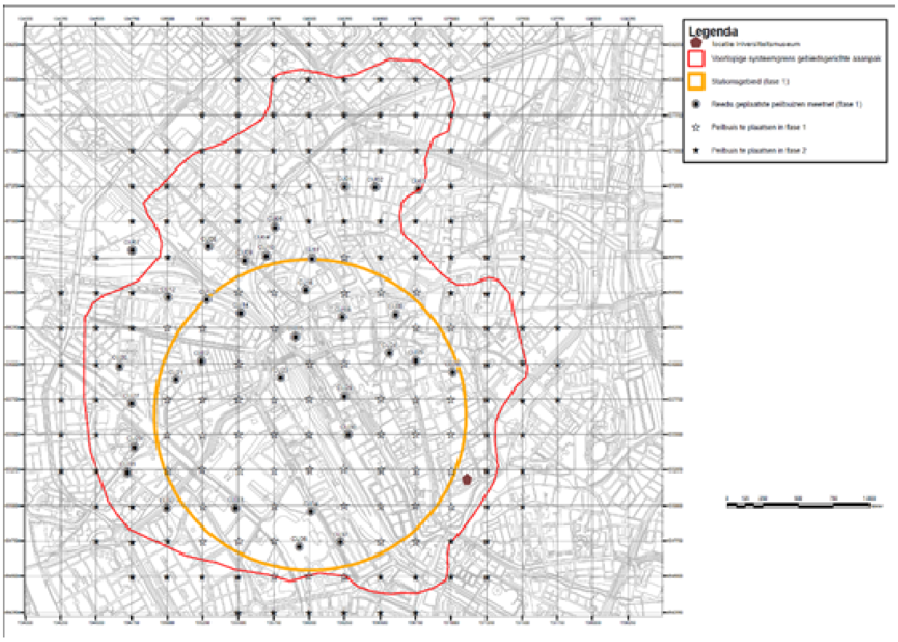



**Figure 1. Demarcated area of Bio-washing machine**

## 2.3.2 Conceptual site model (CSM)

Within this CityChlor project the municipality of Utrecht organized a ThinkTank which is an ‘Expert panel meeting’. This ThinkTank consisted of Bioclear, Deltares, MWH, University of Utrecht and Wageningen University. In this ‘ThinkTank’ a conceptual site model (CSM) was made. This CSM was used to understand the situation in Utrecht, describe the interactions between the various aspects (vapour intrusion, contaminant flux, contaminant degradation rate, contaminant transport). The CSM is depicted in figure 2.

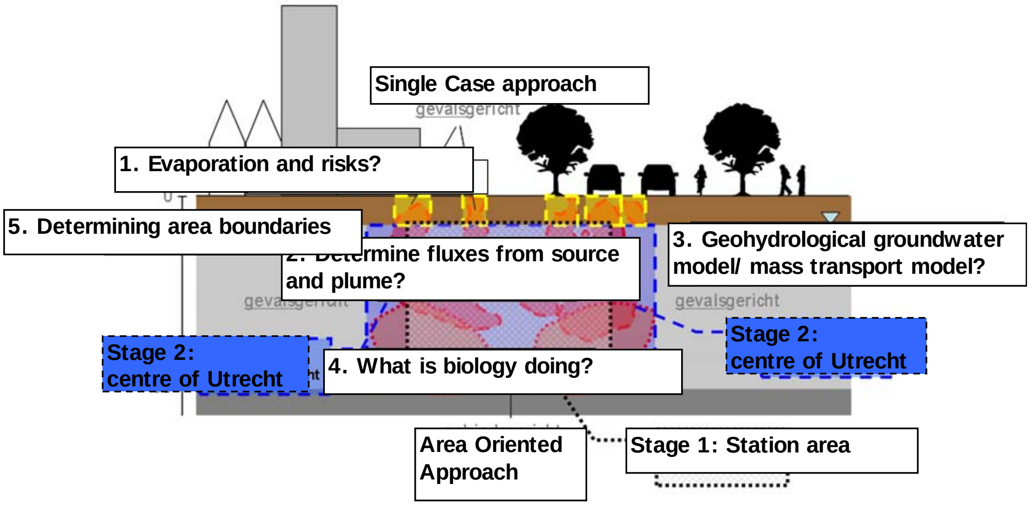



**Figure 2. Conceptual Site Model (CSM) area-oriented approach Utrecht**

Furthermore the CSM was used by the 'ThinkTank' to design a research set up. This CSM is part of a plan-do-act-check-adjust cycle (see §1.3.2). Based on the results from the various research lines the CSM was adapted (see chapter 4). The adapted CSM was eventually used to develop a monitoring strategy for the area-oriented approach in the future.

As mentioned above the CSM was used to design a research set up. Based on the CSM it became clear that a number of aspects (numbered 1 to 5 in figure 2) need to be considered when determining the demarcated area and identifying controllable (= 'sustainable') elements to manage the possible risks within the demarcated area.

**1:** One of the aspects that can cause a risk is the volatilisation of the contaminant 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 localise the risks associated with this process. Another aim is to derive the key parameters influencing the primary processes of vaporization.

**2:** One of the aspects is that contamination from the different source areas, that are still present and have not been remediated, can be mobilized gradually into the (deeper) groundwater. This means that new groundwater layers will be fed with contaminant, this will have an impact on the total mass of contamination that is released per unit time into the demarcated area. Determining integrated area-oriented fluxes are therefore important. Also to be coupled to eq. degradation potential and transport fate.

**3 and 5:** The system boundaries and concentrations must be determined through a modelling approach which integrates results from measured degradation potential within the demarcated area.

**4:** Degradation of the contamination reduces the total mass present in the demarcated area and furthermore contaminant concentrations are reduced. Therefore, contaminant degradation is an important aspect within area-oriented approach and must be examined in a manner that allows proper measurement rather than relying on numerical modelling (independent confirmation of degradation potential, not using modelling data). Such measurements contribute to the estimation of both the risks as a result of the contamination to critical objects /receptors and to the system boundary.

Another aspect to be kept in mind is the impact of the (multiple) ATES systems in the area on the contamination. It is important that the following factors are determined:

(i) will these ATES systems have an impact on the spread of contamination;

(ii) what will the impact be on degradation;

(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 volatilization. Similarly, when ATES is applied to residual pure product sensitive areas the contaminant concentrations can increase;

(iv) where could they lead to risk decrease. In other areas, dilution may occur due to the mixing of large volumes of contaminated groundwater with non-contaminated groundwater. This will cause a reduction in risk, based on risks caused by contaminant concentrations. Additionally, ATES may stimulate the biology and the related degradation process due to changes in parameters such as flow and redox conditions. Conversely, this could also disrupt or slow down biological degradation processes if mixing causes less-favourable conditions for degradation. Determining the actual degradation rates (anaerobic, aerobic, slightly reducing conditions) is therefore important.

The impact of ATES systems in area-oriented approach has not been studied in detail in the current project. Therefore results from previous research projects have been used. With regard to the effect of temperature on the contaminant, this will only have an impact if high temperatures are applied. This is, as yet, not the case in the ATES systems deployed in Utrecht (see for more information the results reported in the “Meer met Bodemenergie” research project).

### 2.3.3 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 3: 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

## 2.4 Research questions

The main questions posed in this project are the following:

1. Does volatilization of contaminants from source areas and plumes occur? If so, to what extent and what are the related risks? What are critical aspects cq. parameters?
2. Does additional volatilization take place when (multiple) ATES systems are employed. Does this result in increased risk due to ATES implementation?
3. What part of the contamination is leached (flux) to the plume area?
4. Towards which areas within Utrecht does the contamination flow and can high concentrations be found near the water table level in the subsurface in Utrecht?
5. Does the soil have a degradation capacity? If it does, how large is this capacity? Which biological processes play a role? Where is this capacity located in terms of time and space? Is this degradation active in the subsurface?
6. What changes in the macro-chemistry (redox potential and mineral composition) of the groundwater are associated with large-scale ATES systems (due to pumping and heating)?

7. What is the net impact of groundwater being pumped around on the degradation and spread of contaminants, including the possible impact on residual product?

Within CityChlor the above mentioned questions have been answered through conducting various experiments, measurements and modelling. For example to determine where the contaminant might reach the water table level in high concentrations, which may cause a risk for indoor air concentrations, geohydrological groundwater modelling and substance transport modelling is required.

In the following chapter a description of the activities conducted and the results of the various research lines is given including the preliminary results for expected impacts due to ATES systems (research question number 6 and 7).

## 3 Description of the research lines

In the following paragraphs a brief description is given of de experiments conducted in de various research lines. For detailed information please see the individual reports.

### 3.1 Vapour Intrusion

#### 3.1.1 Set up

Vapour intrusion may occur when subsurface contaminants volatilize and migrate through the unsaturated zone upwards into buildings. Because of the adverse health effects of the contaminants, this may cause human health related risks.

Vapour intrusion may occur when subsurface volatile contaminants migrate from a dissolved source or residual product / DNAPL through the unsaturated zone and diffuse upwards in the gas phase accumulating in buildings. In the unsaturated zone, gas diffusion is the dominant transport process, as gas phase diffusion coefficients are several orders of magnitude higher than liquid phase diffusion coefficients. On the other hand, partitioning in the liquid and adsorbed phase in the unsaturated zone can significantly reduce risks as it retards upward transport. In a building, the indoor air contaminant concentration is also influenced by ventilation, which will to a large extent dilute the contaminant concentration from the subsurface, see figure 4.

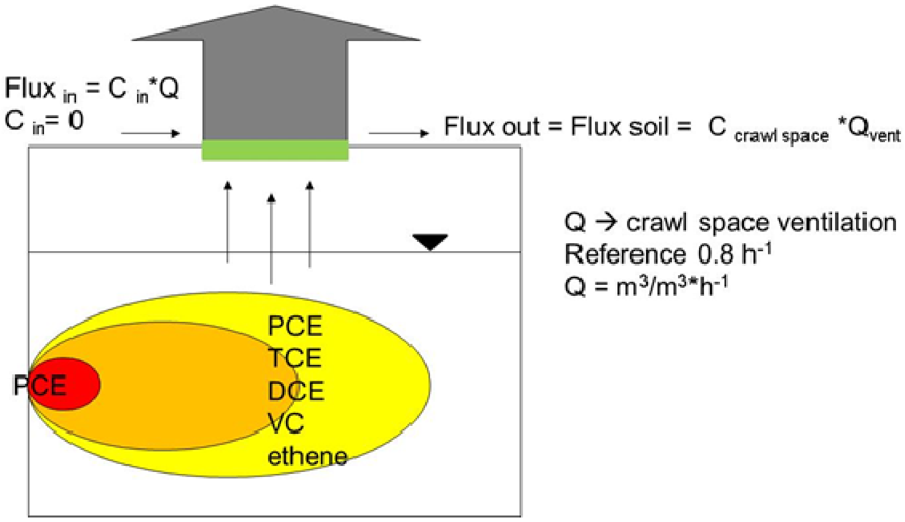



**Figure 4. Conceptual model of vapour intrusion process**

An additional process which can reduce contaminant concentration in the unsaturated zone is biodegradation. Biodegradation of volatile contaminants, like chlorinated hydrocarbons, is known to occur under both anaerobic and aerobic conditions. In the aerobic unsaturated zone, biodegradation of especially low-chlorinated contaminants can be expected.

Cis-dichloroethene (cisDCE) can be degraded under aerobic conditions. Aerobic degradation of solely cisDCE does occur but co-metabolic processes are probably more dominant. Therefore, the assessment of cisDCE biodegradation rates in field conditions remains complicated. Aerobic degradation of vinylchloride (VC) is a well-established process.

As the main contaminants in Utrecht are chlorinated volatile compounds, amongst which vinylchloride and cisDCE, potential vapour intrusion risks are present.

The questions that this vapour intrusion research line addresses are:
1. Are there vapour intrusion risks in the area?
2. To what extent does biological degradation reduce vapour intrusion risks?
3. What is the effect of ATES systems on the vapour intrusion risks?

For the research within this research line two sites in the urban area of Utrecht were chosen: Nachtegaalstraat and Amsterdamsestraatweg. At these sites, a rather shallow groundwater contamination of PCE (tetrachloroethene), TCE (trichloroethene), DCE and VC is present below residential houses in areas where the groundwater table is shallow (between 1 and 1.6 m-gl).

In this research line numerical modelling of the vapour intrusion risks are conducted using a numerical two-dimensional model, that uses the modelcode STOMP. The model predictions are compared with measured data for one of the sites, namely Nachtegaalstraat. A generic model is also used to understand the main processes which influence the risks in this urban area, and to evaluate the effects of ATES systems.

Furthermore biodegradation tests and compound specific stable isotope measurements in laboratory experiments with material from the sites were performed to assess whether and to which extent aerobic biodegradation occurs at the Nachtegaalstraat and the Amsterdamsestraatweg in the unsaturated zone.

Results from both modelling and laboratory experiments were combined to draw conclusions on the risk at the sites and on the implications for the area-oriented approach. Besides critical parameters were identified, these have been used in the integration of the results, see chapter 5.

### 3.1.2 Results

A generic 2D model has been used to assess the main processes affecting the crawl space / indoor air concentrations above a dissolved PCE plume undergoing reductive dechlorination.

From the sensitivity analysis, it can be concluded that the position of the plume with respect to the interface between the saturated/unsaturated zone and the occurrence of aerobic biodegradation are the most important risk-controlling factors. Therefore these are the parameters that should be known or estimated in order to asses vapor intrusion risks for locations with similar characteristics.

Two areas in the urban area of Utrecht, Amsterdamsestraatweg and Nachtegaalstraat, have been used as research locations to assess vapour intrusion risks related to subsurface contamination from chlorinated hydrocarbons (PCE, TCE, cisDCE, VC). The model was built using available soil type, dry matter content and contaminant concentration data.

The laboratory tests showed that aerobic VC biodegradation occurs at the site, with first order liquid phase rates of 2.41±0.29 $d^{-1}$.

For Nachtegaalstraat, the predicted concentrations profiles and the measured ones match reasonably well for PCE and TCE, but the model, neglecting aerobic biodegradation, significantly over predicts the cisDCE and VC concentrations.

VC aerobic biodegradation is the most reasonable hypothesis to explain over prediction of VC in the indoor air (see figure 5), as this process was also observed in batches with soil material from the site. The aerobic VC degradation first order rate measured corresponded to 0.42±0.75 $d^{-1}$. However, no aerobic cisDCE biodegradation occurred in the batch systems. Thus, either a different process occurs than aerobic biodegradation (e.q. co-metabolic aerobic cisDCE degradation, not mimicked in the test set up) or, locally the site conditions are different than what was mimicked in the experiments. In the latest indoor air measurement campaign, no contaminant was detected above the detection limit of 1 µg/$m^3$. These data indicate that aerobic degradation VC and probably of cisDCE occurs in the vadose zone, see figure 5.

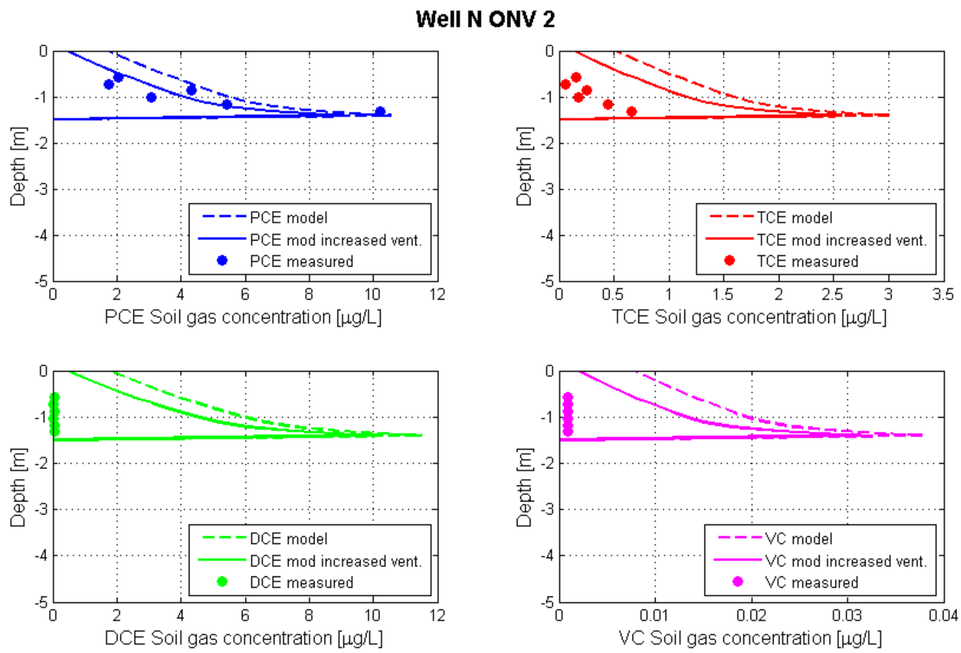



**Figure 5. Comparison between modelled and measured contaminant gas concentrations in well NONV2. When measured cisDCE and VC were lower than detection limit, in the plot the detection limit is shown (1 µg/$m^3$=0.001 µg/L)**

In order to translate these results to an area-oriented approach, calculation of attenuation factors as a function of the most relevant parameters influencing the risk, i.e. source depth and aerobic biodegradation is required. The effect of ATES is best taken into account by a large scale groundwater flow model, combined with the calculated attenuation factors. By combining this information with predictions from a groundwater model it is possible to identify areas with potential risks and monitor them (see chapter 5).

From simulations conducted in this research line, it became clear that a clean groundwater layer has the biggest impact on indoor air concentration. The distance between contaminated groundwater and the water table is the strongest risk reducing factor for vapour intrusion. Attenuation factor may decrease 5-6 orders of magnitude when the contaminated plume is 50 cm below the water table compared with a contamination at the water table. Aerobic biodegradation of VC in the unsaturated zone can reduce the vapour intrusion risks with 1 order of magnitude. Aerobic degradation of DCE has not been observed in the degradation tests of the monitored sites and thus incorporation of this effect in model predictions is not yet recommended.

The distance between the plume and the water table is the most sensitive parameter for obtaining the attenuation factor, see figure 6. The attenuation factor decreases approximately exponentially with increasing water table - plume distance. The thickness of the unsaturated zone and the properties of the contaminant have a much smaller effect.

The relationships shown in figure 6 can be used for a first screening of vapour intrusion risks for the area-oriented approach. When regional groundwater reactive transport models or monitoring data give plume concentrations and the distance to the water table as well, the groundwater concentrations can be translated into equivalent gas concentrations by multiplication with the Henry coefficient of that component. Next, multiplication with the attenuation factors taken from figure 6 gives an estimate of the crawl space gas concentration.

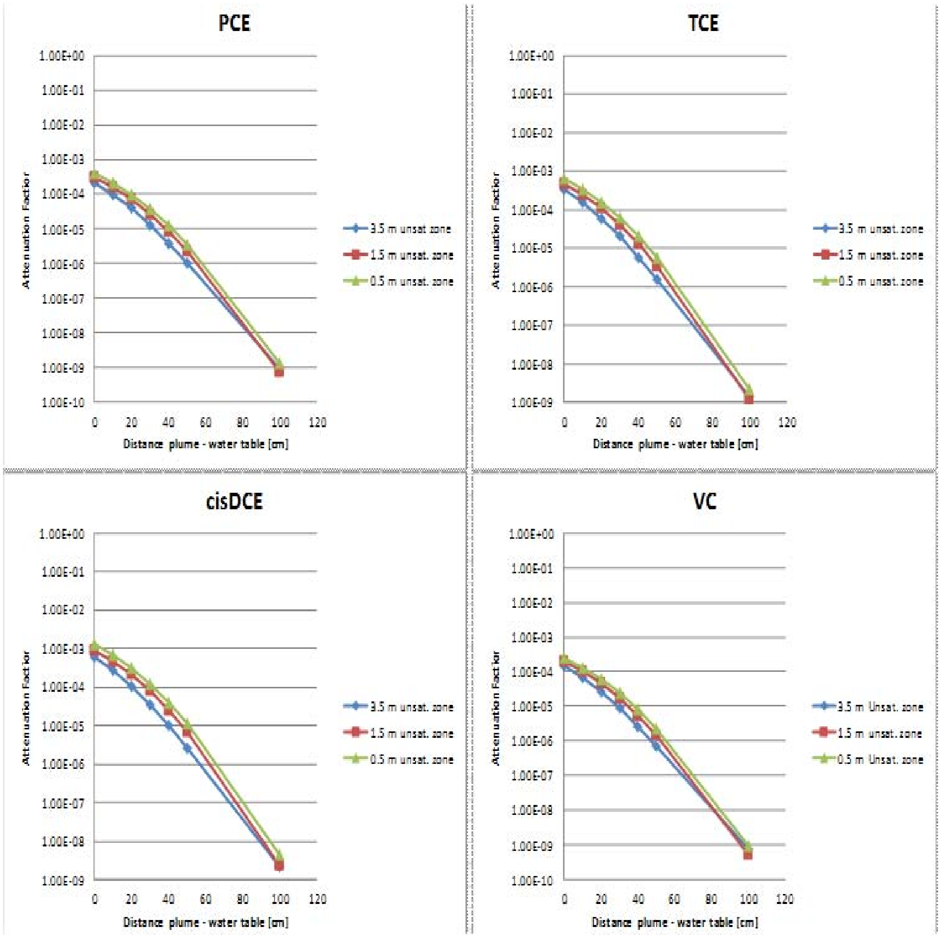



**Figure 6. Attenuation factors as function of plume - water table distance and unsaturated zone thickness for PCE, TCE, cisDCE and VC**

## 3.2 Flux measurements

### 3.2.1 Set up

Fluxes from source areas were determined within a range and/or reliability interval in order to ensure that a link can be made between the degradation capacity and system limits and/or remediation objectives. Using a flux approach, the extent to which the deeper groundwater is fed with contaminants per time period from source zones can be estimated. This estimate can be compared to the contribution of various removal mechanisms for contaminants that play a role in deeper groundwater layers (for example, degradation). This enables to make an estimation on whether there is a balance between removal and new entry of contaminants from source zones.

The question addressed in this research line is:

1. What part of the contamination in the source zones is leached to the groundwater body per unit of time and per area?

To answer this question, an inventory of source locations and a determination of the fluxes from the sources and plumes are conducted. Therefore in this study passive flux measurements were carried out to determine prevalent contaminant mass. The flux measurements aim to characterize contaminant mass fluxes of Volatile Organic Chlorinated Compounds (VOC) resulting from two selected source zones in the Utrecht central station study area: Amsterdamsestraatweg site and Nachtegaalstraat site.

The positioning of flux samplers at a site is important for a good indication of the contaminant flux (see example in figure 7).

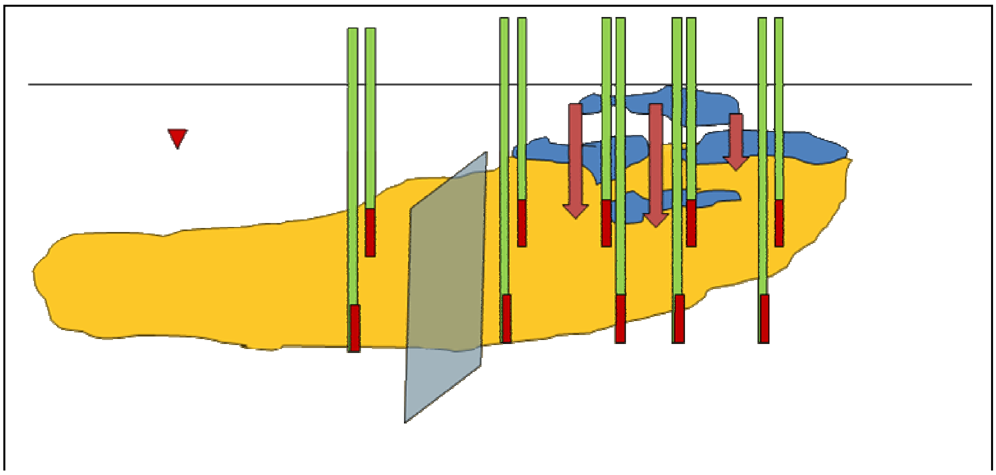


**Figure 7. Picture of ideal measuring points for flux measurements**

Multiple parameters are essential in order to determine the flux, which is expressed as mass per unit time per area. These parameters are: concentrations in the groundwater, the flow rate and the lateral surface area (surface area through which contaminants flow). A combination of timeaveraged concentration measurements as well as flow rate and flow direction is required to determine the flux through a specific plane.

In this study we have chosen for three methods to determine the flux:

1. Regular sampling in observation wells. This data is used to calculate the flux .
2. Passive sampling (SorbiCell) in observation wells. This data is used to calculate the flux.
3. Passive Flux Meters in observation wells (PFM and Sorbiflux). In this method the flux is directly measured.

### 3.2.2 Results

The results show that there is a great variance in mass flux between the different methods used, see figure 8. The highest fluxes for PCE and TCE were measured using the PFM (passive flux measurement) but for DCE and VC the highest fluxes were measured using the traditional method. The SorbiCell and Sorbiflux gave more or less comparable results. At both sites the highest mass flux was measured in the wells located near the contaminant source area.

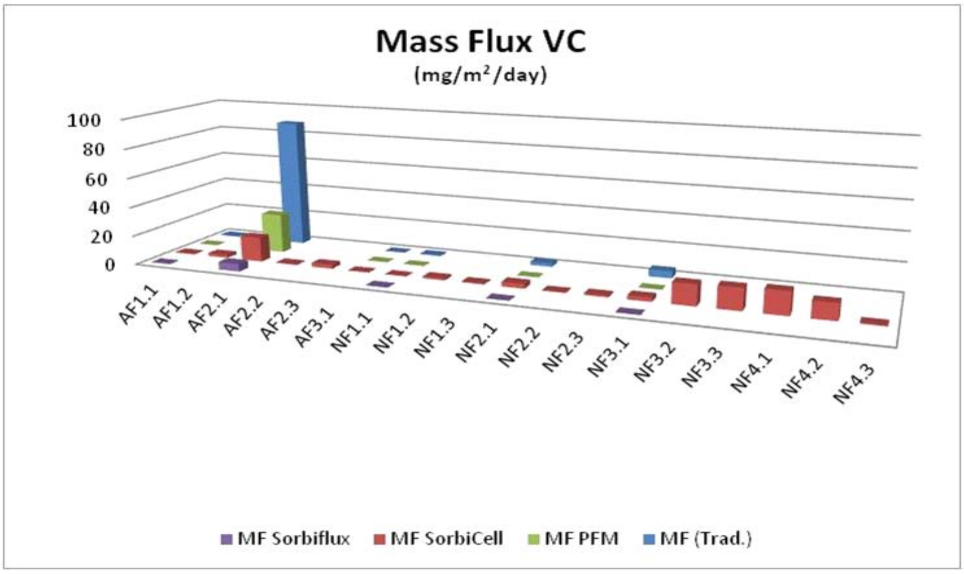



**Figure 8. VC-flux measurements using different sampling methods**

The number of data points in this research set up is too limited in order to integrate the contaminant mass fluxes to determine the total mass (mg/day) through a plane that is perpendicular to the average groundwater flow direction. Nevertheless the mass discharge (Md) at each site has been estimated, see table 1. The total mass discharge of VOC at the Amsterdamsestraatweg is estimated at approximately 165 grams a day in a plane of 350 $m^2$ (vertical discharge area of the source at the measured points). The total mass discharge of VOC at Nachtegaalstraat is estimated at approximately 6 grams a day in a plane of 400 $m^2$. De Amsterdamsestraatweg is highly contaminated and the flux (470 $mg/m^2/day$) is 30 times stronger than the flux (15 $mg/m^2/day$) in the other source zone at Nachtegaalstraat.

Most source zones, within the Bio-washing machine area of Utrecht, have not been characterised in detail but based on the concentrations and the length of the plumes it is possible to predict that only a few source zones are comparable with the source at the Amsterdamsestraatweg. We expect that most of the other known source zones are comparable with the site at Nachtegaalstraat or that the contaminant flux is even lower.

**Table 1. Mean mass flux (J) in mg/m²/day and estimated mass discharge (mg/day)**

| Depth (m-gl) | Plane ($m^2$) | $J_{PCE}$ | $M_{PCE}$ | $J_{TCE}$ | $M_{TCE}$ | $J_{DCE}$ | $M_{DCE}$ | $J_{VC}$ | $M_{VC}$ |
|---|---|---|---|---|---|---|---|---|---|
| Amsterdamsestraatweg | | | | | | | | | |
| 6-12 | 150 (6 x 25) | 472 | 70,800 | 116 | 17,400 | 496 | 74,400 | 5.5 | 825 |
| 12-20 | 200 (8 x 25) | 0.3 | 60 | 0.15 | 30 | 4.1 | 820 | 1.8 | 360 |
| Total plane ($m^2$) | 350 | | | | | | | | |
| Total mass discharge (mg/day) | | | 70,860 | | 17,430 | | 75,220 | | 1,185 |
| Nachtegaalstraat | | | | | | | | | |
| 5-8 | 120 (3 x 40) | 2.9 | 348 | 3.4 | 408 | 7.1 | 852 | 4.4 | 528 |
| 8-12 | 160 (4 X 40) | 0.5 | 80 | 0.8 | 128 | 8.7 | 1,392 | 6.8 | 1,088 |
| 12-15 | 120 (3 X 40) | 0 | 0 | 0 | | 5.6 | 672 | 4.4 | 528 |
| Total plane ($m^2$) | 400 | | | | | | | | |
| Total mass discharge (mg/day) | | | 428 | | 536 | | 2,916 | | 2,144 |

Based on the fluxes measured, a link can be made between the degradation capacity and system limits and/or remediation objectives. Furthermore the extent to which the deeper groundwater (2nd aquifer) 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, see chapter 5. These results can be used to calibrate the model more precisely

In the context of area-specific monitoring in the application of flux measurements, trend and process monitoring can then be conducted at individual (dominant) plumes and control monitoring at signal and area boundaries. It should also be preferable to determine the concentration profile and the location of rapid or preferential flows. This allows for the application of a much more effective (and cheaper) monitoring system, where periodic measurements can be conducted to determine the flow direction and pollution fluxes.

## 3.3 Biodegradation capacity

### 3.3.1 Set up

As the reduction of contaminant is an important part in the approved remediation plan it is important to characterize whether a decrease in contaminant is possible. One of the ways in which reduction can occur is through biological processes. Depending on the circumstance chlorinated ethenes can be degraded either via reductive dechlorination (anaerobic conditions) or (the less chlorinated ethenes) can be oxidative reactions under either aerobic or micro-aerobic conditions. Little was known about this last process (micro-aerophilic oxidation) before starting the CityChlor project. This process has not been described in the remediation plan as one of the processes that plays a role in the reduction of contaminant. This is a novel degradation process which has been investigated in the CityChlor project.

Furthermore the required degradation capacity within the system also depends on the contaminant flux entering the system and the groundwater flow rate. In figure 8 these aspects have been visualized.

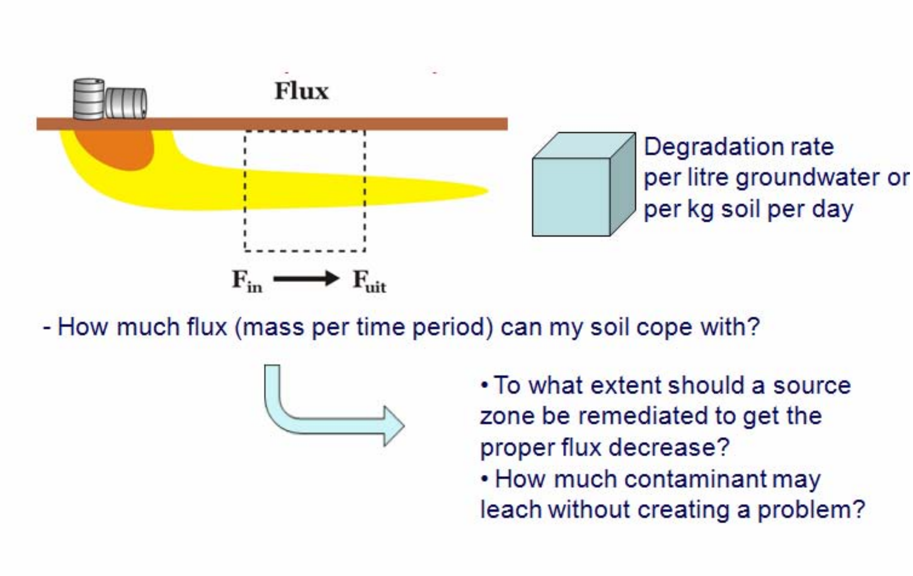



**Figure 9. Relationship between contaminant flux and degradation capacity**

Thus, in this research line the biodegradation capacity was determined. Various different methods were used to determine the degradation capacity (different lines of evidence): compound specific stable isotope analysis in situ, lab microcosms degradation experiments and molecular detection of specific enzymes/bacteria involved in degradation processes.

The main research questions dealt with in this research line are:

1. Does the subsurface in Utrecht have a degradation capacity (qualitative approach)?
2. Which degradation process(es) are predominant in Utrecht?
3. What is the extent (mg VOC/$m^3$/year) of this biodegradation capacity (quantitative approach)?
4. Is this degradation capacity present in the whole area within the city centre of Utrecht (what is the extent of this biodegradation capacity)?

These questions were answered by conducting the following experiments:

1. Lab microcosms (quantitative approach)
   A microcosm degradation study was conducted to investigate whether cisDCE is converted to VC (reductive dechlorination) or to $CO_2$ (micro-aerophilic oxidation). Soil and groundwater samples from different locations in Utrecht were used to conduct a number of degradation batch tests. To make sure that any decrease in DCE concentration is the result of biodegradation biotic and sterile abiotic reference tests were performed.

2. Molecular analyses
   Molecular analyses on 19 groundwater samples, scattered over the city centre area of Utrecht were conducted in 2010 to determine whether *Dehalococcoides* (DHC) or *Polaromonas* bacteria and the genes (etnE and etnC) were present. Based on the results similar analyses were performed on 11 DNA samples which were stored at Bioclear in 2001 and 2008. Based on the results it was clear that bacteria carrying the genes responsible for micro-aerophilic degradation are more likely to adhere to soil surface. Therefore new sampling devices were used: BACTRAPS and MicroTraps. MicroTraps are permeable tubes (HDPE) filled with soil from the location. Both were used to validate and determine reductive dechlorination and micro-aerophilic degradation on site. They were installed at the filter depth in a monitoring well over a period of six months time. The monitoring wells selected showed difference in VOC concentrations and/or redox conditions, implying different biological degradation processes could be prevalent at these sites. Molecular analyses were conducted on the BACTRAPs and MicroTraps (MT).

3. Isotope analyses
   The isotope analyses method can determine whether biodegradation is occurring and can also distinguish between anaerobic and aerobic degradation. In order to assess the biodegradation capacity isotope monitoring of groundwater samples was conducted at a specific contaminated field site in Utrecht (Amsterdamsestraatweg). This is a site which is not part of the Bio-washing machine area. In order to assess whether in-situ biodegradation of cisDCE and VC occurs within the Bio-washing machine area in Utrecht and to identify the micro-organisms involved, BACTRAP studies were conducted. A BACTRAP® is an in situ microcosm containing $^{13}C$-labelled substrate and inert carbon particles. BACTRAPS were deployed at three different sites, with different VOC concentrations. Isotope analyses were conducted at these sites to determine which degradation process had occurred.

### 3.3.2 Results

The results from monitoring wells located at the contaminated site Amsterdamsestraatweg indicated that biodegradation of VC in the plume was caused either by reductive dechlorination in conjunction with a substantial concentration decrease due to non-destructive processes (like dilution) or by aerobic VC degradation in conjunction with a low to moderate concentration decrease due to non-destructive processes. Aerobic VC degradation can be excluded to a large extend at the source zone of this site. The results of the isotope analyses strongly indicate that reductive dechlorination is the predominant pathway for VC biodegradation in the source zone. In the plume aerobic processes are likely to occur.

The results from the microcosm lab tests showed that micro-aerophilic degradation of VC occurred when fresh groundwater was used. This indicates that minor concentrations of oxygen may have been present in the groundwater. In the abiotic test no decrease of DCE nor VC was observed, indicating that the decrease in the biotic flasks is a result of the biological degradation. The biological degradation of VC was verified by isotope and molecular analyses. Based on the degradation tests the degradation rate for VC under aerobic conditions was determined at 0,1 day$^{-1}$. The degradation rate in-situ is expected to be lower. Furthermore this process requires oxygen, the speed of the process will be dependent on the oxygen present.

The above results and the results from the molecular analyses on groundwater and solid phase samples showed that there is a capacity for biodegradation in the subsurface of Utrecht. In many monitoring wells distributed in the city centre area bacteria and genes responsible for reductive dechlorination or micro-aerophilic degradation were identified (figure shown in appendix 1). In monitoring wells with high VOC concentrations reductive dechlorination seems to be the predominant process. However in monitoring wells with lower VOC concentrations (and mainly VC concentrations) and iron to sulphate reducing conditions, micro-aerophilic degradation is the more likely processes. However, the degradation capacity is heterogeneously distributed in the city centre. In a number of monitoring wells, based on the standard groundwater sampling method, no degradation capacity was identified. The standard sampling method gives an underestimation of the total biodegradation capacity (micro-aerophilic) at the site. The bacteria involved in micro-aerophilic degradation are more prone to adhere to soil particles, therefore a new sampling tool was developed: MicroTrap. In several monitoring wells scattered over the city centre area the potential for biodegradation was confirmed using MicroTraps and BACTRAPs.

The 1$^{st}$ order degradation (rate) is dependent on the contaminant concentration, this means that the degradation rate decreases with a decrease in contaminant concentration. The redox conditions probably determine which degradation process occurs. To determine the degradation rate in-situ based on the number of *Dehalococcoides* spp. data from literature [Suarez and Rifai 1999)] was used. The number of *Dehalococcoides* spp. varied in the different samples, this implies that there is a broad range in degradation rate at the site. Based on the *Dehalococcoides* number and contaminant concentration we expect the degradation rates to vary. In table 2 the expected degradation rates are given. The degradation rates are higher in the source zone compared to the plume areas. Locally no reductive dechlorination capacity was detected at all.

Thus in some areas no degradation will take place as both the capacity for reductive dechlorination as well as for micro-aerophilic degradation is absent.

**Table 2. Degradation rates (day$^{-1}$), these are based on literature [Suarez and Rifai, 1999] and number of *Dehalococcoides* bacteria.**

| Contaminant | Reductive proces source | Reductive proces plume | Oxidative proces plume area |
|---|---|---|---|
| PCE | 0,08 | 0,008-0,0008 | |
| TCE | 0,023 | 0,002-0,0002 | |
| DCE | * 0,013 | 0,001-0,0001 | |
| VC | 0,007 | 0,001- 0,0001 | 0,1-0,02 |

* 90th percentile data used as the maximum degradation rate reported by Suarez and Rifai was regarded as unrealistic (partially based on the statistical data: the maximum reported degradation rate was 0.1 day$^{-1}$ whereas the 90$^{th}$ percentile data point was 0,013 day$^{-1}$)

The extrapolation of the detected degradation processes to the whole area is possible since the current research results provide several lines of evidence that micro-aerophilic degradation and reductive dechlorination processes are present at different locations within the area. Reductive dechlorination seems to be more prone to source zone areas. However the results are based on a selection of monitoring wells distributed over the whole city centre area of Utrecht. A strong correlation for occurrence (or absence) of either of the processes with redox conditions or contaminant concentrations remains to be investigated.

The results of the reductive degradation rates are different in comparison to the 'educated guess' rates from the remediation plan of the Bio-washing machine. The expected degradation rates of DCE are faster in the source zone compared to the plume zones. In certain areas no reductive dechlorination occurs at all. The range is larger compared to the remediation plan. With regard to VC, the range is similar, although the current results show that the degradation capacity is locally absent.

The oxidative process in the plume areas is an unexpected opportunity for the degradation of VOC with respect to the remediation plan and original CSM. This gives a new perspective on the subsurface of Utrecht and provides extra tools (capacity) for the risk-based management of the contaminated area. The degradation rate is higher (half-life of approximately 1 month) than the reductive process (half-life of approximately 19 years). A prerequisite for this process is however the availability of oxygen, this also has an impact on the actual in-situ degradation rate.

## 3.4 Groundwater modelling

### 3.4.1 Set up

The geohydrological groundwater model gives an insight in the fate of the contaminant and forms an important part of the design of an area-oriented approach. While constructing the model geological data from the sampling wells from the monitoring network were used. This data showed that in some areas the aquitard between de 1st and 2nd aquifer is absent.

In combination with the other research lines the geohydrological model will help to determine:

1. The horizontal and vertical boundaries of the area-oriented approach.
2. The impact of the contamination on receptors (including vapour intrusion).
3. A spatial distribution of the probabilities where plumes may pass the boundary of the area-oriented approach at unacceptable concentrations, that is to be used for the design of a monitoring strategy and fall back scenario's.
4. Remediation targets for present plumes that threaten to pass the boundaries with unacceptable concentrations.

In this research line a geohydrological model has been developed in order to predict the behaviour of a number of plumes with chlorinated hydrocarbons in the city of Utrecht. The model is set up to support the area-oriented approach for groundwater contamination. As starting point, the model developed by Arcadis (Arcadis, 2009) has been used. It has been refined to layers of 0.5 m thickness and extended with an improved characterisation of the hydraulic conductivity by incorporating the recently developed GeoTOP. Using the original GeoTOP data, the geohydrological flow model was run and pathline analysis were performed for pathlines starting at the present plume locations. The effect of preferential flow on the pathlines has also been analysed for four locations at which pathlines were started at different depths.

Furthermore a reactive transport model based on pathline analysis has been applied. This model incorporates the sequential biodegradation of chlorinated hydrocarbons and retardation. Degradation capacity determined in the other research line (paragraph 2.3) was incorporated in this model. Monte Carlo simulations were used in order to incorporate data in which the degradation rate is a stochastic parameter.

### 3.4.2 Results

Using the original GeoTOP data, the geohydrological flow model was run and a pathline analysis were performed for pathlines starting at the present plume locations. Most modelled pathlines end up in two large abstraction wells in the western part of the Municipality of Utrecht at 'Lage Weide' and near 'Leidsche Rijn'. The non-retarded travel times towards these wells are 115 to over 1000 years. The effect of preferential flow on the pathlines has also been analysed for four locations. Pathlines were started at different depths and it turned out that the travel times for a horizontal displacement of 1000 meter could vary up to a factor 3 due to variations in hydraulic conductivity.

A reactive transport model based on pathline analysis has been applied. This model incorporates the sequential biodegradation of chlorinated hydrocarbons and retardation. Based on parallel research, the degradation of cisDCE in the model is assumed to be very slow or even not occurring at all. Therefore, model predictions show the development of long contaminant plumes that exceed the ‘tussenwaarde’ value (0,5x intervention value), but do not reach the abstraction wells nor the border of the municipality within 200 years. In about 30% of the Monte Carlo runs, the concentrations at the front of the plumes are degraded to less than the ‘tussenwaarde’ value after 200 years, whereas in the other 70% of the Monte Carlo runs the norm is exceeded also at the front of the plume after 200 years.

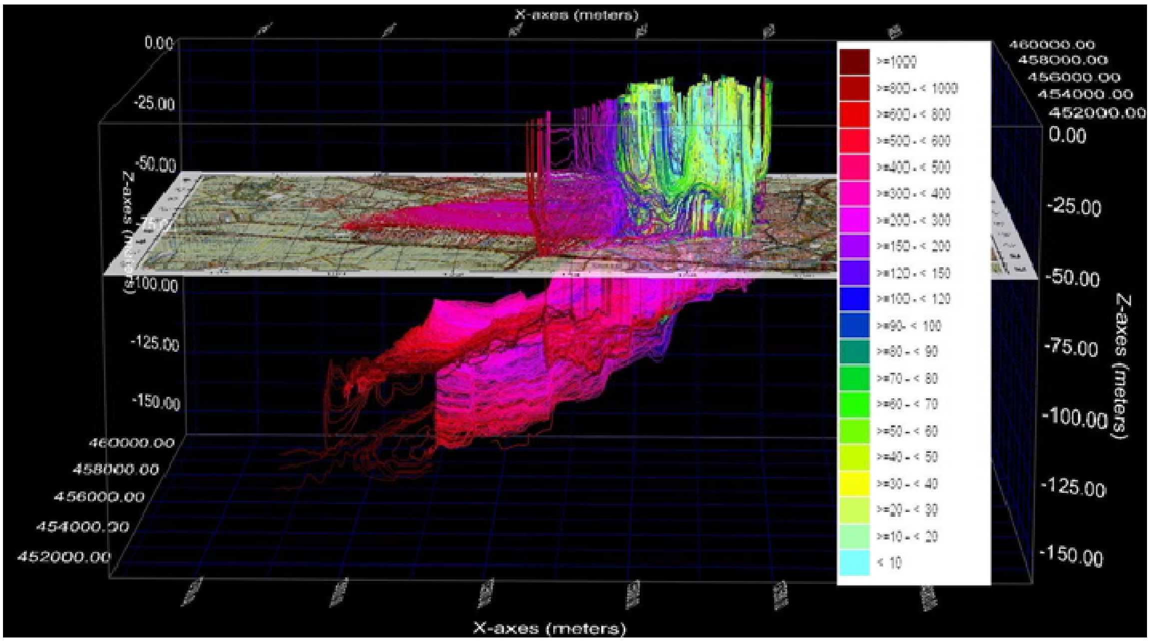



**Figure 10. 3D figure of pathlines starting at depths -10, -22.5 and -40 m +NAP; colours denote conservative travel time in years; the topography is plotted at a depth of -50m +NAP, pathlines below this depth are also projected on the topography**

An analysis was made to determine when breakthrough to the 2$^{nd}$ aquifer would take place in the model. Figure 11 shows the spots where breakthrough will occur. The breakthrough times however vary. The fastest 80% of the breakthroughs are almost linearly distributed over the first 100 years. Already within 1 year breakthrough occurs to the 2$^{nd}$ aquifer, this is because some pathlines start at 50 m-gl and some even start in the 2$^{nd}$ aquifer at 50 m - NAP (based on Arcadis model). This provides a slightly distorted view of the actual situation.

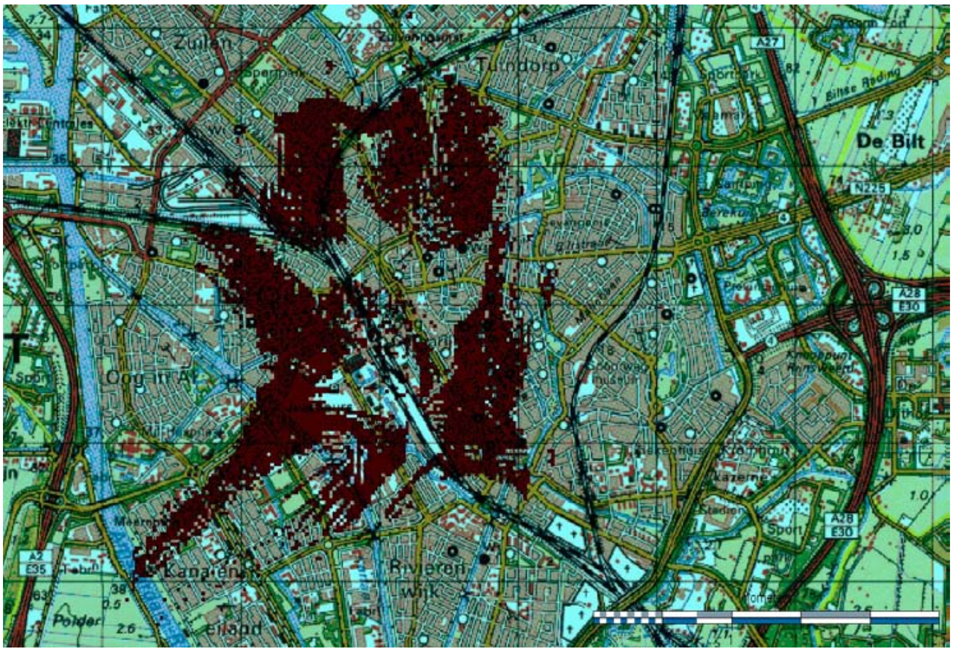



**Figure 11. Breakthrough points to 2nd aquifer**

## 3.5 ATES effect on groundwater macro-chemistry

### 3.5.1 Set up

For the large scale area oriented approach, an extensive monitoring network has been installed for monitoring of the performance of the Bio-washing machine. The comprehensive network consists of more than 260 positions based upon a grid of 250 x 250 meters (figure 12). On each position 3-4 different monitoring wells have been installed in the different layers, depending on the depth of the aquitard.

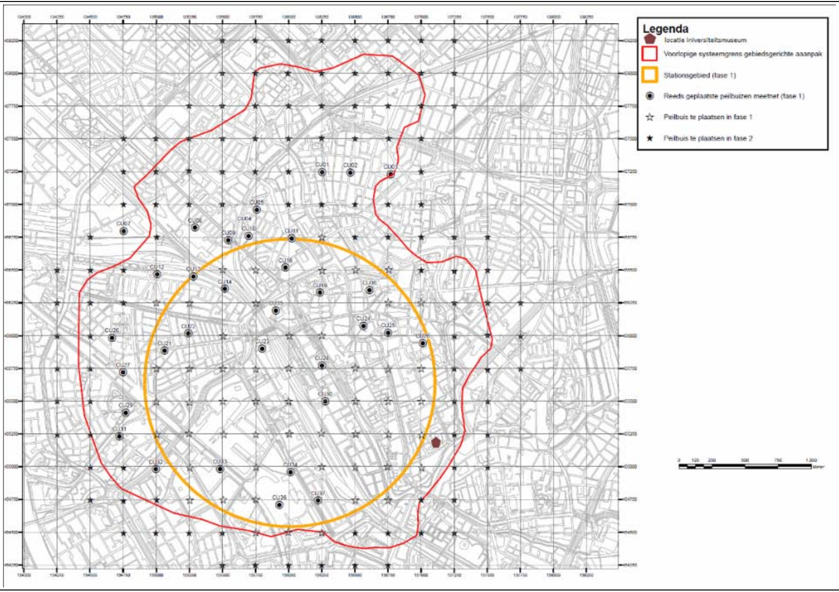



**Figure 12. Monitoring network and demarcated area of Bio-washing machine, Utrecht**

The most important questions addressed in this research are:

1. What are the typical and natural characteristics (macro-chemistry) of groundwater from different depths in the aquifer?
2. What is the influence by ATES on the macro-chemistry in the area?

From start, each monitoring well has been sampled at least once a year. For the round of 2012, the total 264 monitoring positions have been selected. All wells have been sampled according to low flow purging method (micro-purging). For the analyzes of biological parameters groundwater samples have been collected with an artificial kidney device, in order to take large volume samples. Groundwater samples have been analyzed on field parameters and amongst others on VOC's and redox parameters (10% of the wells).

A selection of 8 monitoring positions in the city centre has been selected for extra research. The following parameters have been: geochemical parameters, redox parameters, depth of sampling (inside screen sections), indicators of biological degradation processes and quantitative molecular analyzes based upon Q-PCR technology.

For reference wells data has been used from the provincial network of groundwater wells, long term results of monitoring wells of the water company and upstream wells from the Bio-washing machine network.

### 3.5.2 Results

The effect of ATES on the groundwater macro-chemistry depends on the amount of time the ATES is active. From this research most groundwater on the site directly in the station area, has a homogeneous composition based upon geochemical parameters. This indicates the effect of long term groundwater pumping from the ATES system. The highest amounts of the genes involved in micro-aerophilic degradation of VOC are found in monitoring wells next to the relatively warm ATES wells. No significant relationship is found between the total amount of bacteria present and the temperature of the groundwater. In most wells evidence of sulphate reduction is found, due to concentrations of sulphate reducing bacteria. The redox conditions are not optimal for reductive dechlorination of the VOC present.

Indications of the mixing of vertical stratified groundwater is found in some of the wells near the city centre. This is groundwater which can be characterised as affected by ATES for a short time. Especially in the wells on locations close to the ATES system at Vreedenburg and the ATES system of the Rabobank show a slight shift in parameters like sulphate and DOC.

The direct effect on the total biodegradation capacity of ATES systems is unknown, because there are different biological processes occurring  and the baseline situation of these processes is not known. Based on expert judgement it is expected that the biodegradation capacity based on micro-aerophilic degradation will not be negatively affected by the pumping of groundwater which could lead to change in redox conditions. In practice, all ATES systems influence the deeper groundwater (VOC plumes), where possibly micro-aerophilic degradation processes are dominant.

In general, the biodegradation capacity based on reductive dechlorination could be affected negatively as for this process highly reduced (anaerobic) conditions are necessary. In the situation where the ATES systems are installed in the deeper part of the aquifer (> 20 m- gl) there is a large vertical distance between the plume and source area. Therefore the effect of groundwater pumping due to the ATES is expected small at the shallow source area. A negative effect due to decrease in contaminant concentration might occur as the degradation rate is based on 1$^{st}$ order degradation (this is a concentration dependant rate).

While designing an ATES system it is important to keep in mind that contamination can spread over a larger area and more dissolved contaminant can enter the water system if the ATES wells are positioned near source zones/residual product areas.

Results from the “ATES pilot” project in the Lange Nieuwstraat of Utrecht are used to determine whether the degradation potential measured within the Bio-washing machine area is also present in other areas in Utrecht. The results show that in the “ATES pilot” area degradation capacity for reductive dechlorination as well as for aerobic degradation is present.

# 4 Adapted Conceptual Site Model

The results of the various research lines, described in the previous chapter, are integrated in order to be able to answer questions which are related to monitoring and optimisation of the area-oriented approach in Utrecht.

As mentioned in chapter 2 a CSM was used to understand the situation in Utrecht, describe the interactions between the various aspects and design the research set up and frame the research questions. A plan-do-check-adjust cycle applies to the CSM. Therefore, having conducted the proposed research it is important to check whether the initial CSM is still valid and fine-tune the model where required. In figure 13 the original CSM is shown.

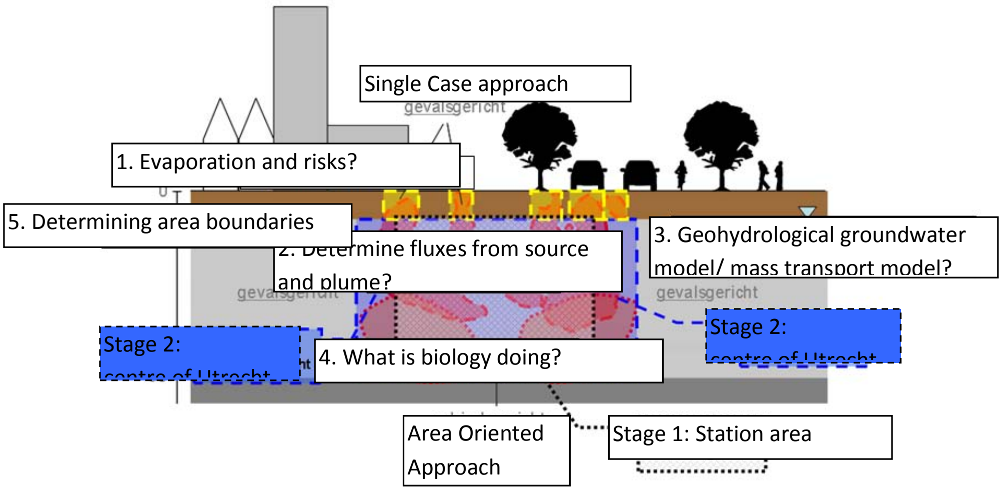



**Figure 13. Original Conceptual Site Model**

The first research line dealt with the risks for vapour intrusion. The results showed that a clean water layer tremendously reduces the risk for vapour intrusion. In figure 14 this aspect has been incorporated in the CSM.

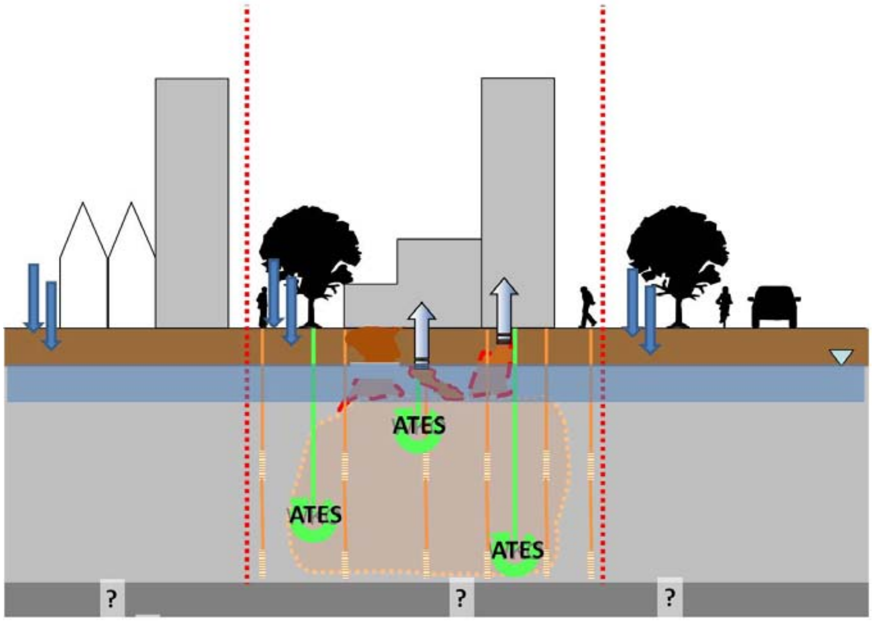



**Figure 14. Modified CSM for vapour intrusion risk**

In figure 15 the CSM has been modified with regard to the biodegradation capacity. The results showed that the biodegradation capacity was heterogeneously distributed throughout the City centre of Utrecht and that both the processes of reductive dechlorination as well as micro-aerophilic oxidation occur. Near source zones the degradation rates were higher compared to plume areas. Furthermore in some monitoring wells no biodegradation capacity was present at all. This aspect is depicted in figure 15.

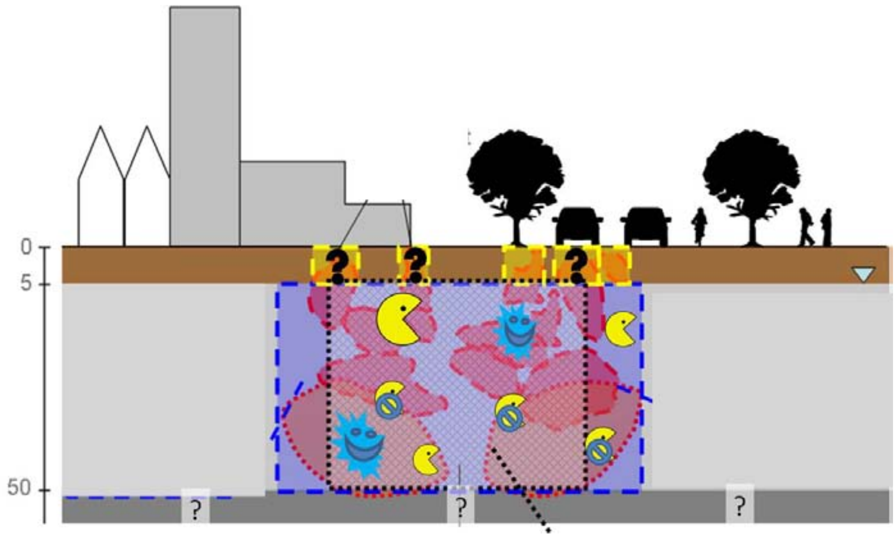



**Figure 15. CSM modified for biodegradation capacity**

In figure 16 these various aspects have been  integrated into a modified CSM for the city centre of Utrecht.

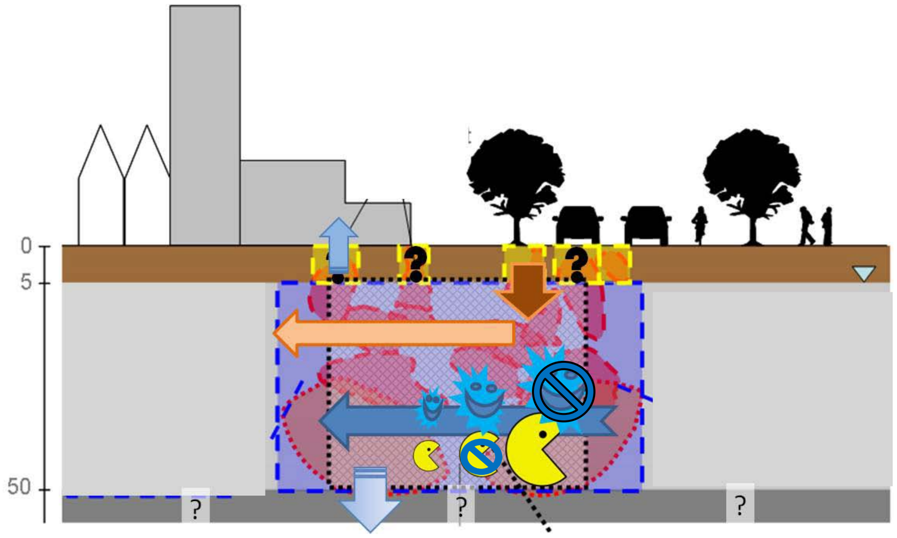



**Figure 16. Modified CSM for the Bio-washing machine.**

Apart from the above mentioned CSM for the Bio-washing machine  another CSM has been made for the complete city area as a whole. This CSM is shown in figure 17.

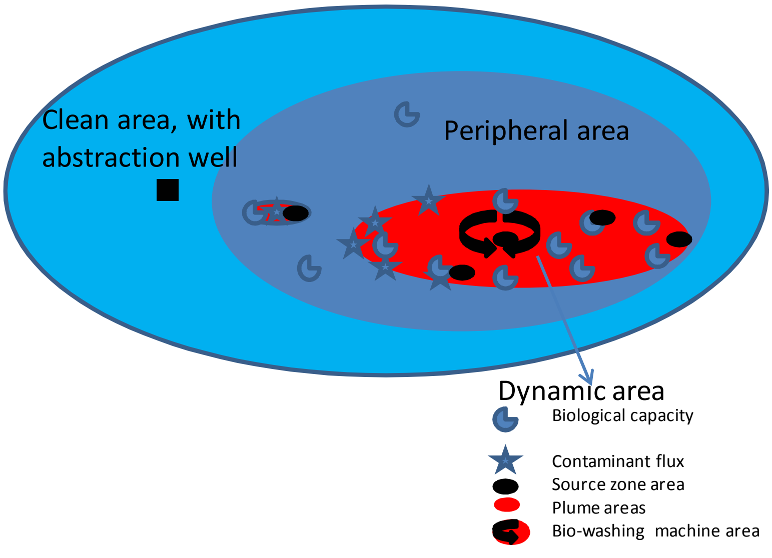



**Figure 17. System boundaries Bio-washing machine area, peripheral area and location abstraction well (receptor).**

The CSM in figure 16 is a cross-sectional depiction of the situation whereas the CSM in figure 17 is a birds-eye view of the situation. The area in red denotes the Bio-washing machine area in which ATES are/will be situated. In this area besides dissolution, volatilization and degradation mixing is also an important factor to take in account. In the surrounding peripheral zone the main processes occurring are dissolution (from source zones), dispersion (through groundwater flow) and degradation. In the outer area, which is the strategic clean zone no contaminant is present. This CSM will be used in chapter 5 to design a monitoring program for the area-oriented approach.

The results from the different research lines have resulted in a adapted conceptual site model as shown in figure 16. The three important aspects that have resulted in an altered view of the situation are:

1. Clean groundwater layer enormously reduces the risk for vapour intrusion.
2. The confining layer (aquitard) between the $1^{st}$ and $2^{nd}$ aquifer is locally absent.
3. 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.

# 5 Integrated results for the Bio-washing machine area of Utrecht

## 5.1 Integrated results

The expert panel organised a meeting in which the results described in the previous chapter were discussed and integrated focussing on the area-oriented approach. These integrated results are described in this chapter.

The groundwater model plays a central role in the integration of all the aspects investigated in this project as these aspects form input parameters for the groundwater model and can be used to predict the fate of the contaminants within the demarcated area and can determine whether the system boundaries are passed by at unacceptable concentrations.

Furthermore the contaminant flux and the biodegradation capacity (see figure 9) is of importance. In table 3 an example for Amsterdamsestraatweg is given. At this site respectively 200 mg/m$^2$/day PCE, 50 mg/m$^2$/day TCE, 215 mg/m$^2$/day DCE and 3 mg/m$^2$/day VC is released from the source zone. Based on the molecular analyses (*Dehalococcoides* present in 1x10$^5$ cells/ml) it was reasoned that in this area the biodegradation capacity was high and therefore high degradation rates were used. These degradation rates (day$^{-1}$) were converted to a degradation capacity expressed as mg/m$^3$/day. The results are depicted in table 3. The results show that the degradation capacity for PCE and VC is sufficient to degrade the PCE contaminant flux. For the contaminants TCE and DCE the degradation capacity may not be sufficient to degrade the contaminant flux. As can be seen in table 3 a slight change in degradation rate has a major impact on the degradation capacity, to demonstrate this a column has been added in table 3 in which 2 times lower degradation rates have been used for the calculation. An important aspect to keep in mind is that de degradation rate decreases with decrease in contaminant concentration.

**Table 3. Example Amsterdamsestraatweg**

| | Contaminant flux | Concentration source zone | Degradation rate* | Biodegradation capacity | Degradation rate (2x lower) | Biodegradation capacity |
|---|---|---|---|---|---|---|
| | mg/m$^2$/day | mg/l | day-1 | mg/m3/day | day-1 | mg/m3/day |
| **PCE** | **200** | **16** | **0.08** | **1280** | **0.04** | **640** |
| **TCE** | **50** | **5.1** | **0.023** | **35** | **0.0115** | **17** |
| **DCE** | **215** | **29** | **0.013** | **113** | **0.0065** | **57** |
| **VC** | **3.4** | **1.7** | **0.007** | **11.9** | **0.0035** | **6** |

* maximum and 90$^{th}$ percentile results from literature used, see chapter 3

# degradation rate 2 times lower

The various results of the CityChlor project are integrated in the groundwater model with the aim to determine the total area needed for an optimal risk-based area-oriented approach. Based on the groundwater flow, preferential pathways, source zone hotspots and degradation capacity (rates) it is possible to determine the time it will take for the contaminant to reach one of the ‘critical objects’. In the city of Utrecht three ‘critical objects’ or receptors have been identified:

1. Indoor air.
2. Potable water (drinking water) abstraction wells.
3. $2^{nd}$ aquifer.

Based on the results described in chapter 4 and the receptors mentioned above the following aspects are of importance.

1. Indoor air (vapour intrusion risk)
    a. contaminant will emerge at or near the water table level.

   Based on the model outcome it is possible to determine where the groundwater contaminants will emerge at or near the water table level. When regional groundwater reactive transport models or monitoring data give plume concentrations and the distance to the water table, the groundwater concentrations can be translated into equivalent gas concentrations by multiplication with the Henry coefficient. Multiplication with the attenuation factors, described in chapter 3.1, gives an estimate of the crawl space gas concentration and thus the possible risks. When ATES systems are deployed in this area near residual product zones the risk could increase.

    b. contaminant is present in the unsaturated area or at the groundwater level

   Another area where a vapour intrusion risk may be present is at source areas where the contaminant is present in the unsaturated zone or at the groundwater table level (with no clean groundwater layer above). Due to a decrease in the groundwater table (for example due to seasonal fluctuations or fluctuations due to pumping of groundwater (at an ATES system) this may lead to increased vapour intrusion risk. At risk prone sites it could be wise to monitor the groundwater heads by using divers. If the groundwater level decreases below a threshold value then action may be necessary. This action can consist of monitoring soil gas concentrations or indoor air concentration or increase indoor air ventilation.

2. Potable water abstraction wells:
    a. Breakthrough to $2^{nd}$ aquifer

   Another critical object in the future use of the subsurface of Utrecht is the drinking water abstraction well. This is situated in the $2^{nd}$ aquifer (strategic aquifer) outside the demarcated area for area-oriented approach. Based upon the degradation rates as mentioned in chapter 3, the geohydrological model shows that within 100 years time, contaminant present in the $1^{st}$ aquifer (part of the Bio-washing machine area) will pass through to the $2^{nd}$ aquifer and can be extracted in the drinking water abstraction wells. These results are based on the assumption that the Vitens abstraction wells will remain operational for the coming 100s of years. This is not realistic. Therefore it is important to discuss other possibilities in a dialogue with Vitens.

    b. Contaminant flux and subsequent degradation within the Bio-washing machine area and the peripheral area

Information on the contaminant flux from the Bio-washing machine area (boundary limits) and the biodegradation capacity in the source and plume zones (peripheral area) is important in order to predict the concentration level of contaminant leaving the demarcated area. The (degradation)processes occurring in the area downstream from the Bio-washing machine, the area near the abstraction wells, are also of importance as these are nearer to the abstraction wells. Based on monitoring results downstream of the Bio-washing machine area necessary (precautionary) actions can be taken if and when necessary. The overall flux of contaminant (contaminant flux and degradation rate) determines the success of area-oriented approach. As stated in the approved remediation plan for Utrecht a reduction in contaminant of 40% is required.

3. 2$^{nd}$ aquifer
    a. Strategic water supply

The 2$^{nd}$ aquifer is the strategic water supply of Utrecht, and therefore a critical object in the subsurface of the city centre. The model shows that within 100 years time contaminant present in the 1$^{st}$ aquifer will pass through to the 2$^{nd}$ aquifer, due to the natural hydrological system of the subsurface. Therefore this can have a negative effect on the groundwater quality and the strategic function of this aquifer for the city.

    b. Breakthrough to 2$^{nd}$ aquifer

Based on geohydrological data (acquired during installation of the monitoring wells) now it is known that in certain areas the aquitard (confining layer) between the 1$^{st}$ and 2$^{nd}$ aquifer is absent. At these spots contaminant can easily pass through to the 2$^{nd}$ aquifer. This can occur within 100 years, as has been predicted in the geohydrological model. With degradation of VOC occurring in the 1$^{st}$ aquifer the net discharge of contaminants to the 2$^{nd}$ aquifer will be lower, therefore it is important to know whether other processes like degradation and for example dissolution (from residual product) is occurring.

## 5.2 Monitoring Bio-washing machine Utrecht (ADAPT)

Based on current monitoring and newly gained knowledge, a smart monitoring program has been designed. The focus is on indicator parameters that are important for the operation of the system as a whole. There are two ways of managing the area-oriented approach. Both have been briefly described in this paragraph.

There are two possibilities for area-oriented approach in Utrecht:

A. Area-oriented approach based on currently implemented remediation plan.
B. Area-oriented approach based on receptor security.

### 5.2.1 Area-oriented approach based on currently implemented remediation plan

In the remediation plan the norm set for the contaminant concentration leaving the system has been set at “tussenwaarde” values. Furthermore a contaminant reduction of 40% is required within 30 years.

In the area in which the area-oriented approach is applied it is not necessary to precisely determine the contaminant flux from each individual source zone within the area but it is important to know the contaminant flux leaving the system area and the processes that result in concentration reduction. This can be monitored by determining the contaminant flux in monitoring wells placed at the boundary of the system. The perfect place for this is the border between the dynamic and peripheral area. The processes occurring in this dynamic zone (area-oriented system) are dilution, degradation, dissolution, volatilization etc).

One of the important processes is the degradation within the system. Therefore it is important to determine whether the degradation capacity stays active within the system.

Furthermore it is important to determine the contaminant flux from source zones outside the dynamic zone (in the peripheral zone) if it poses a threat to the receptors.

In the following figure 18 an overview of the monitoring program is given. Downstream of the abstraction well (in a pathline) measurements with Sorbicells can be conducted to determine the risk for contamination of the drinking water system (Sorbicell result is an average concentration over time). In source zones in the peripheral area both flux measurements in the source zone as well as degradation capacity measurements in the source and plume areas are necessary. In the Bio-washing machine area overall biodegradation capacity measurements are needed (is the degradation potential present). Flux measurements need to be conducted at the border of the system.

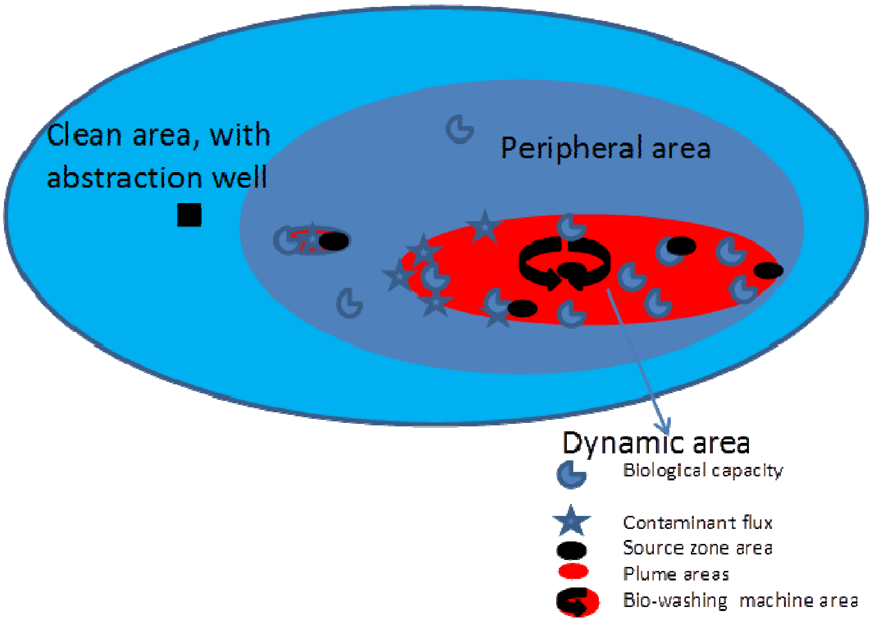



**Figure 18. Monitoring program area-oriented approach**

## 5.2.2 Area-oriented approach based on receptor security

The area in which the area-oriented approach is applied is considered a black-box the only important aspect is that the receptors may not be threatened by the contaminant.

In this case it is not necessary to precisely determine the contaminant flux from each individual source zone within the area.

Focus on measurements at the boundary of the system and only measure contaminant concentration (use passive samplers like the PFM or Sorbiflux). Within the system it is important to know whether the biological degradation capacity is higher than the contaminant flux. The balance between the biodegradation capacity and the contaminant flux is the key control instrument for the area-oriented approach. Furthermore it is important to localise the vapour intrusion prone area.

# 6 Lessons learned for area-oriented approach

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.

## 6.1 Recommendations based on the results CityChlor

Based on the results these are the recommendations for further research:

1. The quality of the groundwater model relies on the quality (realistic) of the input parameters. Based on the research so far, preferential pathlines and contaminant degradation rates have been determined. It is important to verify these input parameters.
2. As degradation forms an important/crucial aspect of the remediation strategy it is important to verify degradation rates from time to time within the Bio-washing machine area in order to determine whether the degradation process (as input in the model) still applies. Another option is to determine decrease in downstream contaminant concentrations over time and calculate the degradation constant and compare this with the degradation constant used in the model. At this moment biodegradation capacity has been determined in a number of monitoring wells in the city centre of Utrecht.
3. Due to the heterogeneity of the degradation potential it is important to analyse more sites (using the newly developed MicroTrap sampling method) in order to extrapolate the current results to the whole Bio-washing machine area. For example analyse 20 sampling wells at

different depths. It is important to conduct analyses at sites that are contaminated with VOC and take samples that are spatially distributed (both horizontally and vertically).

4. Within this project a new sampling method was developed, this method should be applied to more monitoring wells in Utrecht to be able to determine the extent of micro-aerophilic degradation capacity.
5. Performing soil gas and possibly indoor air measurements in Amsterdamsestraatweg is recommended in order to come to a validation of the model with field data and thus the model can be used as a risk prediction tool for the whole area.
6. More detailed site specific data, such as repeated measurements of the filters situated in the unsaturated zone (NFREA filters N.1, N.2, N.3 and of the soil gas (NONV N1., N.2, N.3) would be necessary to confirm that aerobic cisDCE biodegradation occurs in the field.
7. The results from the unsaturated zone biodegradation tests can be used as input in the STOMP model and then compare the results with field results, this has not yet been done.
8. We expect that most of the other source zones are comparable with the site at Nachtegaalstraat or that the contaminant flux is even lower. This needs to be checked as in Utrecht in the groundwater layers below 5 m-gl no information is available about the presence (and strength) of source zones with residual product.
9. Conduct flux measurement at a source zone in the 1$^{st}$ aquifer (below 5 m-gl) and compare this with the data from Nachtegaalstraat and Amsterdamsestraatweg and use the data for interpolation to the whole area.

## 6.2 Recommendations and concerns with regard to ATES systems in area-oriented approach

Based on the results a few recommendations and concerns with regard to deploying ATES systems in area-oriented approach have been formulated:

1. It is important to know the position of all the critical objects within the system and keep this in mind while granting permits for new ATES systems.
2. While designing an ATES system it is important to keep in mind that contamination can spread over a larger area and more dissolved contaminant can enter the water system if the ATES wells are positioned near source zones areas. For the Utrecht situation no indications for DNAPL were present. While designing ATES systems close together, keep in mind that near an indoor air risk prone area it is important not to decrease the water table level too much so that the contaminant is always covered by a clean groundwater layer thus decreasing the indoor air risks.
3. With respect to the effects of ATES systems, monitoring data are necessary to confirm the conceptual model of how the contamination is affected by the recirculation system. Assuming the conceptual model used here is valid, the main vapour intrusion risks arise when lowering the water table for a contaminant present up to the water table. When extending these considerations to a broader area, however, two further considerations are of importance. First, fresh water infiltration during water table decrease might create a

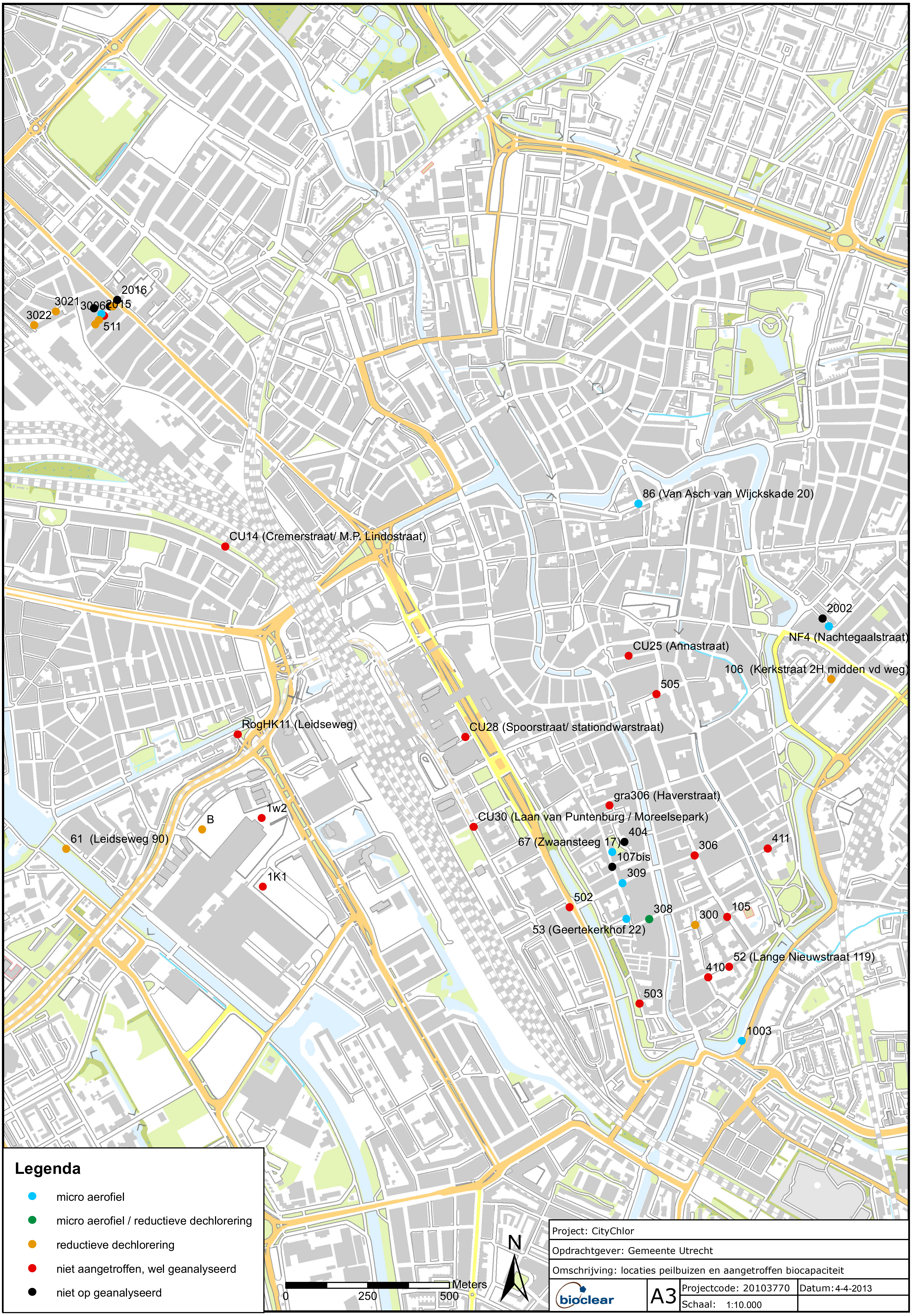
natural cap for vapour migrating upwards, thus changing the picture significantly. Second, the effect of injecting contaminated groundwater by an ATES system into the shallow groundwater should be accounted for. A groundwater flow and transport model at the scale of the City of Utrecht should be used to calculate at what depth below the groundwater table and at which concentrations these plumes can develop.

4. The water table variation caused by ATES may have a strong negative effect of vapour intrusion risks when a plume is close to the water table and the continuous water table movement destroys the protecting clean water layer. ATES or natural fluctuations can be accounted for in the model in a conservative way by using the smallest distance between plume and water table.
5. In the ATES pilot area it is advised to apply high temperatures in order to be able to determine the effect of temperature on contaminant behavior and degradation capacity. In the research project Meer met Bodemenergie low temperatures were measured at the Utrecht pilot.
6. Furthermore the geohydrological model needs to be applied when changes occur in the subsurface (for example new ATES systems, abstraction wells). The model should be used to determine the effect on the receptors and the set boundary.

# 7 Bibliography

Suarez, M.P. and Rifai, H.S., Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater, Bioremediation journal 3(4), pg 337 (1999)

# Appendix 1: Overview of degradation capacity in Utrecht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505
RogHK11 (Leidseweg)
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gra306 (Haverstraat)
1w2
B
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Omschrijving: locaties peilbuizen en aangetroffen biocapaciteit
bioclear
A3
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