

Groundwater
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energy storage
systems on the scale
of a large urban area

*A pathline analysis of
contaminant behaviour beneath
the city centre of Utrecht*

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A pathline analysis of contaminant behaviour beneath the city centre of Utrecht

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Preface

This report is the final result of a six month internship at Deltares. Six month in which I have learned a lot, most of the time staring at the white screen of my computer pondering on how I was going to make my model work. While working on my research, I have worked intensively with my supervisor at Deltares, Johan Valstar. I would like to thank him for his patience and giving me support and advice during my whole internship.

I also would like to thank Frans Roelofsen, for helping me with the model of the subsurface of Utrecht and Ruud Schotting, my supervisor at Utrecht University.

I would like to give many thanks to my parents, Erroll and Mariëlle van Lieshout for their support throughout my entire study. Also, I would like to give a big hug to my girlfriend, Sélène Brinkhof, who picked me up when I was down.

And finally, I would like to thank my fellow students and interns for all the talks and laughs during the coffee and lunch breaks.

March 15th, 2013

Rowdy van Lieshout

A handwritten signature in black ink, appearing to read 'Rowdy van Lieshout', written in a cursive style.

Abstract

This research thesis attempts to answer the question if a pathline analysis can be applied to a transient flow field where aquifer thermal energy storage systems (ATES) are present. This is done by constructing a simplified conceptual model of a contaminated aquifer with one ATES system and comparing a full MT3D contaminant transport simulation with a pathline analysis with and without the addition of biodegradation. If this question is answered affirmatively, the pathline analysis is applied to the case of the city centre of Utrecht, the Netherlands, to study whether ATES systems have an influence on the spreading of contaminants and their effect on contaminant concentration. In Utrecht, the subsurface is contaminated with volatile organic hydrocarbons (VOCs) and the goal of the municipality of Utrecht is to remediate these contaminated zones with the help of ATES systems. A boundary is drawn around the city centre and through a pathline analysis it is analysed whether the VOCs pass that virtual boundary with a concentration higher than a certain intervention value. The result of this study is that two of the VOCs, namely DCE and VC, pass this boundary with too high values in the first fifty years of modelling. However, from this study, it can not be concluded that the ATES systems have a direct influence on that result.

1. Introduction

For health and safety reasons, a clean subsurface and good groundwater quality in densely populated areas has to be guaranteed; therefore sound soil and groundwater management is a prerequisite. In earlier days, when the subsurface was less frequently used, potential risk areas could be taken care of case by case. But now due to the increasing activities above and below the surface and the building density is higher, a contaminated site can not be remediated easily and cost-effectively.

When a case-oriented approach because of practical, technical and, most importantly, financial reasons is not feasible a more area-oriented approach is required. In this case it is cheaper to let the contaminant degrade in a natural way and to approach the whole problem from a more extensive point of view.

Area-oriented approach

An important feature in the area-oriented approach is the virtual system boundary. The source zone or zones, a volume of soil where a pure phase contaminant is present, should be located within that boundary. From these zones, contaminant plumes spread through the groundwater for an extended period of time. Contaminants that pass this boundary can not have a concentration that exceeds certain intervention values. When there is a direct risk to human health, the removal of a source zone is preferred, but it cannot interfere with the area-oriented approach. So when it does, if, for instance, the cost of the removal is very high, the source zone is not removed.

Highly vulnerable areas or locations are a top priority in the determination of the boundary. If the risk can be kept at a minimum, a vulnerable area can be inside the boundary, provided that proper monitoring around this location is installed and a fall-back scenario is available, otherwise they are kept out.

The boundaries of the area should be monitored, so when something unexpected or unwanted occurs, measures can be taken.

Monitoring

The carefully chosen monitoring system is another important feature of the area-oriented approach. This system needs to monitor contaminant concentrations at the boundaries of the control area and vulnerable areas nearby and decide if they exceed intervention values.

The location and number of monitoring wells depend on the groundwater flow conditions, the behaviour of the contaminant, the size of the plume and location of this plume in relation to the system boundary or an area of interest. In this approach it is wise, in respect to available funds, to only monitor some typical plumes and/or the most hazardous ones. The monitor frequency depends on the developments in the subsurface; if concentrations become too high, a higher frequency and a lower frequency when the situation stabilizes. On the other hand it depends on the amount of time that is desired or required to intervene if concentration become too high.

Case study: Utrecht - the bio-washing machine

In the area in the vicinity of the railway station in the centre of Utrecht, a lot of new construction and improvement of existing buildings takes place. The new station should be connected to the old city, in this way creating a new city centre that should be ready in 2030. The problem is that the whole area in and around Utrecht central station (about 180 million m³ of soil) is highly contaminated with predominantly volatile organic chlorinated hydrocarbons (VOC) (Figure 1-1). The most abundant VOCs are: tetrachloroethylene (PCE) and trichloroethylene (TCE), cis 1,2-dichloroethylene(DCE), vinylchloride(VC) [appendix A]. The contaminants are situated between 5 and 50 meters below surface level in the first aquifer. At 50 meters there is a confining layer. Below that layer we find the second aquifer.[10]

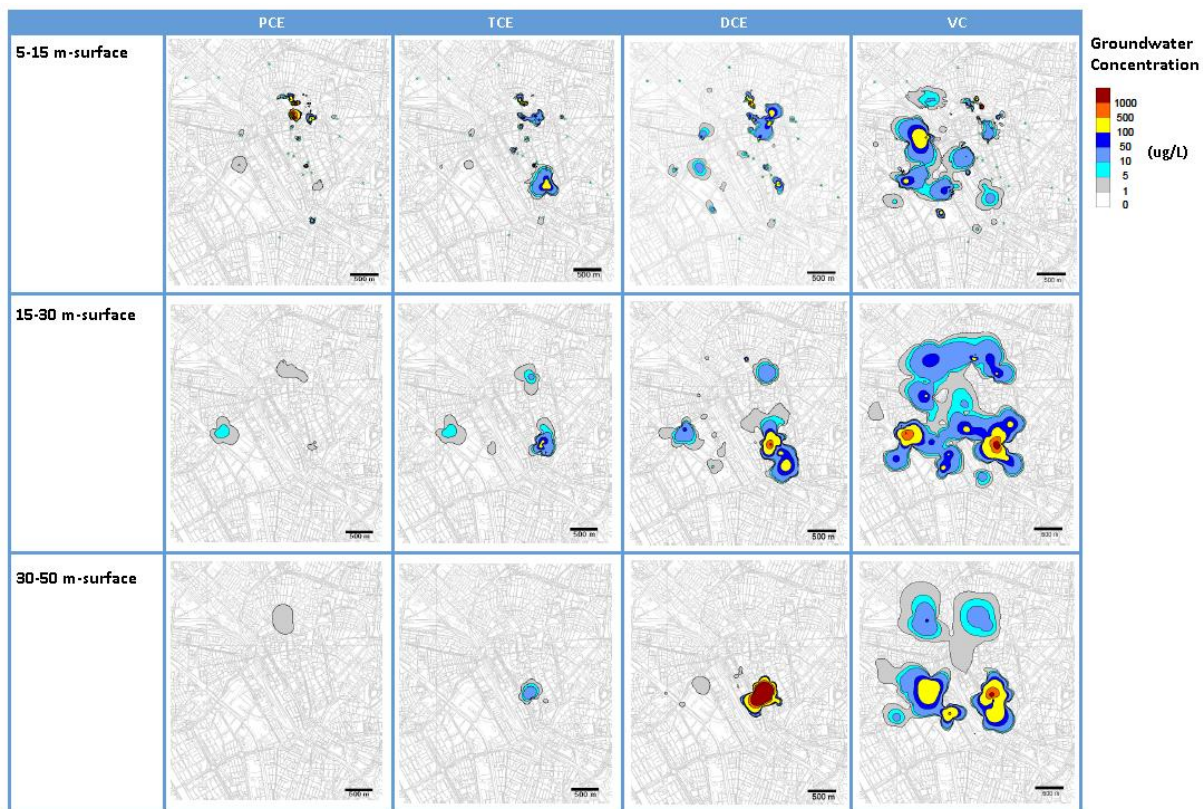


Figure 1-1 Initial VOC concentration in the groundwater below the centre of Utrecht (ARCADIS)

The municipality of Utrecht decided to go for an area-oriented approach with the goal to attain a situation where the contaminant degradation is in equilibrium with the spreading, in such way that over time a stationary situation will arise in a predefined area and consequently an improvement in the groundwater quality and a reduction in human risks.

The municipality wants to tackle the whole problem in a sustainable way. Therefore they have agreed to improve the quality of groundwater within, and protect the groundwater outside the control area with the help of multiple ATES (aquifer thermal energy storage) system in the area around Utrecht central station. They named the project the 'Bio-washing machine'. [7]

Aquifer Thermal Energy Storage

An ATES system stores cold and hot water in the subsurface to heat, or cool buildings above ground. There are basically two types of ATES systems: open-loop (Figure 1-2 and 1-3) and closed-loop systems (Figure 1-4). Open-loop systems extract water from an aquifer (or surface water) and exchange heat via a heat exchanger before water is pumped back into the subsurface.

In summer cold water is pumped up at about 7 °C and used for cooling of a building. The heated water (~20°C) is re-injected in the subsurface, to be pumped up again in winter to heat the building. This can be done with two wells, one cold and one hot, but also with one well with filters on different depths. [1]

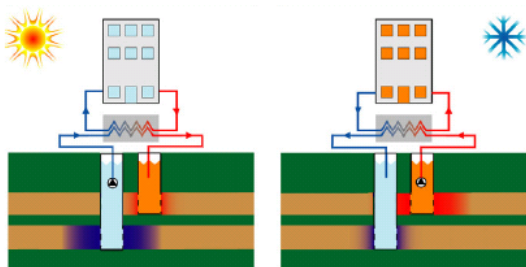


Figure 1-2 Open-loop mono ATES system [2]

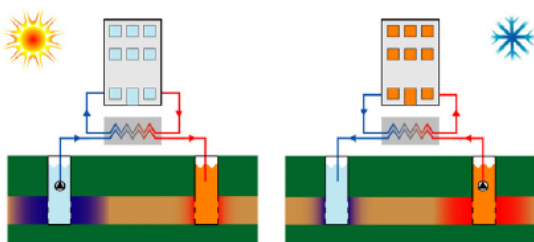


Figure 1-3 Open-loop ATES system [2]

An open-loop system may be also used for cooling a building only. When this is the case, a well will keep its function (abstraction or injection), throughout the year.

Closed-loop systems get the energy directly from the subsurface by subsurface heat exchangers. This means, there is no direct circulation of groundwater. [5]

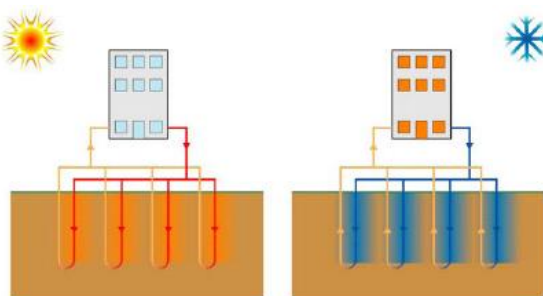


Figure 1-4 Closed-loop ATES system [2]

In this study closed-loop systems are not considered, because they do not displace groundwater and therefore have a limited effect on contaminant transport.

The use of ATEs systems to help with remediation

Injecting and abstracting water has not only an influence on the hydraulic head and therefore the flow direction of the groundwater, but also on the temperature and mixing rate.

Mixing

Because of the seasonal cycle of abstraction and injection, water is displaced continuously in the aquifer and within the ATEs system itself. The scale of mixing also depends on how fast the groundwater flows to and away from the well. An ATEs system can, by mixing contaminants, nutrients and microorganisms, have an effect on redox potentials and pH.

Also a significant feature is the fact that contaminants and microorganism can travel from one location to another, through the ATEs system and thus influencing the chemical conditions at the position of the injection.

Temperature

Temperature differences result in density differences and therefore cause density dependent flow to and from an ATEs system. This effect only has to be considered when dealing with temperatures higher than 25 degrees. A higher temperature causes changes in the solubility of some minerals, but experiments show that this is rarely the case at temperatures lower than 25 degrees, which is the case with the systems that are considered in this thesis. [4]

Changes in reaction rates can be expected with the considered ATEs systems. The rates can change by a factor two to three when the temperature rises from ten to twenty degrees, resulting in lower reaction rates near the cold well and higher near the hot one. The fact that a well is hot at one instant and cold at another makes net effect of temperature on the reaction rate very small. [4]

Changes in temperature also influence the type of microorganism that live in the subsurface.. Microorganisms require an optimal temperature to function and some will die out totally at a location whenever too high temperatures are reached. Again, at the temperatures (~20°C) that are considered, those effect are limited, if at all present, according to field and lab experiments. [4, 6, 11]

Modelling

The risk analysis, which is needed to determine the eventual location of the monitoring wells, can be done through a model. This model needs to give an accurate description of: the soil, groundwater and surface water characteristics, the constructions (that have any influence on water flow) and any drainage or water extraction in the area. It also needs as input; the location, the size and the properties of, one or more, contaminant plumes and source zones. [17]

Pathline Analysis

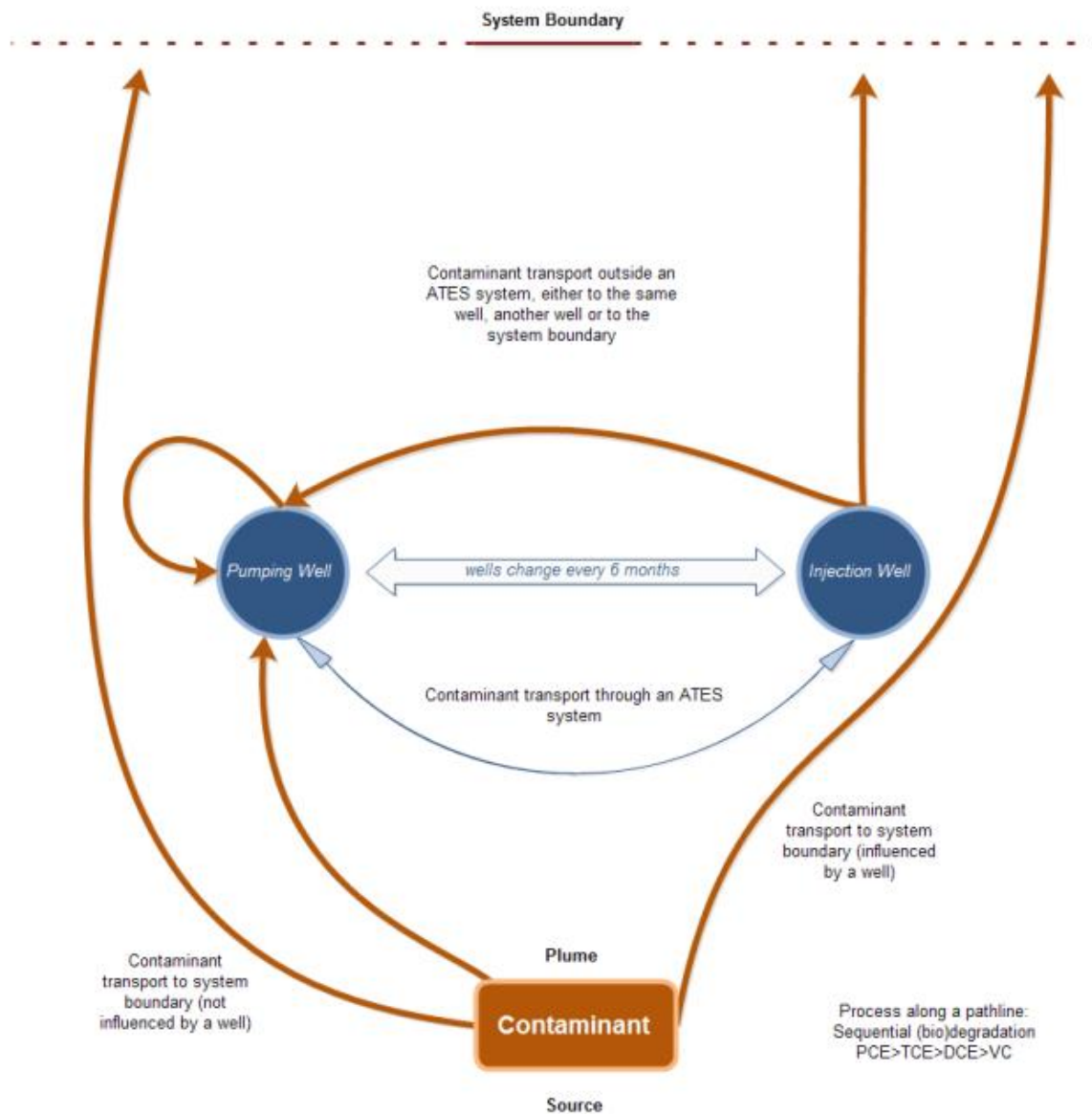


Figure 1-5 Pathline Analysis

When the area-oriented approach is applied, the modelling of contaminant transport through tools like MT3D and RT3D, both using the model code MODFLOW for calculating groundwater flow, is not desirable. These programs are usually used to simulate cases with one contaminant plume and these cases, most of the time, have a limited number of cells and relatively short simulation time.

Because the area and simulation time, in the area-oriented approach, is very large, another, more simplistic, method can be used. In this method, using the flow data calculated by MODFLOW, the path of a particle released from a predetermined spot through an area of interest, a pathline, can be computed (Figure 1-5).

Then, the concentration along these pathlines, provided that the initial concentration and other factors (for example: redox conditions, biodegradation) are known, can be calculated. [18]

So by reducing the amount of cells where the contaminant concentration has to be calculated, the computation time can be reduced.

In the case of a model with ATEs systems, the difficulty lies in the fact that a pathline is, in a sense, interrupted at the abstraction well and continued at the injection well. So to compute the overall change in concentration correctly, the mass transfer from one well to another corresponding well has to be done accurately.

Another difficulty is the fact that in a situation with ATEs systems, the heads and discharges change with time; at one time a well injects and in another it pumps water up. The flow field, in this case, is therefore transient and not steady state. This makes a pathline analysis more difficult and more assumptions must be imposed.

Yet another difficulty, which is relevant in the Utrecht case, is the fact that the most abundant contaminant type, VOC, degrades sequentially. This means that the reaction product of a degradation reaction of one VOC is another VOC [appendix A].

Research objectives/questions

The case study concerns a large urban area, the city centre of Utrecht, where the subsurface is contaminated with VOC's. The approach is area-oriented and therefore a pathline analysis may be, for reasons which are mentioned above, preferred over a more detailed analysis.

The general objective of this research project is therefore to gain insight in the influence of aquifer thermal energy storage (ATEs) systems on transport of contaminants in a large urban area and the applicability of a pathline analysis to this type of problem.

The research questions in this research project are:

- Can pathline analysis be applied to a transient flow field?

Case study: Utrecht

- What is the influence of an ATEs system or multiple systems on the spreading of contaminants?
- What is the influence of an ATEs system or multiple ATEs systems on the concentration and load of the contaminants?

2. Methods

Before a pathline analysis is applied to the Utrecht case study, a study is conducted to determine whether a pathline analysis can approximate a more detailed MT3DM analysis. For this part of the research, a simplified conceptual model has been made with MODFLOW 2000. MT3D is used to simulate contaminant transport and biodegradation. MODPATH is used to compute pathlines.

The model of the subsurface of Utrecht is also MODFLOW based. The governing equations of these programs and the equations used in the pathline analysis are given below.

Governing equations

MODFLOW

The equation MODFLOW 2000 uses to model 3-dimensional groundwater flow in a porous medium is [9]:

Equation 2.1

$$\frac{\partial}{\partial x}(K_{xx} \frac{\partial h}{\partial x}) + \frac{\partial}{\partial y}(K_{yy} \frac{\partial h}{\partial y}) + \frac{\partial}{\partial z}(K_{zz} \frac{\partial h}{\partial z}) + W = S_s \frac{\partial h}{\partial t}$$

Where K is the hydraulic conductivity along the x-axis, y-axis or z-axis (xx, yy, zz respectively) in m/d. h is the potentiometric head (m), S_s is the specific storage of the porous medium (d^{-1}) and W is the volumetric flux per unit volume (d^{-1}).

MT3D(MS)

MT3D uses the following differential equation for 3-dimensional transport of contaminants in groundwater [20]:

Equation 2.2

$$\frac{\partial(\theta C^k)}{\partial t} = \frac{\partial}{\partial x_i}(\theta D_{ij} \frac{\partial C^k}{\partial x_j}) - \frac{\partial}{\partial x_i}(\theta v_i C^k) + q_s C_s^k + \sum R_n$$

Where, C^k is the concentration of the dissolved contaminant (k) (ML^{-3}), C_s^k is the concentration of the source/sink flux of the contaminant (k), θ is the porosity, D is the hydrodynamic dispersion coefficient in the I, j direction (m^2/d), v is the flow velocity in the i direction (m/d), q is the volumetric flow rate per unit volume of the sources/sinks (d^{-1}) and $\sum R_n$ is the chemical reaction term (g/m^3d).

The rate constant for the dissolved phase and the adsorbed phase can be different for some types of biodegradation. MT3D uses this equation to simulate biodegradation [19]:

Equation 2.3

$$-\lambda_1 C - \lambda_2 \frac{\rho_b}{\theta} \bar{C} = \Sigma R_n$$

Here, ρ_b is the bulk density (kg/m³) and λ is the rate constant.

However, in most cases biodegradation occurs only in the dissolved phase, therefore the second term in the equation can be neglected.

MODPATH

MODPATH is a post processing particle tracking program and is specifically designed to work with MODFLOW. It computes pathlines for “water particles” moving through the subsurface that has been designed in MODFLOW and keeps track of the travel time of every single particle.

MODPATH uses the following equation [13], to express the conservation of mass for infinitesimally small volume of an aquifer and the finite difference approximation of this equation can be seen as a mass balance equation for the finite-sized cell showed in Figure 2-1.

Equation 2.4

$$\frac{\partial}{\partial x}(\theta v_x) + \frac{\partial}{\partial y}(\theta v_y) + \frac{\partial}{\partial z}(\theta v_z) = W$$

Where W is the volumetric flux per unit volume (d⁻¹).

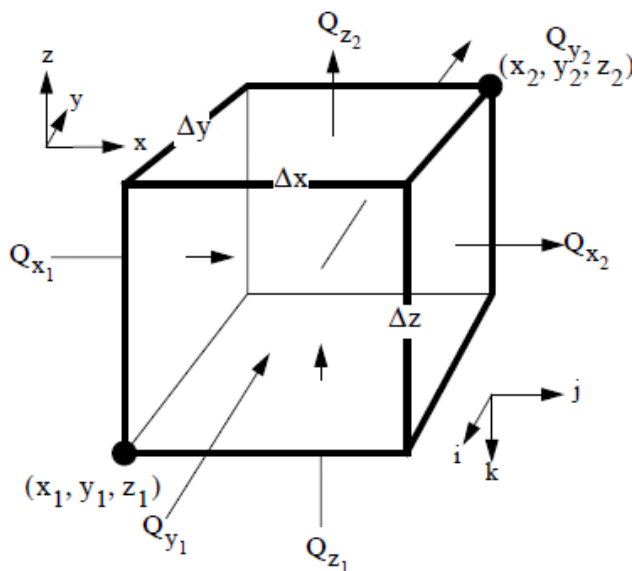


Figure 2-1 Finite-difference cell showing definitions of x-y-z and i-j-k

The average linear velocity across every cell face is obtained by the following equation [13]:

Equation 2.5

$$v_{x_1} = \frac{Q_{x_1}}{(\theta \Delta y \Delta z)R}, v_{x_2} = \frac{Q_{x_2}}{(\theta \Delta y \Delta z)R}$$

$$v_{y_1} = \frac{Q_{y_1}}{(\theta \Delta x \Delta z)R}, v_{y_2} = \frac{Q_{y_2}}{(\theta \Delta x \Delta z)R}$$

$$v_{z_1} = \frac{Q_{z_1}}{(\theta \Delta x \Delta y)R}, v_{z_2} = \frac{Q_{z_2}}{(\theta \Delta x \Delta y)R}$$

Here, Q is the flux (m³) and R is the retardation factor (-).

To simulate the fact that a particle is not a water particle but a contaminant particle, one component is added to the equation; the retardation factor (R). This factor, normally, is dependant on the type of contaminant and the organic matter content that apply to a cell.

Calculate the flux of a particle

MODFLOW/MODPATH calculates the flux through every cell face (Q_{x1}, Q_{x2}, Q_{y1}, Q_{y2}, Q_{z1}, Q_{z2}). In this way the total influx and outflux can be calculated per cell. The outflux, then, is the flux every starting particle has at its release time.

Equation 2.6

$$Q_{in} = \max(Q_{x_1}) - \min(Q_{x_2}) - \min(Q_{y_1}) + \max(Q_{y_2}) + \max(Q_{z_1}) - \min(Q_{z_2})$$

$$Q_{out} = -\min(Q_{x_1}) + \max(Q_{x_2}) + \max(Q_{y_1}) - \min(Q_{y_2}) - \min(Q_{z_1}) - \max(Q_{z_2})$$

$$F_{particle} = Q_{out}$$

Here, F is the flux in m³.

Steady State pathline versus Transient pathlines

To shorten computation time, pathlines that are not significantly influenced by a well are considered steady-state and therefor treated this way.

The endpoints of the pathlines, with the same starting points, of a transient model run and a steady-state run are compared to determine which pathline is, and which pathline isn't influenced by a pumping or injection well and therefore can be considered transient or steady-state, as stated above. If Δh , the distance between the two different pathlines in the x and y direction, Δz , the distance in depth and Δt , a percentage of the difference in travel time between transient and steady-state compared to the travel time of a particle under steady-state conditions, is larger than a predetermined norm (Table 2-1), a pathline is considered transient, otherwise it is treated as steady-state.

Equation 2.7

$$\Delta h = \sqrt{(x_{st} - x_{tr})^2 + (y_{st} - y_{tr})^2}$$
$$\Delta z = |z_{st} - z_{tr}|$$
$$\Delta t = |(t_{st}^{travel} - t_{tr}^{travel}) / t_{st}^{travel}| * 100$$

Where, t is the time in days.

| Norm | Value |
|----------------------------------|-------|
| Δh (m) | 5 |
| Δz (m) | 5 |
| Δt (%) | 5 |

Table 2-1 Norm used for steady-state transient pathline comparison

Biodegradation

During the time a particle travels from one cell to another, biodegradation occurs.

The following equations describe that process. The first part describing natural degradation and the second part ($C^{production}$) describes the fact when a VOC degrades; it partly converted into a VOC next in the degradation chain (Appendix A).

Equation 2.8

$$C(p_{nr}, \varsigma) = C(p_{nr}, \varsigma) * \exp(-k_{deg}(\varsigma) * (dt_{p_{nr}} / R)) + C^{production}(p_{nr}, (\varsigma - 1))$$

Equation 2.9

$$C^{production}(p_{nr}, \varsigma) = C(p_{nr}, \varsigma) * (1 - \exp(-k_{deg}(\varsigma) * (dt_{p_{nr}} / R))) * k_{st}$$

Here the retardation factor and k_{deg} (d^{-1}) depends on the type of contaminant (ς). Normally the degradation constant is also dependent on redox conditions, but because there is no accurate data available, for the cases studied, this constant only depends on ς .

Also, C is the concentration in g/m^3 , k_{st} is the stoichiometric constant, p_{nr} is the particle number

Modelling of an ATES system

As can be seen in Figure 1-5, a well belonging to a ATES system can abstract particles that are released from the source zone, the ATES well itself and other wells.

As a particle enters a well cell from a source zone, the mass per time step is tracked for every contaminant. The following equation applies to this part of the process:

Equation 2.10

$$M(w_{nr}, \tau, \varsigma) = M(w_{nr}, \tau, \varsigma) + F(p_{nr}) * C(p_{nr}, \varsigma)$$

Where, M is the mass in grams, τ is the time step and w_{nr} is the well number.

To second process, the pumping of particles by the same well they are released from is simulated by the following equation. The percentage of particles released at one time, arriving at another time step is calculated (pP).

Equation 2.11

$$\frac{P(w_{nr}, \tau_{release}, \tau_{arrive})}{P^{total}(w_{nr}, \tau_{release})} = pP(w_{nr}, \tau_{release}, \tau_{arrive})$$

Here P is the number of particles (-).

The third process, particles that travel from one well to another, has been simulated in a similar way. The percentage of particles that is released at one time step and arrives at another time step in another well (PP).

Equation 2.12

$$\frac{P(w_{nr}, \tau_{release}, \tau_{arrive})}{P^{total}(w_{nr}, \tau_{release})} = PP(w_{nr}^{release}, w_{nr}^{arrive}, \tau_{release}, \tau_{arrive})$$

Then, to simulate an ATEs system, wells have to be coupled. In this way mass going into one well will only be released in the corresponding second well.

According to the assumption that a particle will also arrive exactly twelve time steps later, as the time step it initially arrived in, the following equation is true:

Equation 2.13

$$M^{in}(w_{nr}, (\tau + 12), \zeta) = M^{in}(w_{nr}, (\tau + 12), \zeta) + M^{source}(w_{nr}, \tau, \zeta)$$

After that, the mass pumped up at a well is injected at another well at the same time.

Equation 2.14

$$M^{in}(w_{nr}^{pumpingwell}, \tau, \zeta) = M^{out}(w_{nr}^{injectionwell}, \tau, \zeta)$$

This mass is equally divided over all the particles leaving the injection well at time step τ .

The biological degradation is calculated for, first, the particles leaving the same well as they arrive in,

Equation 2.15

$$M_{out}(w_{nr}^{release}, \tau_n, \zeta) = M_{out}(w_{nr}^{release}, \tau_n, \zeta) * \exp\left(\frac{-k_{deg}(\zeta) * (\tau_{return} - \tau_{injection})}{R}\right) + M^{production}(\tau_n, \zeta - 1)$$

And secondly, for the particles leaving one well and arriving in another,

Equation 2.16

$$M_{out}(w_{nr}^{arrive}, \tau_n, \zeta) = M_{out}(w_{nr}^{release}, \tau_n, \zeta) * \exp\left(\frac{-k_{deg}(\zeta) * (\tau_{return} - \tau_{injection})}{R}\right) + M^{production}(\tau_n, \zeta - 1)$$

with,

Equation 2.17

$$M^{production}(\tau_n, \zeta) = M_{out}(w_{nr}^{release}, \tau_n, \zeta) * \left(1 - \exp\left(\frac{-k_{deg}(\zeta - 1) * (\tau_{return} - \tau_{injection})}{R}\right)\right) * k_{st}$$

All combined, the total mass in arriving in a well at a certain time step can be calculated as follows:

Equation 2.18

$$M_{in}(w_{nr}^{arrive}, \tau_n, \zeta) = \sum_{k=0}^n (M_{in}(w_{nr}^{arrive}, \tau_n, \zeta) + pP(w_{nr}^{release}, \tau_k, \tau_n) * M_{out}(w_{nr}^{release}, \tau_k, \zeta) + PP(w_{nr}^{release}, w_{nr}^{arrive}, \tau_k, \tau_{arrive}) * M_{out}(w_{nr}^{release}, \tau_k, \zeta))$$

Contaminant transport to the boundaries of a control area

Particles can travel to the boundaries of a control area, established in the area-oriented remediation approach, in three ways, namely from the well, directly from the source, but still influenced by a well (transient) or from the source zone and not influenced by a well (steady-state). In all cases biodegradation will occur, as described above.

Model description: Conceptual model

Model domain

The conceptual model (created in MODFLOW 2000), used for this study, consists of one unconfined aquifer with a depth of 50 meters. The area of the aquifer is one kilometre by one kilometre. The aquifer is modelled as one layer, 250 rows and an equal number of columns. The contaminated source zone is situated between row 165 and 177 and column 58 to 80 and comprises the entire layer (Figure 2-2).

Two wells were placed in the grid, one in row 125, column 75 and one in row 125 and column 175, to model one single ATEs system (Figure 2-2). During every period, one well is abstracting and the other is injecting water at the same volumetric flow rate. A cycle includes 6 periods of abstracting and 6 periods of injecting water.

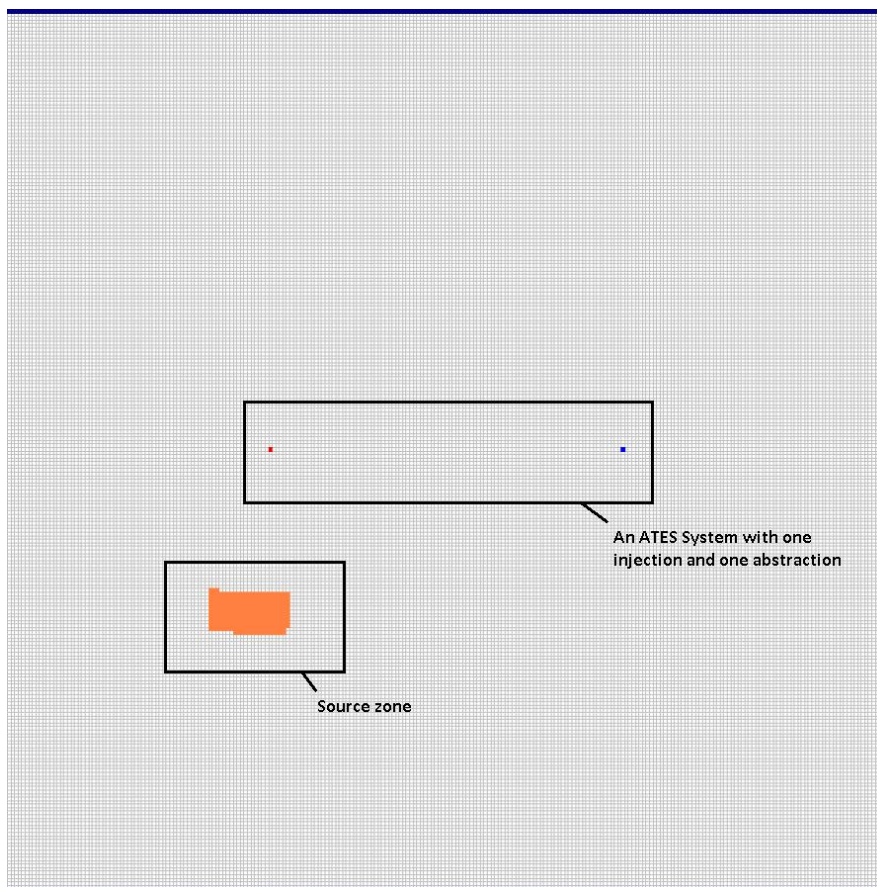


Figure 2-2 Conceptual model

Model parameters

One period is 30 days in the conceptual model, which is considered a month. The simulation time of the model is 480 periods, which equals 40 years.

Other parameters used in the MODFLOW model are given in Table 2-2 and parameters used for the simulation of contaminant transport in MT3D are given in Table 2-3.

| Parameter | Value |
|---------------------------------------|-----------|
| Hydraulic conductivity (m/d) | 100 |
| Transmissivity (m ² /d) | 5000 |
| Porosity (-) | 0.33 |
| Specific yield (-) | 0.15 |
| Dry bulk density (kg/m ³) | 1600 |
| Well flow rate (m ³ /d) | (+/-)2400 |

Table 2-2 Model Parameters (MODFLOW)

| Process | | Parameter | Value |
|-------------------|--|--|-------|
| Advection | Solution scheme: Upstream finite difference method | Courant number | 0.75 |
| Chemical reaction | No sorption | First order rate constant for the dissolved phase (d ⁻¹) | 0.01 |
| | Source zone | Initial concentration (g/m ³) | 1 |

Table 2-3 Model Parameters (MT3D)

Boundary and initial conditions

Two rows are indicated as constant head cells, one on the top (row 250) with a constant head of 12 meters and the other on the bottom (row 1) with a head of 11 meters.

Assumptions

The following assumptions are made in the conceptual model. First, the model domain is homogenous and $k_{\text{degradation}}$ is constant per contaminant throughout the model. Secondly, the amount of water that is abstracted in one well at a certain time step is in its entirety reinjected in another well. Other assumptions are that the water inside the ATEs system is perfectly mixed and that one cycle of twelve time steps (6 injection and 6 abstracting time steps) is exactly the same as the next twelve time steps. So, a particle released in one time step travels along exactly the same pathline as a particle released twelve time steps earlier.

Also, it should be noted that the surface level has been chosen to be the reference level, so the cells are fully saturated.

Pathlines

In the conceptual model, particles are released from two different locations. First, from a cell that is indicated as a source zone cell. Secondly, from cells which are indicated as wells (the ATEs system). From the source zone, particles are released only the first 12 time steps of the simulation. From the wells, particles are released every time step.

Model description: Case study Utrecht

Model domain

For this study the model data of Arcadis [7] is used, this model is refined in the vertical direction (one layer every 0.5 meters) by adding the TNO model Geotop [16] to the first 50 meters of the model.

The model dimension is 20000m x 20500m in the x, y and has variable depth. The model is non-equidistantly with 412 rows (44x100, 2x50, 280x25, 2x50 and 84x100), 342 columns (59x100, 2x50, 180x25, 2x50 and 99x100) and 126 layers.

ATES systems

In the model, three types of extractions are simulated. Two of them are related to ATES systems. Firstly, the paired wells (doublets) that are abstracting and injecting water continuously throughout the year. Secondly, doublets, or multiple doublets belonging to one ATES systems, which switch from abstraction to injection and vice versa between summer and winter each year. Also modelled, but not related to ATES systems are industrial extractions. These abstract water continuously throughout the year (appendix B).

Model parameters

The stoichiometric constants and degradation constant that are used in the biodegradation equations are given below. [3]

| VOC | Degradation constant (d-1) |
|-----|----------------------------|
| PCE | 0.005 |
| TCE | 0.003 |
| DCE | 0.002 |
| VC | 0.001 |

Table 2-4 Degradation constant of VOCs used in the model

| VOC | Stoichiometric constant |
|---------|-------------------------|
| PCE>TCE | 0.7920 |
| TCE>DCE | 0.7377 |
| DCE>VC | 0.6445 |

Table 2-5 Stoichiometric constant of VOC degradation reactions

System Boundary

The system boundary as described in the ARCADIS report is shown in Figure 2-3([7]), where shaded part of the figure is the area outside the system boundary.

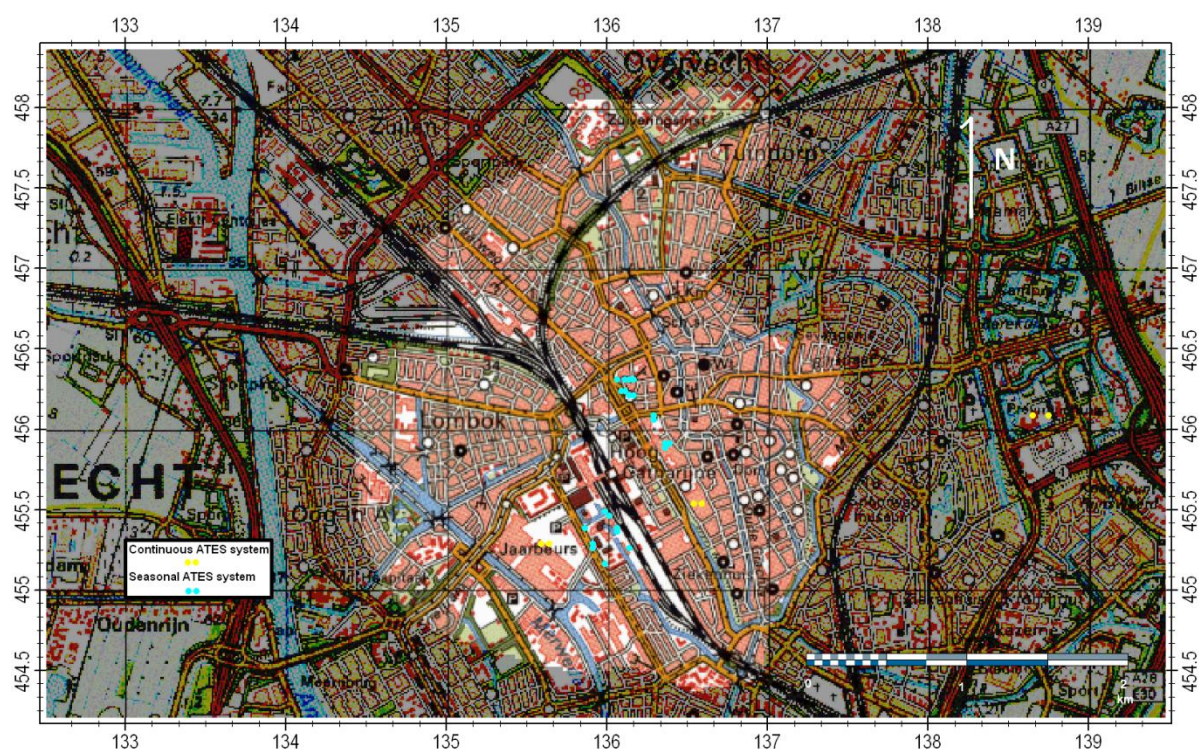


Figure 2-3 System boundary and location of the ATES systems

Assumptions

One assumption that is imposed, in the model that is used for the Utrecht case study is, that the water inside the ATES system is perfectly mixed. Moreover, the amount of water that is pumped in one well is in its entirety reinjected in another well. In addition we assume that one cycle of twelve time steps (6 injection and 6 pumping time steps) is equal to the next twelve time steps. So when a particle arrives at a well in the 22nd time step, another imaginary particle that started 12 time steps later would arrive in the 34th time step in the same well. The degradation constants of all contaminants are assumed to be constant. Last, the source zone is considered continuous until it would be remediated.

Pathlines

To simulate the current and future situation in the city centre of Utrecht, three types of starting point are created. The first set consists of points which start at the source zone locations, as they have been defined by Arcadis. In the source zone cells, ten starting point are defined which are situated in a circle around the centre of the cell. Analysing afterwards, only one starting point per source zone would have been adequate already. Every starting point gets an initial concentration; this concentration is also given in the Arcadis report and is based on the situation in 2008. [7]

The starting points for the plume particles and the corresponding initial concentrations, also based on the situation in 2008, are created in a different manner. The plume concentrations of the four VOCs are known for three parts of the subsurface, namely 5 tot 15, 15 to 30, 30 to 50 meters beneath the surface level (Figure 2-4, Figure 2-5, Figure 2-6 and Figure 1-1).

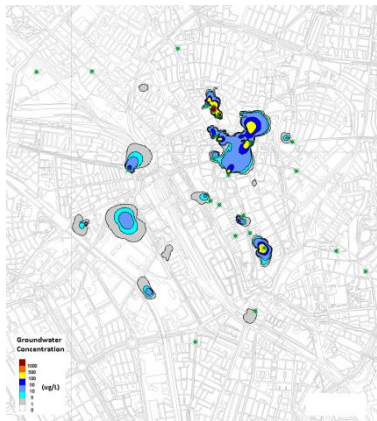


Figure 2-4 DCE plume concentrations (-5 <> -15m) 50m)

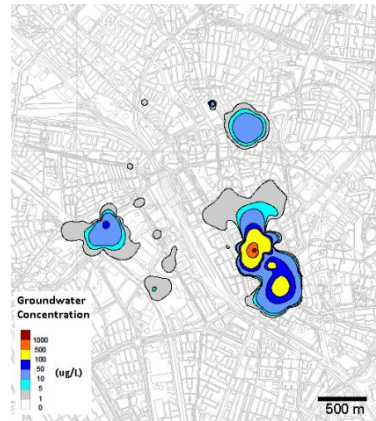


Figure 2-5 DCE plume concentrations (-15 <> -30m)

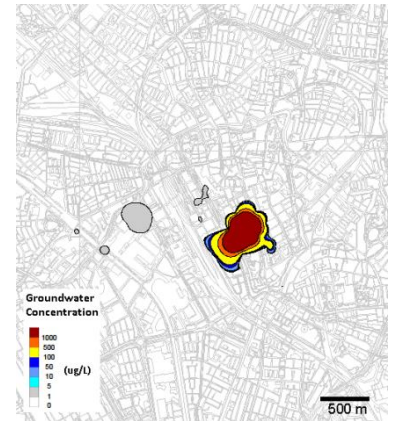


Figure 2-6 DCE plume concentrations (-30 <> -50m)

These figures correspond to a grid size of about 5 to 7 meters. To convert these figures to a figure, with cells of 50 meter that can be used in this research the following steps are taken. First, the maximum value is taken of a cluster of 8x8 cells. These temporary cells have a size of 40 up to 56 meters. After that a grid is made of cells of 50 meters and the concentration that is assigned to these cells is the concentration that is applicable in the middle of this new cell. In this way the plume shape and concentration values change from Figure 2-7 to Figure 2-8.

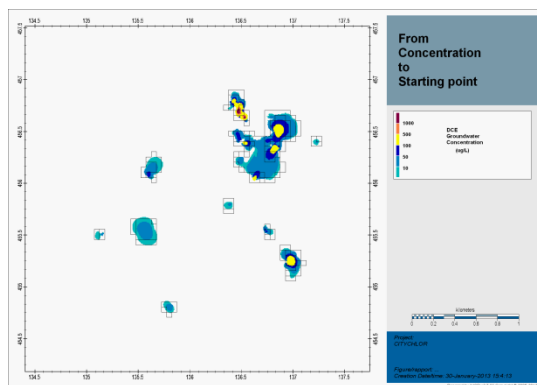


Figure 2-7 Plume concentrations as described by ARCADIS

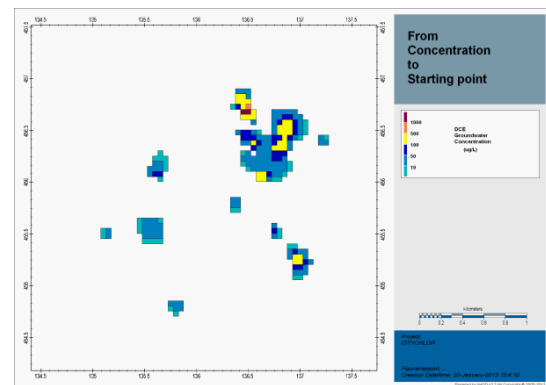


Figure 2-8 Plume concentrations digitalized and adjusted to cell size used in Utrecht model Deltares

This is done for every VOC and applied to every layer in the, with Geotop refined, Utrecht model. The plume starting points are then situated in the middle of every cell that has one or multiple initial concentration values of a VOC (Figure 2-9).

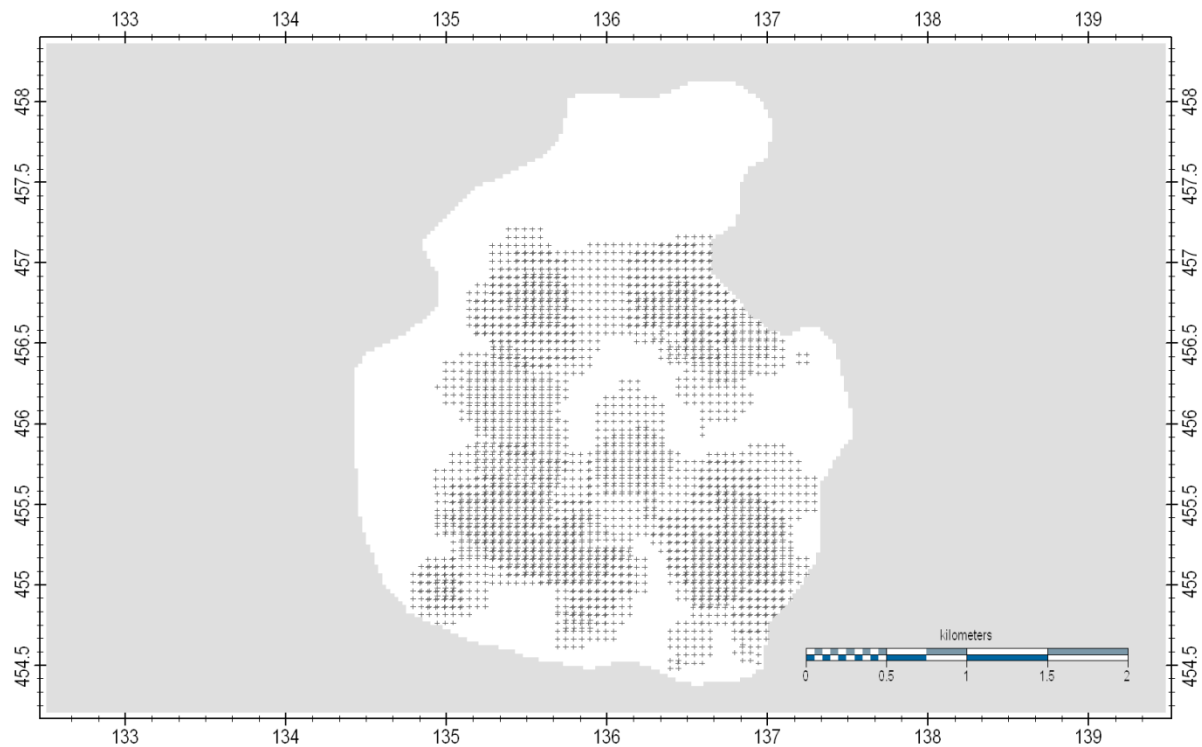


Figure 2-9 Starting points of the plume pathlines

Due to the fact that many particles that start in a source zone will travel directly to the surface (explained in the results), the source zone has been extended vertically. This has been done in such ways that if a plume cell is located at the same row and column as a source zone cell, it is from then on treated as a source zone cell, with the difference that in the original source zone cells more than one particle will start.

3. Results

Conceptual model

Head distribution

Steady state

Below, the head distribution is plotted for the steady state model, with a fixed head of 12 meter at the upper boundary and 11 meter at the lower boundary. The flow direction is therefore north to south (downwards).

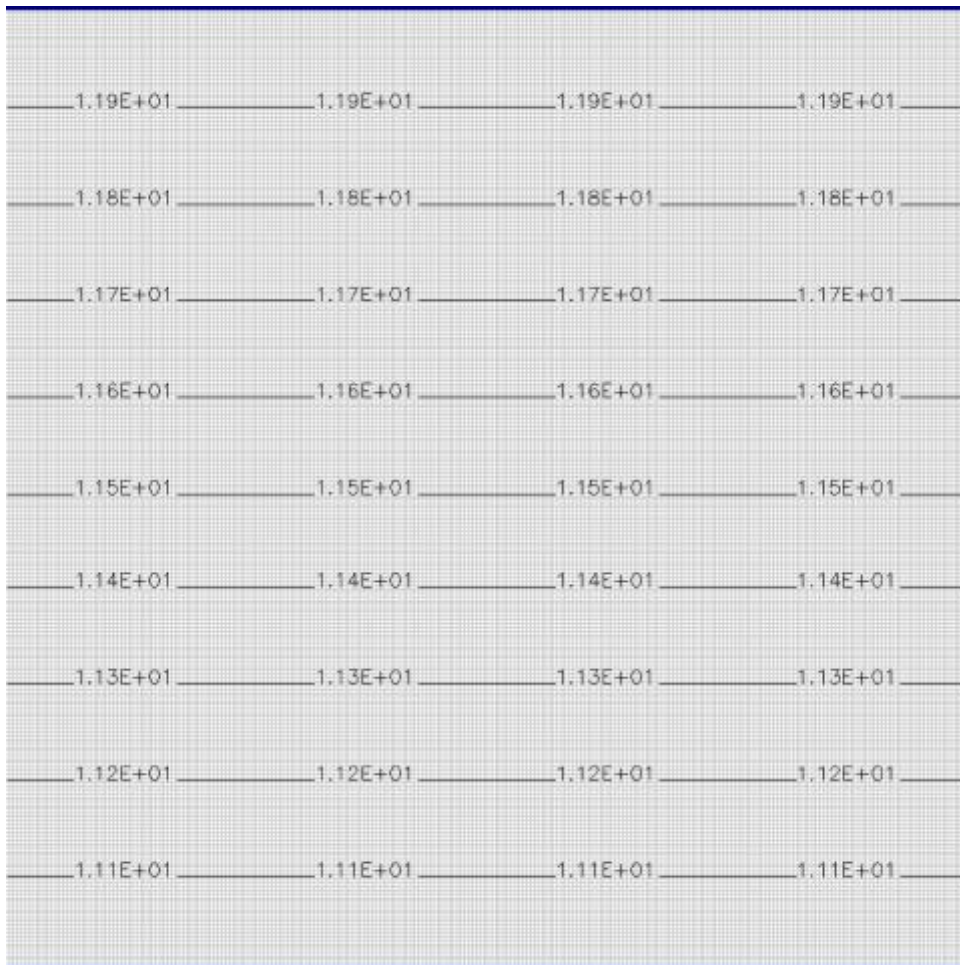


Figure 3-1 Head distribution: Steady State model (period 1)

Transient

Below, the head distributions are plotted for the transient model with one ATEs system in place within one abstracting-injection cycle. First, the situation where the left well is abstracting and the right one injecting water for six time steps (months)(Figure 3-2). Next, the situation, in the seventh time step (month), when the right well is abstracting and the left well is injecting water (Figure 3-3). In both situations the location of the source zone of the contamination can be seen in orange.

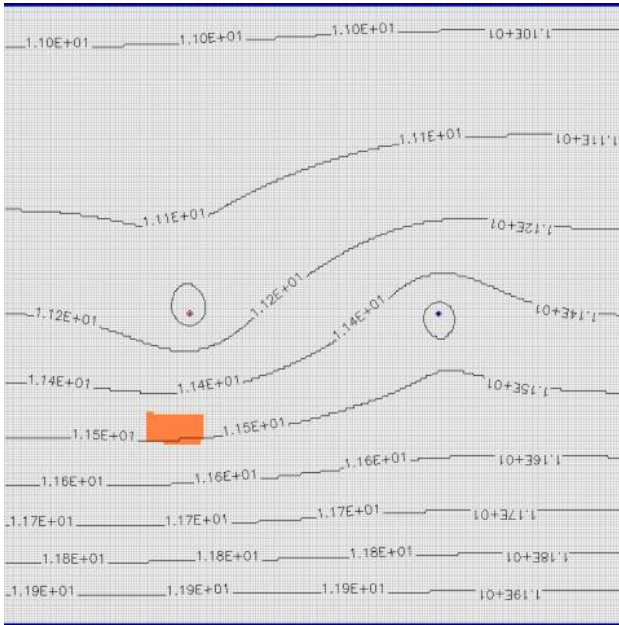


Figure 3-2 Head distribution: Transient model (period 1)

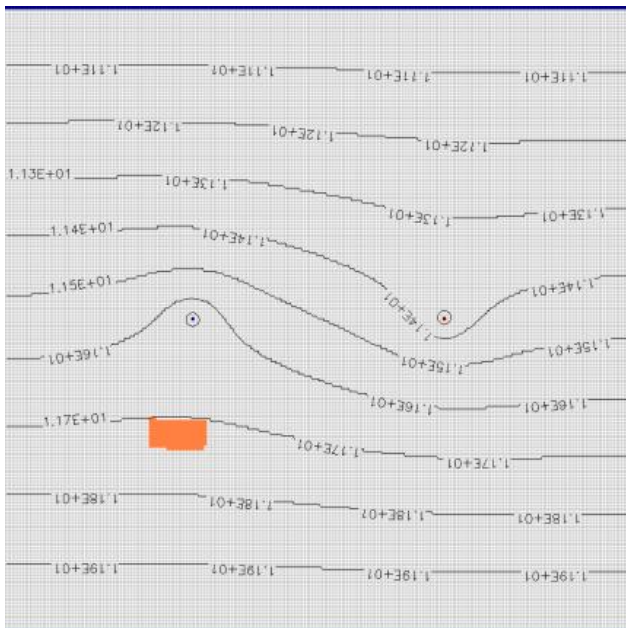


Figure 3-3 Head distribution: Transient model (period 7)

Contaminant concentration in an ATES system

The next two figures show a comparison between the pathline analysis run and the MT3D run. Both runs use the same MODFLOW model. The two graphs have concentration in grams per cubic meter on the vertical axis and time in months on the horizontal axis. The first graph disregards biodegradation (Figure 3-4), while the second does take into account linear biodegradation (Figure 3-5).

Without biodegradation

The pathline analysis over estimates the concentrations arriving in the well by 150% (peaks) and underestimates it by about 50%. Also can be observed that the concentration increases much faster with the pathline analysis than with MT3D.

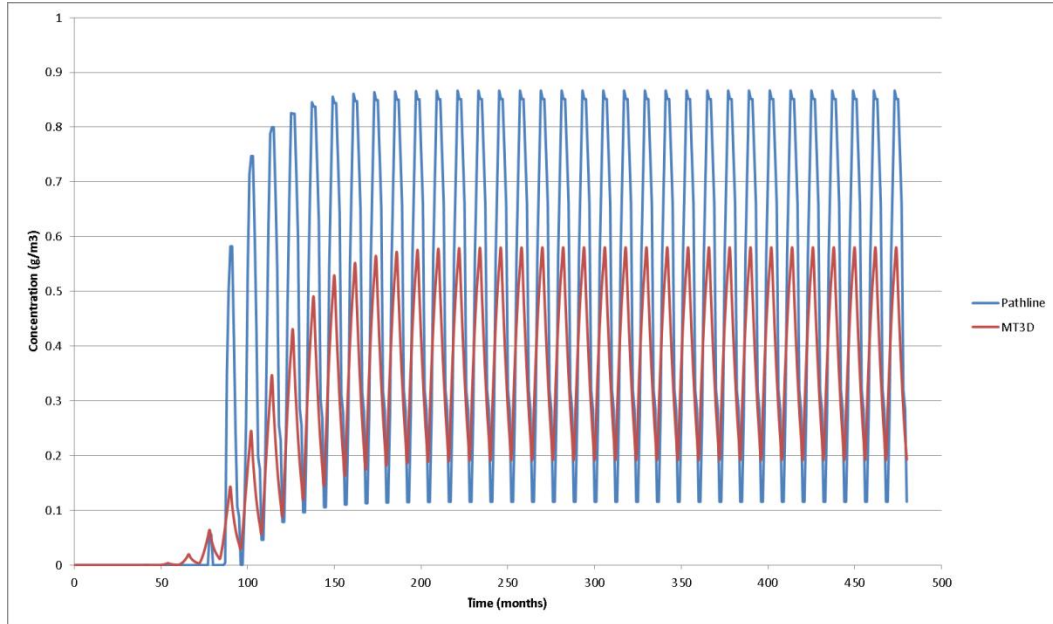


Figure 3-4 Concentration of the contaminant in the ATEs system (no biodegradation)

With biodegradation

With linear biodegradation added to the process, the difference between a pathline analysis and a MT3D simulation becomes evident. The pathline graph shows that it overestimates the degradation of the contaminant substantially compared to MT3D. The difference is about three orders of magnitude.

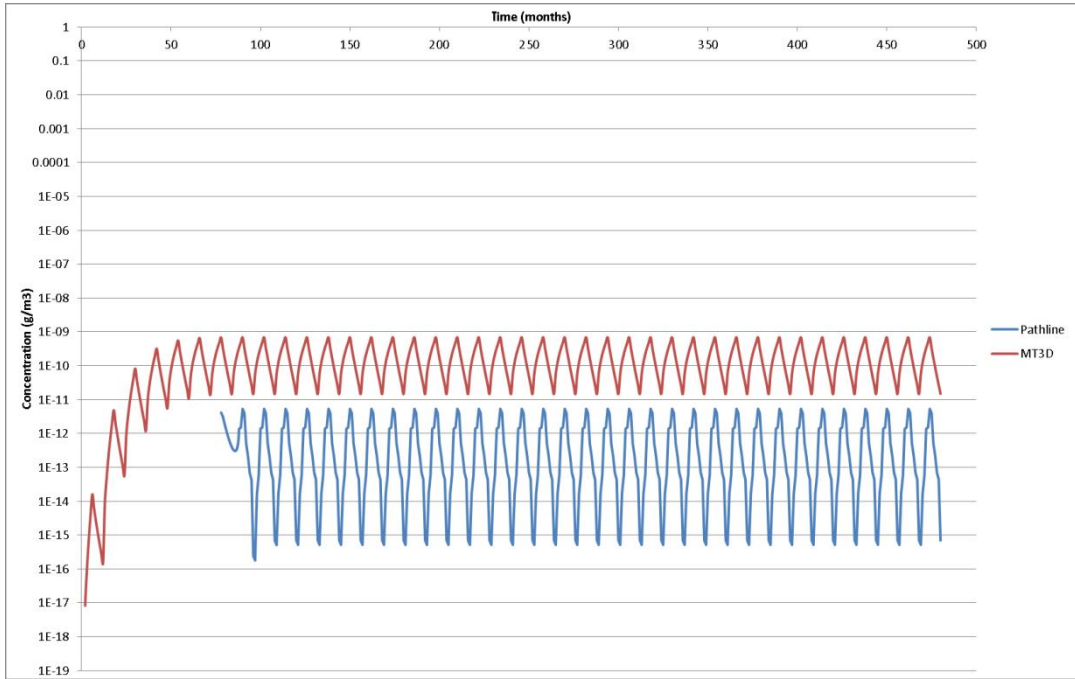


Figure 3-5 Concentration of the contaminant in the ATEs system (with biodegradation)

Case study: Utrecht

In the Utrecht case study, particles were released from three location types. First, particles are released from every plume cell. However, because the large amount of data and the fact that the image of the pathlines only depicts a huge tangle of lines, this image is not shown. But to give an impression of the direction of flow and the potential locations with too high contaminant concentrations caused only by the plume, the endpoints (Figure 3-6 and Figure 3-7) of these pathlines are plotted.

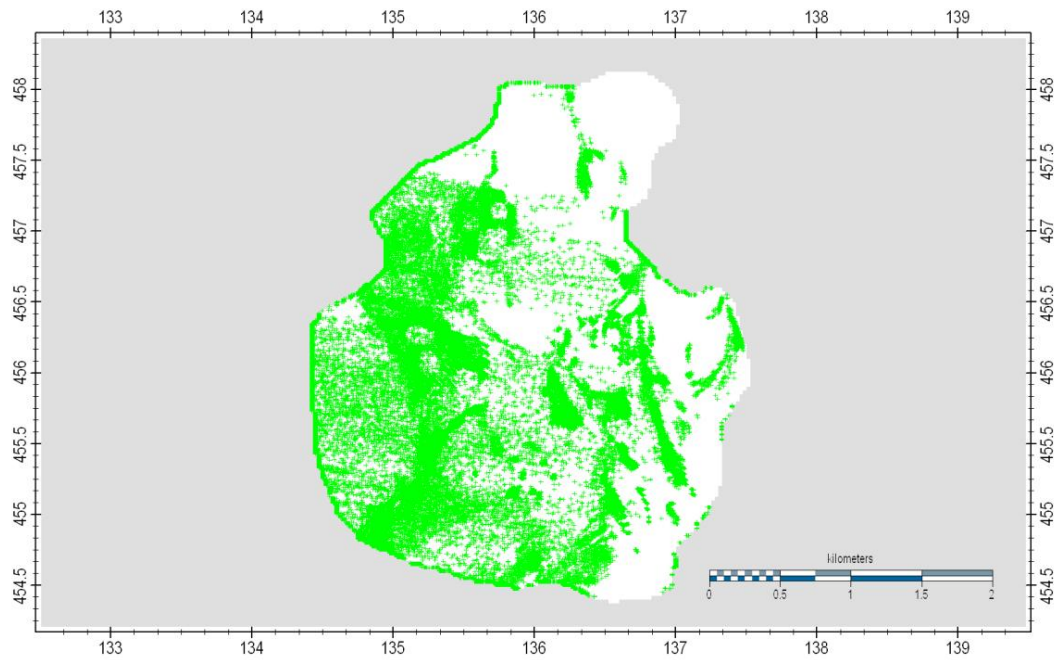


Figure 3-6 Endpoints of the plume pathlines, starting in the second month of 2008

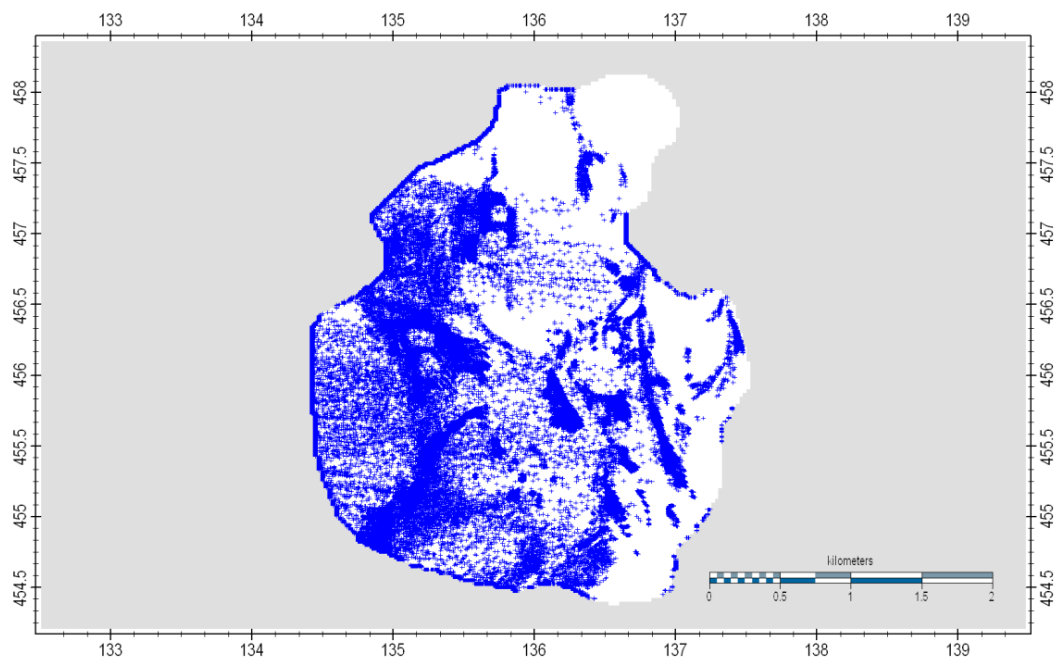


Figure 3-7 Endpoints of the plume pathlines, starting in the eighth month of 2008

Secondly, particles that are released from cells that are designated as a source zone (Figure 3-8). Here both particles released in winter and in summer, although this is not clear because some green lines are hidden underneath blue lines, will reach the system boundary within 250 years.

Potential locations where the contaminant concentration exceeds the established intervention values are situated in the north-west, the east and the south. What also can be seen is that pathlines never end in a well.

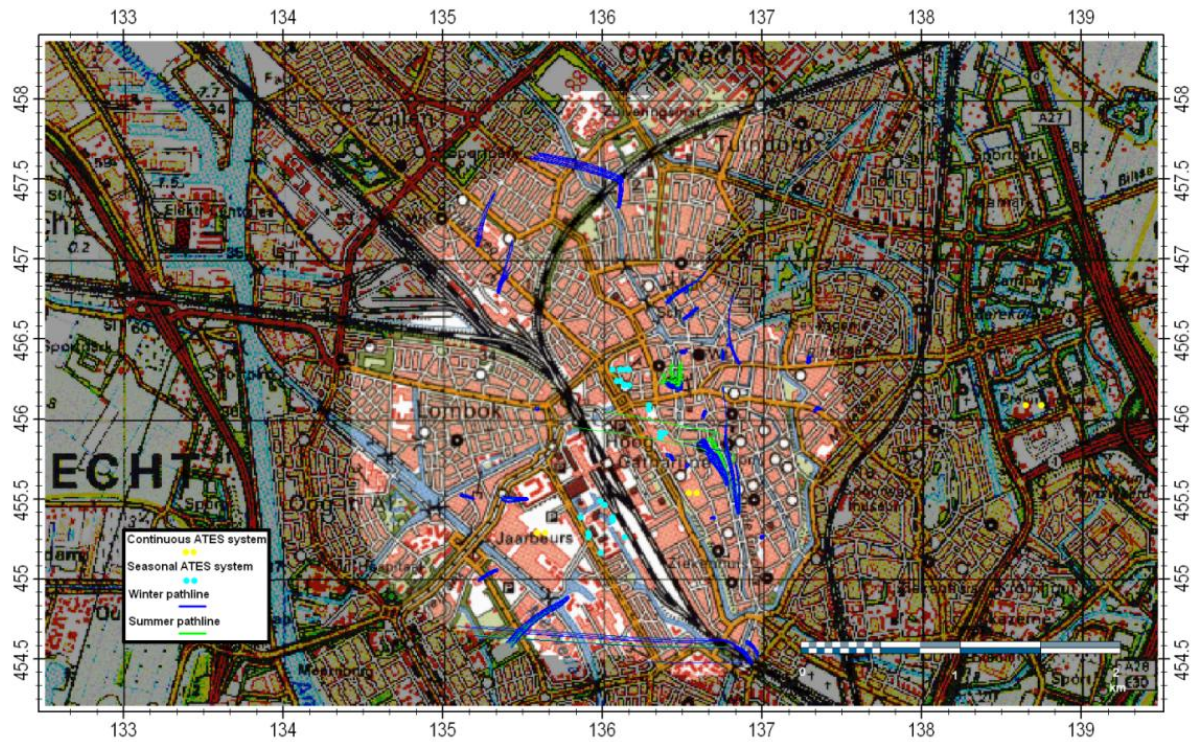


Figure 3-8 Pathlines from the source zones to the system boundary

In Figure 3-9 can be seen how the particles travel in the vertical direction. What is most obvious in this image is that most particles travel vertically until -50 meter and from there on a more horizontal path is preferred, this is discussed further on. Another feature that stands out is the intermission of the two most eastern clusters of pathlines at the approximately -50 meter boundary.

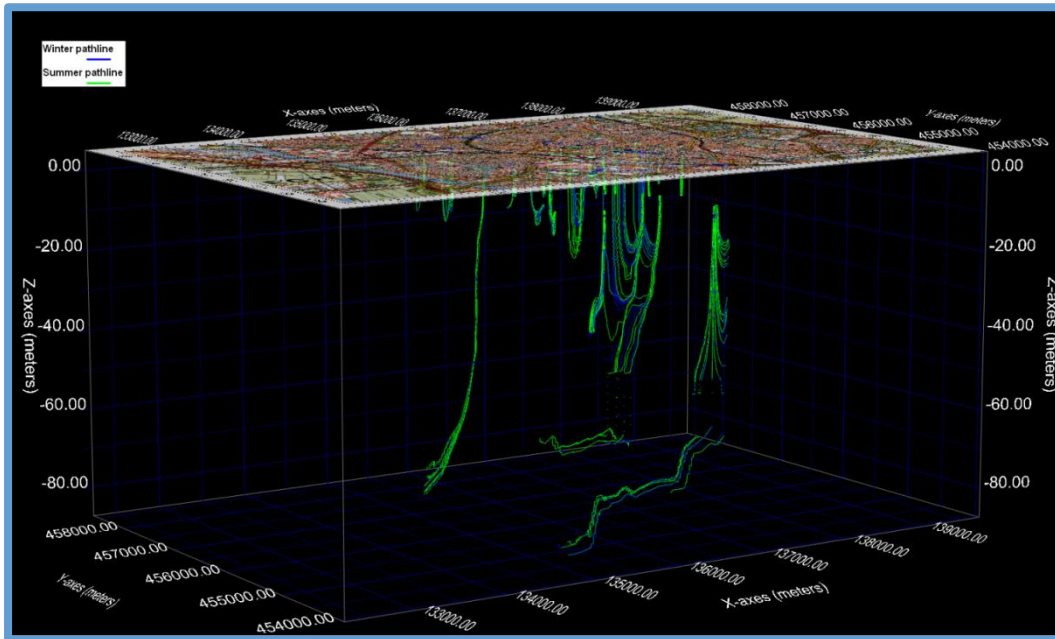


Figure 3-9 Pathlines from the source zones (3D)

When this image is studied in more detail (Figure 3-10), it can be seen that some particles that are released within the first five meters of the subsurface will travel almost directly to the surface.

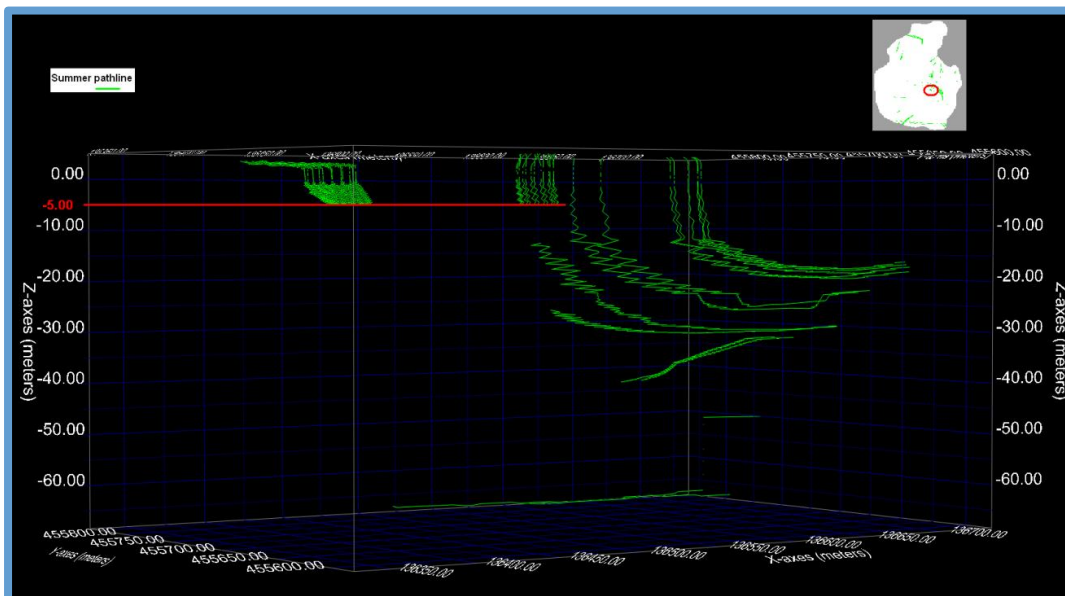


Figure 3-10 Pathlines from the source zones (3D) (close up).

Third, and last in Figure 3-11 and Figure 3-12, the pathlines are shown which start in a well of an ATES system. What is most striking in the 2-dimensional and especially the 3-dimensional image is that particles travel mostly vertically in the first 50 meters of the subsurface, and only start to travel more horizontally, to the boundary when they reach the layers beneath that. This is a similar effect as can be seen with pathlines leaving from a source zone.

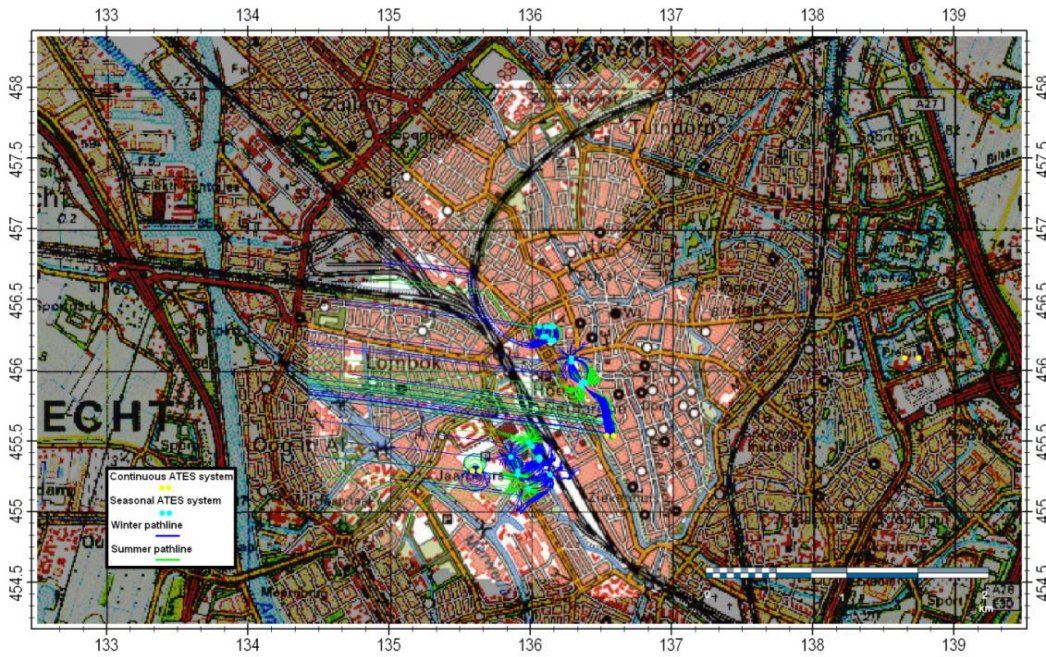


Figure 3-11 Pathlines from the ATES wells to the system boundary

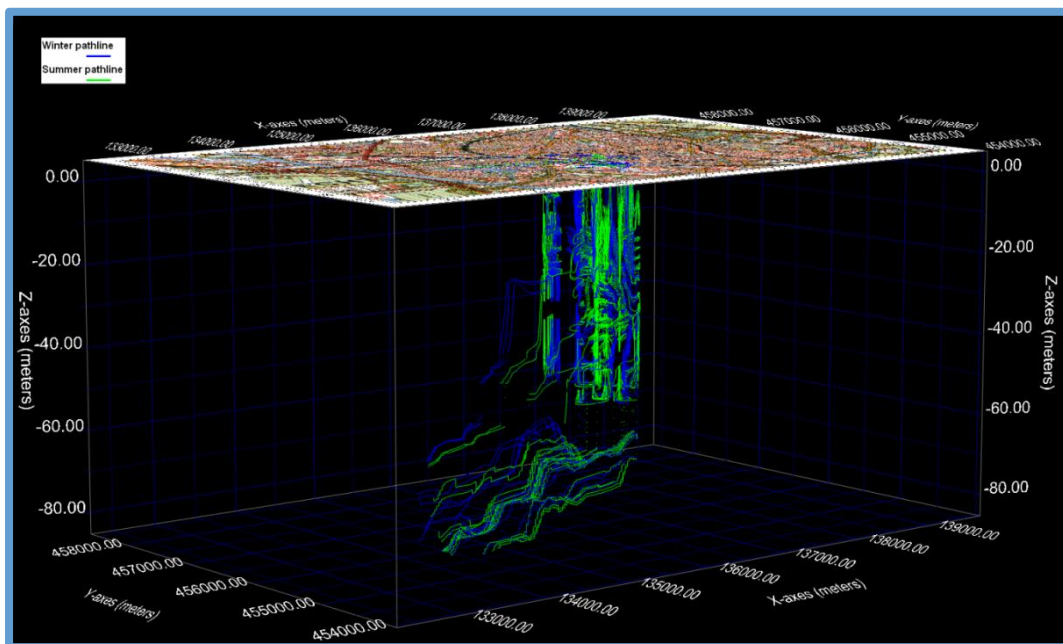


Figure 3-12 Pathlines from the ATES wells (3D)

Figure 3-13, depicts a close-up of one well. Most particles are recaptured by the well within one cycle and only a limited number escape from the ATES system. These pathlines are depicted for a period of 250 years.

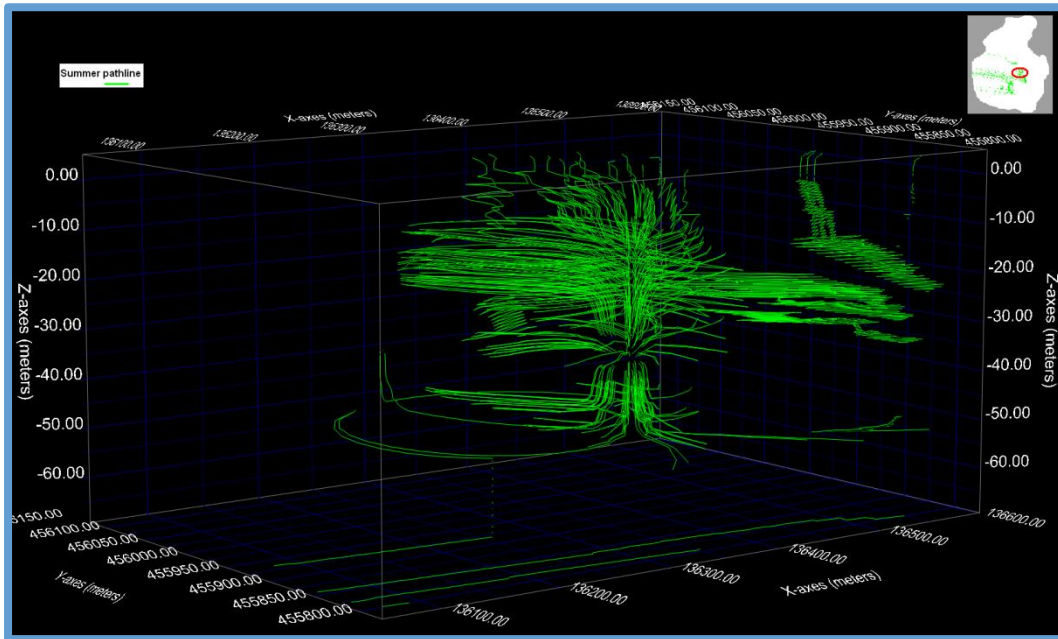


Figure 3-13 Pathlines from the ATES wells (3D) (close up)

Exceeding intervention values

Underneath (Figure 3-14), a more simplified image of the system boundary and the ATES systems within is shown.

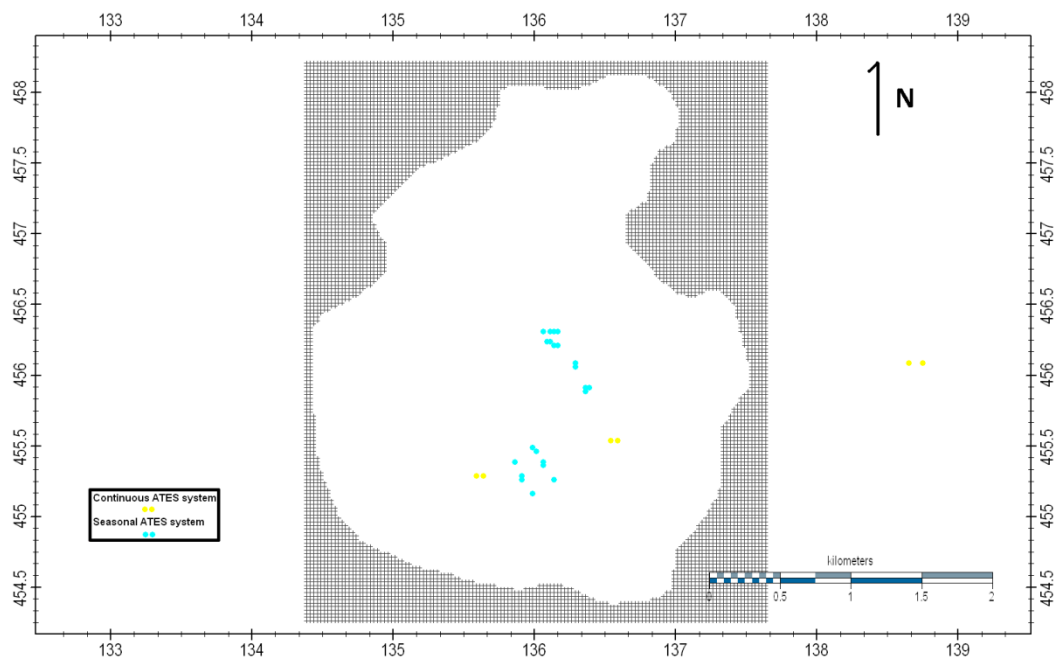


Figure 3-14 The ATES systems within the system boundary

In the figures below (and in Appendix C) the locations are plotted where the intervention values (Table 0-1) for the four discussed VOCs (tetrachloroethylene (PCE) and trichloroethylene (TCE), cis 1,2-dichloroethylene(DCE), vinylchloride(VC)) are exceeded.

Tetrachloroethylene

PCE will never reach the system boundary with concentrations higher than the intervention value. The locations where it exceeds the intervention value become less numerous until about 2018. The number of locations stabilizes around that year.

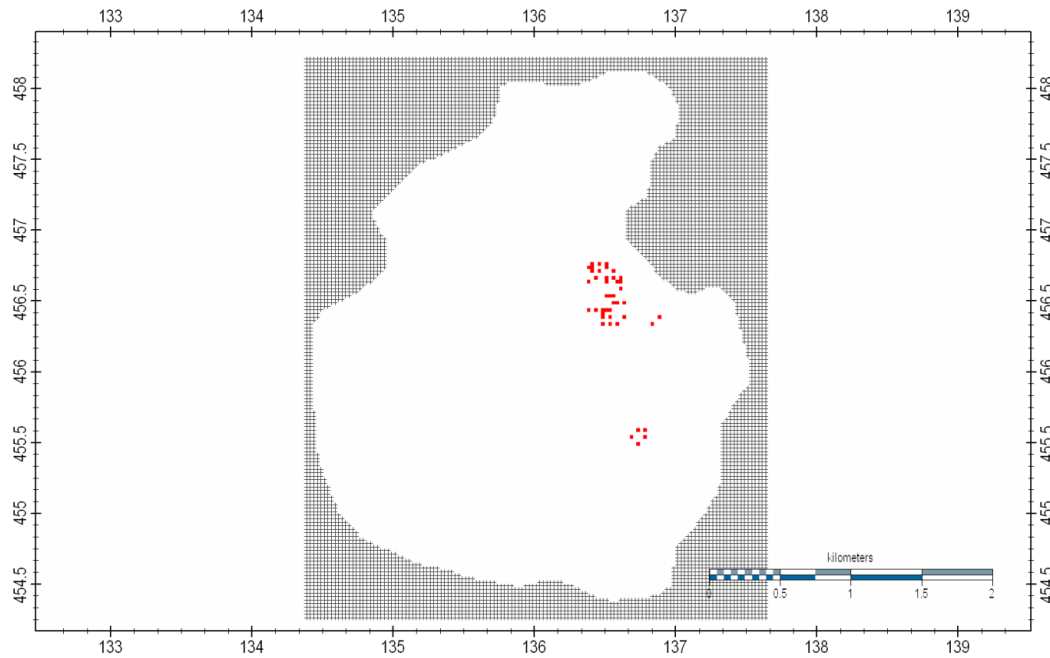


Figure 3-15 Location where the concentrations of PCE is higher than the intervention value in 2013

Trichloroethylene

TCE also never reaches the system boundary with higher concentrations than the intervention value. Its behaviour is similar as PCE, only this VOC totally stabilizes at the year 2038.

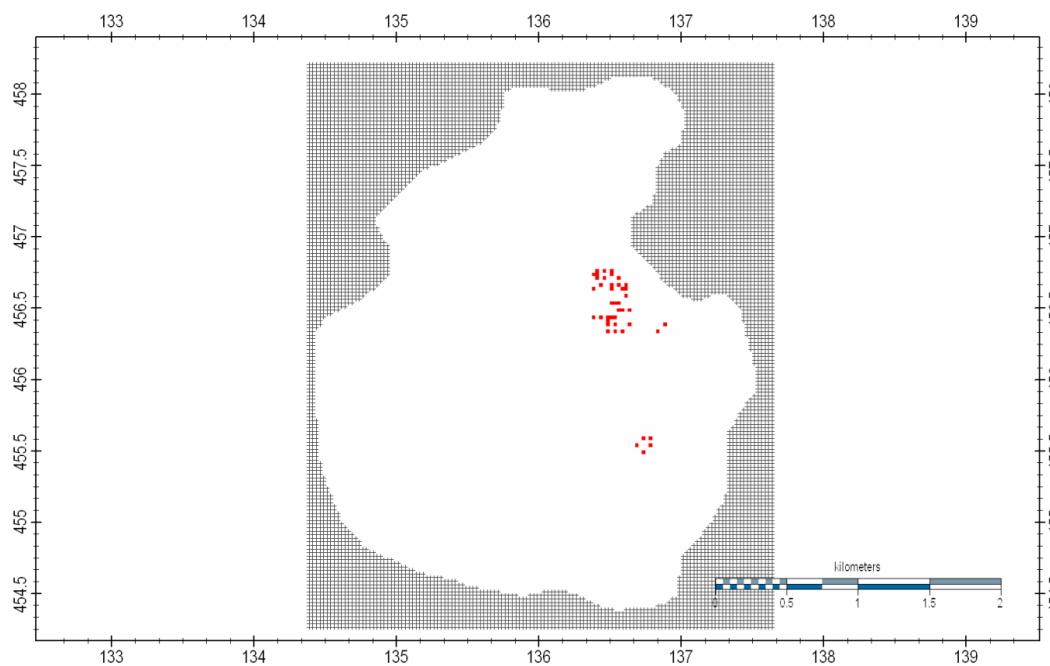


Figure 3-16 Location where the concentrations of TCE is higher than the intervention value in 2013

Cis 1,2-dichloroethylene

This VOC will reach the system boundary with too high concentrations. A certain risk zone is the south eastern part of the boundary and a potential one is the eastern boundary. The amount of locations with too high contaminant concentrations will decline until 2038 and will stay the same from then on.

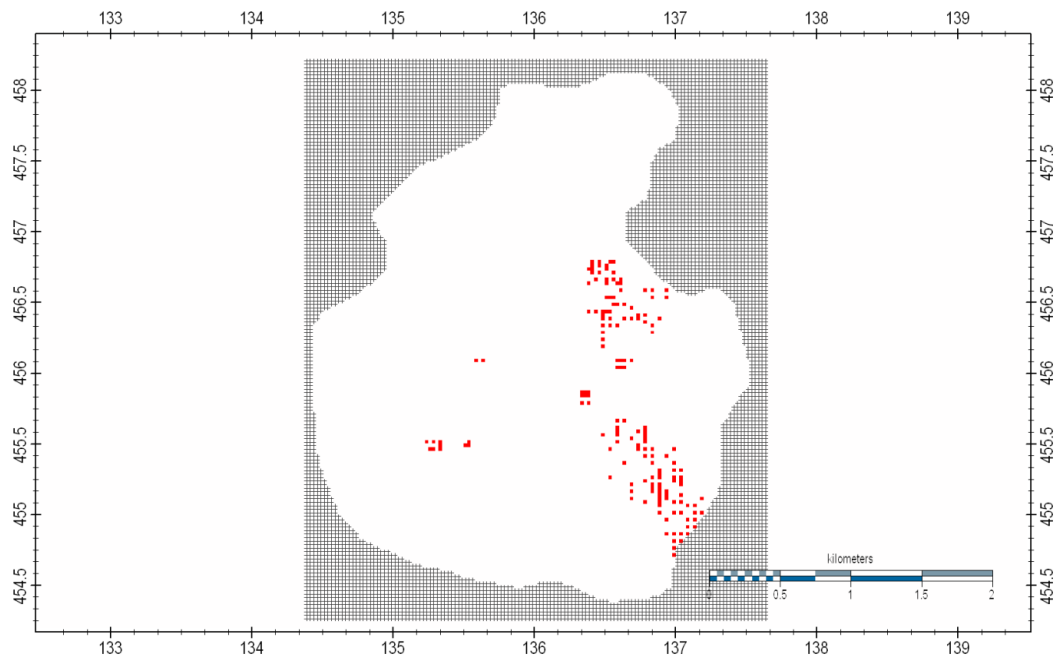


Figure 3-17 Location where the concentrations of DCE is higher than the intervention value in 2013

Vinylchloride

Vc has the most locations where the intervention values is exceeded. There are 2 major risk zones and one smaller one. The big ones are at the east and south eastern part of the system boundary. The smaller one is situated at the south western part. The risk zones in the south east and south west will disappear between the year 2038 and 2058, while at the eastern boundary many locations where contaminant concentrations are too high will subsist after that. In 2108 the locations situated at the system boundary have disappeared and the situation stabilizes.

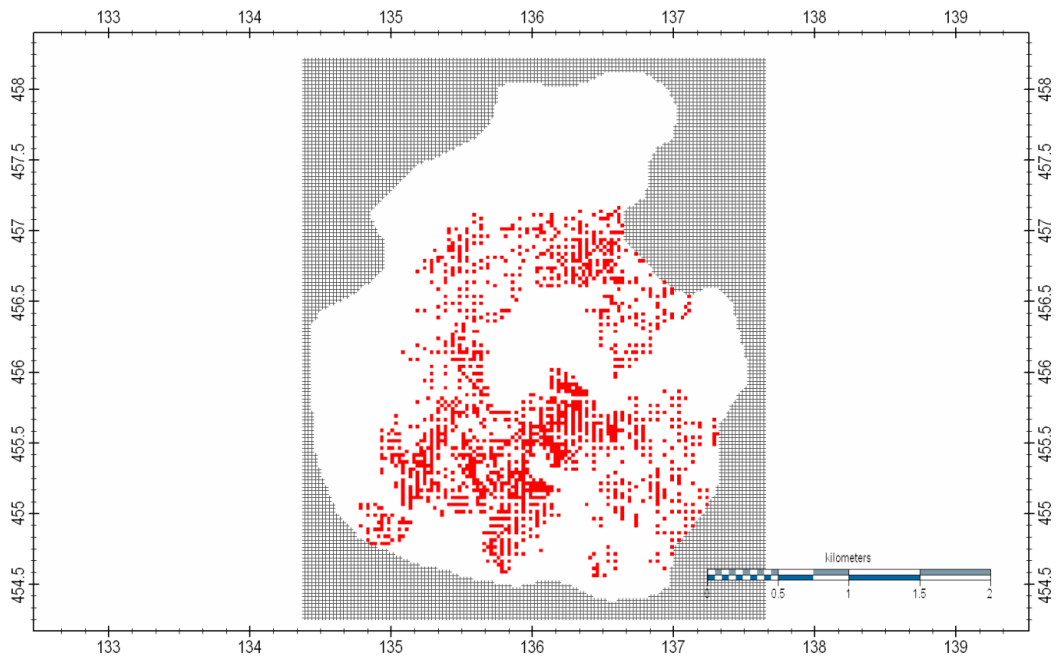


Figure 3-18 Location where the concentrations of VC is higher than the intervention value in 2013

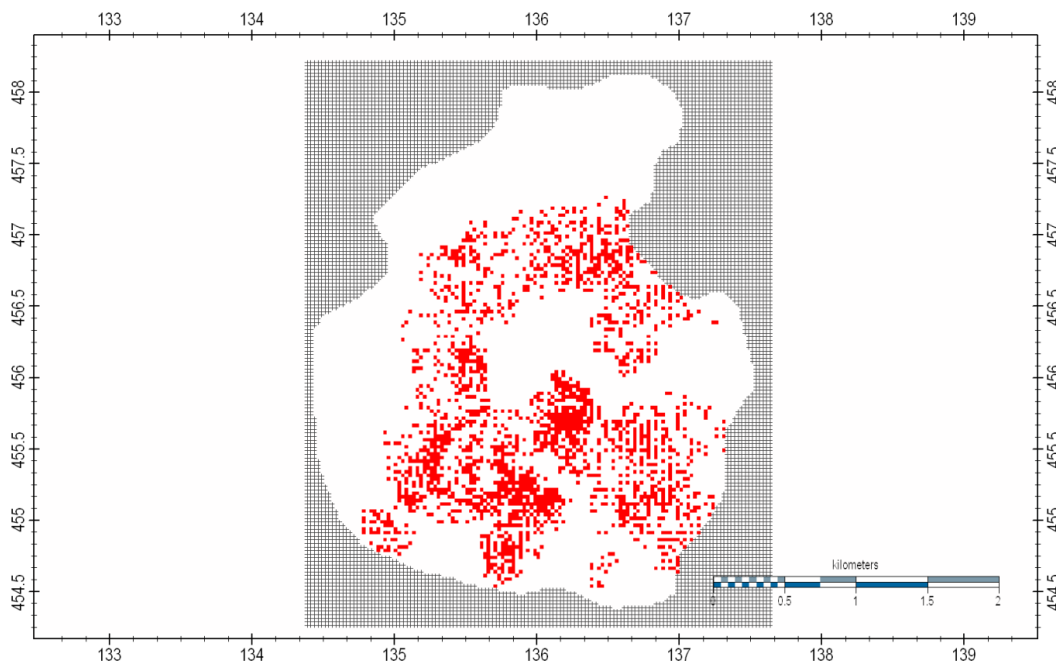


Figure 3-19 Location where the concentrations of VC is higher than the intervention value in 2018

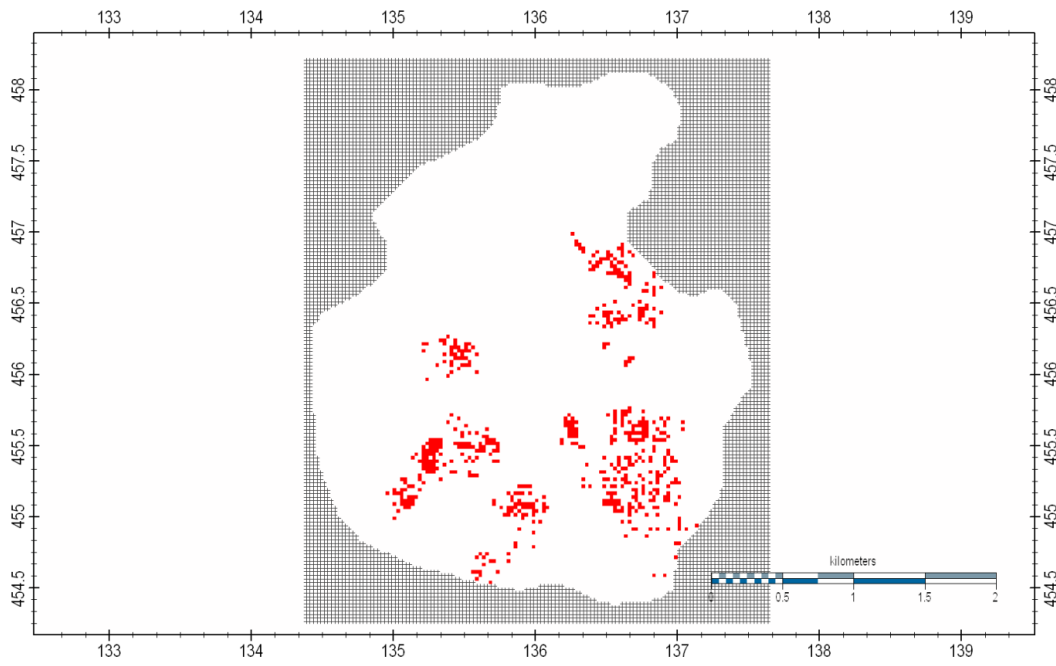


Figure 3-20 Location where the concentrations of VC is higher than the intervention value in 2038

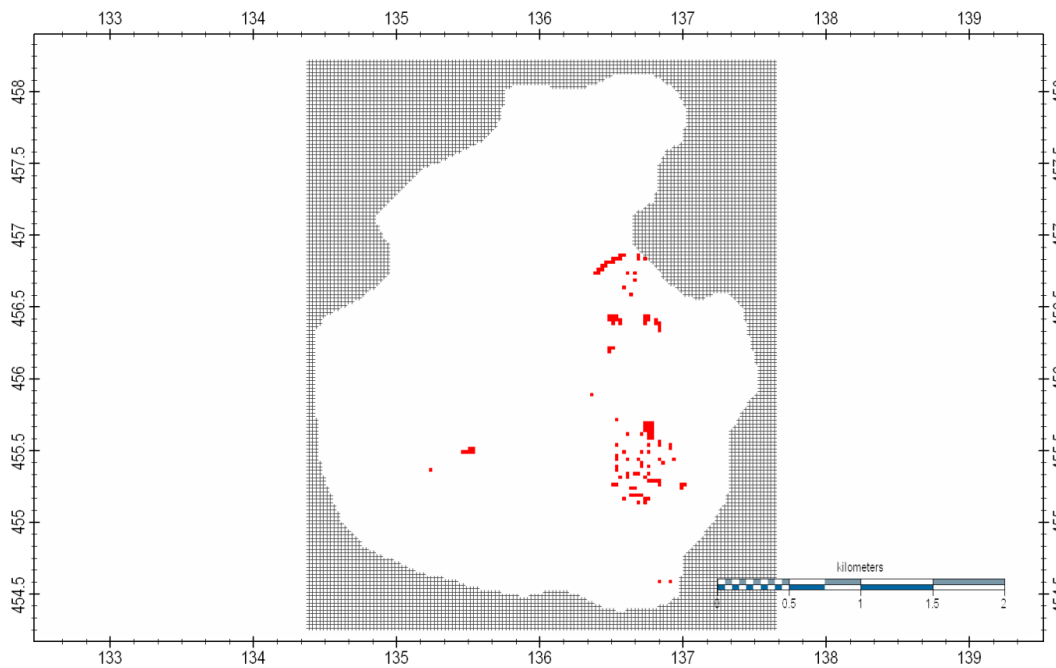


Figure 3-21 Location where the concentrations of VC is higher than the intervention value in 2058

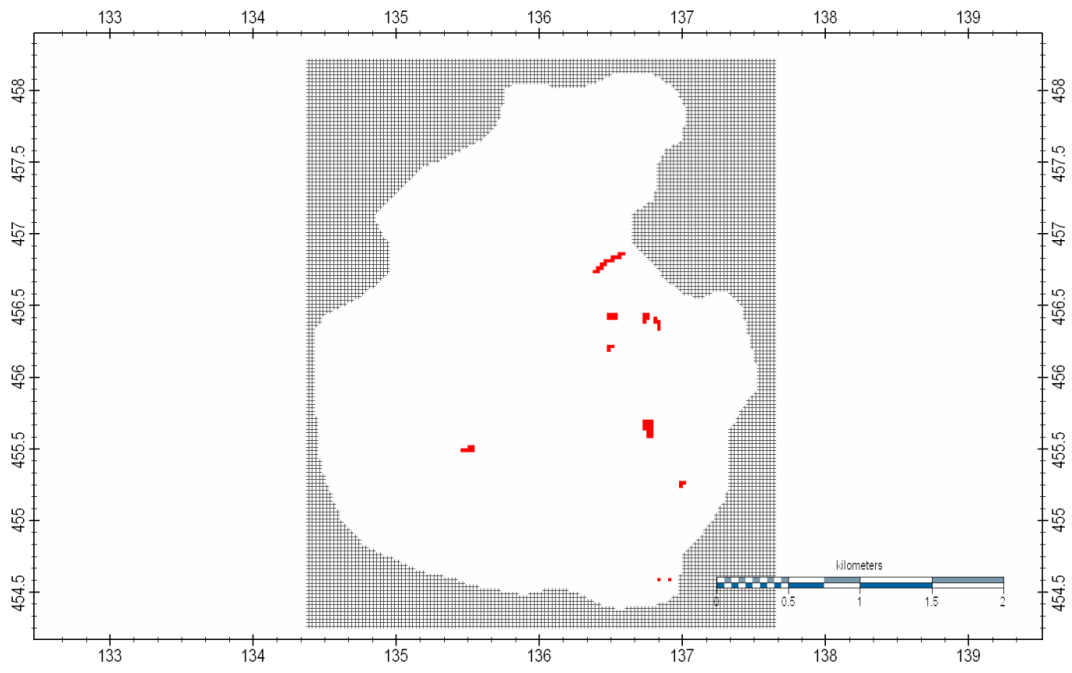


Figure 3-22 Location where the concentrations of VC is higher than the intervention value in 2108

4. Discussion

A pathline analysis is a tool to make a quick risk assessment of a large, contaminated area. This method can be used to give recommendations for placement of monitoring wells and to determine the system boundary for an area oriented approach. It could also be applied as a reference in the determination of further, more detailed, modelling objectives.

Assumptions made

In this specific case too many assumptions are made to use this as a definitive description of contaminant behaviour in the subsurface of the city centre of Utrecht.

The injection of hot water into an aquifer might have an influence on metabolism of bacteria and therefore on degradation rates of VOCs. Temperature effects on degradation rates and also on density and viscosity haven't been taken into account. The statement that because at one time the injected water is hot and at another cold and they can therefore be trade-offs [4], may be questioned. Because the high and low temperature effects probably can only be trade offs if a contaminated water particle will remain at the same location over time. If a particle travels through an area influenced by a hot water injecting well, it must travel to a location that is influence by a cold water injecting well after that, for the temperature effect to be negligible.

Because of the way the biodegradation is modelled, the retardation coefficient was kept constant in time and space. This might have a large effect on the spreading of the contaminants. Normally the retardation coefficient is dependent, for instance, on the type of contaminant and organic matter content. But, first of all, the information concerning organic matter content is limited. Secondly, the equation that describes the distribution of matter from one ATES well to another (Equation 2.18), because it concerns two percentages, doesn't allow multiple degradation coefficients. The way the ATES system is programmed ensures that when a (contaminant) particle arrives at a well it must have concentration, otherwise the particle that leaves the corresponding well at the same time, has an initial concentration of zero.

This problem can be solved if the water particle itself is retarded too, but in that case the retardation coefficient of this particle must change over time and space too, depending on the composition of the soil and the VOC it comprises along the sequential degradation chain.

Another way to implement a retardation coefficient into the model is to base the coefficient, despite the type of contaminant, on a worst case scenario, that is the less retarded substance. This will still cause an error in the results, but it probably is a very small one. This is because VC is the most abundant and least retarded substance and all other VOCs will eventually degrade into VC, so then most of the particles get the right retardation coefficient.

Another disadvantage of the lack of detail in the Utrecht model is that biodegradation can not be modelled accurately. One important characteristic, relating to the speed of biodegradation of VOCs, is the redox condition that applies to the cells a particle is travelling through, but these are not known. At this moment the redox conditions are kept constant per VOC over time and space. In the simulations a constant biodegradation rate is used, but they could be refined if more data becomes available.

Lastly it is assumed that a particle travels along the same pathlines as ones released twelve time steps earlier or later. This assumption implies that the flow regime in the Utrecht subsurface

and especially the area discussed in this research, does not change during the 250-years that are simulated. Which is not the case, it is fairly plausible that, for instance, more ATES system will be installed in the near future.

Utrecht model input

The input used for the pathline analysis, the Arcadis model with the addition of Geotop in the first 50 meters, has some issues that are of importance to this study.

Most of the particles that are released in the first 5 meters of the model are directly transported to the surface; either they travel to drains or to open water. All the source zones, as defined in the Arcadis report, are situated in these upper few meters of the subsurface, which means there would be limited transport of dissolved contaminants to lower layers. According to this model, the contaminants will travel to a more undesirable place, the surface, but no cases of such sort are mentioned in the report.

Another issue concerning the source zones is that the location of some of the source zones does not overlap with the known plumes (Figure 4-1). So there seems an information gap between the two data sets, in the sense that there is no physical/ chemical connection between the plume and the source zone.

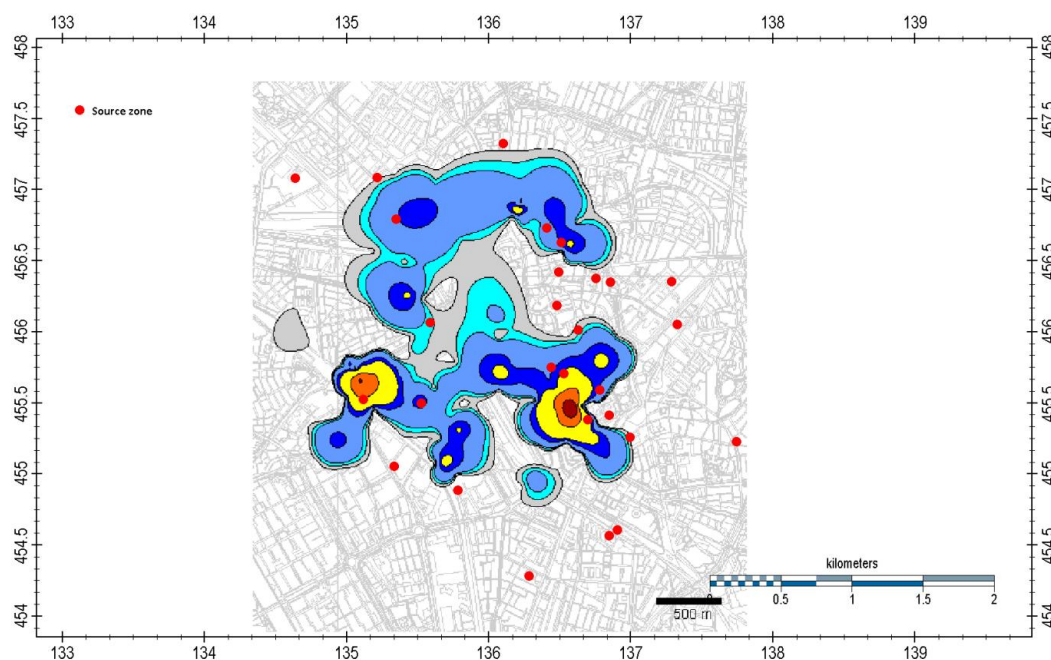


Figure 4-1 Largest extent of the plume (VC) compared with the locations of the source zones

Both the finding that many pathlines starting at certain source zones will end up at the surface and the fact that the location of half of the source zones do not overlap with the plume, are the cause of a limited supply of 'new' contaminants to the plume even when the source zone is extended vertically (as described above). As a result, the effect of the continuous source zone (until it is remediated) is limited.

One of the most obvious flaws in the model can be observed in Figure 3-9 and Figure 3-12. Note that there is a large difference in the behavior of particles above -50 meters +NAP and the layers below. In this upper area, particles travel more vertically than horizontally, but below that the

particles travel almost primarily horizontal. This phenomenon is probably caused by the addition of the Geotop until 50 meters below NAP. Presumably the accuracy of the model increases in this way, but another consequence is that it is difficult to identify if the behavior of the particles must be explained by this difference in accuracy or by the properties of the soil itself.

Because of the large differences in behavior of the particles in the upper part and the lower part of the model, questions can be raised if one or both of the models are accurate enough for analysis.

Pathline analysis results

Conceptual model

The conceptual model is highly simplified, and only serves as a verification if the pathline analysis works correctly up to a desired level.

According to this small model, the pathline analysis can reasonably predict the arrival times and arrival concentration of a contaminant plume which arises from the source zone. But when linear biodegradation is added, the discrepancy in concentration becomes very large. Probably this is, partly, due to the fact that through dispersion, in the MT3D model, contaminant load arrives earlier at a well.

The concentrations themselves are very, probably unrealistically, low. So from a risk management point of view the difference between MT3D ($\sim 1^{-10} \text{ g/m}^3$) and the pathline analysis ($\sim 1^{-13} \text{ g/m}^3$) is not a significant problem. If the discrepancy occurs at a concentration level around intervention values, the problem becomes significant.

So the question: 'Can pathline analysis approximate an MT3D model in a transient flow field?' can not be satisfactorily answered. On the one hand; yes, it can approximate transport fairly well. On the other hand; no, the difference between the two are too large when it comes to biodegradation.

Another reason why the question cannot be answered in its entirety is that the MT3D simulation has not been done for the Utrecht case, which is a more complex model. It can therefore not be checked whether the discrepancy becomes larger or smaller, when the complexity of the model goes up.

So more research has to be done to examine if the discrepancy is dispersion related and to examine if the discrepancy goes up or down when a more complex model is used.

Case study: Utrecht

What is evident from the image of the endpoints of the pathlines that simulate a plume is that there is a clear difference between the west/ south west and the eastern part of the area. There is a large cluster of dots in the west, which means that a lot of particles will not reach the boundary in the west within 250 years. The fact that there are a lot of white spots in the east shows that, because particles do start here, a lot of particles will reach the eastern boundary within 250 years or travel to the west.

So two things may be concluded according to this observation; the travel time to the eastern boundary is much shorter and a lot of particles will travel in the western / south-western direction.

What can be seen in the concentration graphs of the different VOCs, is that the particles with a concentration that exceed the intervention value of the respective VOC are very concentrated and in the case of PCE, TCE almost always located at about the same x and y location as the initial plume or source zone. That is, in this case fairly logical because the particles almost primarily travel in the vertical direction until they reach layers lower than 50 meter below NAP. For both PCE and TCE applies that it has its highest plume concentrations in the top most section of the subsurface, it takes a long time to reach minus 50 meters and from there out travel horizontally. So when it does reaches that level it will be degraded into other VOCs.

DCE is, first of all, more widespread than the previous two. It also has a significantly large part of its plume in the -30 to -50 meters part of the subsurface. So therefore it can travel to the -50 layer quicker and reach the boundary or parts within the control area faster.

In the case of VC; this plume seems to exceed intervention values right from the start and because this is the most widespread contaminant it reaches the boundary almost immediately. Because PCE, through TCE and DCE, eventually degrade into VC, this plume will grow first and concentrations of VC will rise before they decline somewhere between 2018 and 2038.

From the graph from the four VOC can be concluded that primarily the particles will travel vertically, which means the plume will stay roughly at its place and concentration will decline to values lower than intervention values in time. According to the model as it exists right now, no final answer can be given to the question what is the influence of ATES systems on the spread of contaminants. The only thing what can be said is that the ATES system might reduce, in the sense that it will keep particles within a certain sphere, the already weak horizontal flow in the first fifty meters of the subsurface in this area.

No research has been done to test which effect is stronger; the natural effect or the effect the ATES system has on the strong vertical flow.

The fact remains that the ATES systems, in this case, will keep the contaminants in its sphere of influence, giving the contaminant time to degrade below intervention values. Although, as already said before, in this specific case it cannot be said if this effect is large compared to the natural flow regime in the subsurface.

The research question: can pathline analysis be applied to a transient flow field, can be answered affirmatively. The contaminant transport part can be modelled quite well and can definitively serve the goal as a quick method to determine how and where (more) monitoring has to take place. The fact remains that the biodegradation part of the analysis only can be modelled correctly if the enough biological and chemical parameters are known, especially when it comes to contaminants that degrade sequentially. In such case, without proper modelling, a distorted image may arise of whether a contaminant passes a boundary at concentration higher or lower than intervention values.

In cases where very few biological and chemical parameters are known, these can be estimated on the basis of a probability distribution using a Monte Carlo analysis.

5. Conclusion

Contaminant transport through a transient flow field can be reasonably well modelled. It is not as accurate as an MT3D model, but for the objective pursued, it does its job. When modelling of reactive transport through the subsurface, as it is done in the case, an error occurs. In cases where ATEs systems are involved, the groundwater flow regime is transient. To model the exact position of each chemical component that is retarded due to adsorption the retardation factor should be included in the calculation of the pathlines. When there are multiple contaminants with different retardation factors each should have its own pathline. In this research the effect of multiple retardation factors for different chemical components was neglected. The applicability of the pathline analyses with retarding chemical components in combination with sequential biodegradation needs additional research.

The amount of organic redox data in Utrecht case study was also minimal, which affect the accuracy of the biodegradation constants. When more data is available, it can be implemented. Or, when little chemical and biological properties of the soil are known, these can be estimated on the basis of a probability distribution using a Monte Carlo analysis.

According to the results from the Utrecht case study, ATEs systems retain the spread of contaminants by mixing on the one hand and keeping the particles in their sphere of influence for a long time on the other. Hereby reducing concentrations by mixing and lengthening the travel time of a particle to the system boundary and so giving the contaminant a chance to degrade to lower concentrations than the intervention values before it reaches the system boundary.

In the Utrecht case, because there is a lot of natural vertical flow, no certainty can be given if an ATEs system enhances vertical spreading significantly.

From this research can then be concluded that a pathline analysis can be applied to a transient flow field. The addition of ATEs systems to the analysis can be arithmetically done with an acceptable accuracy. It can predict contaminant behaviour, provided that it is done with sufficient chemical en biological data, either from the field or from a Monte Carlo analysis. Both sufficient chemical and biological data aren't currently available in the Utrecht case study.

6. References

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Appendix A: Volatile Organic Compounds

The subsurface in the area around central station in Utrecht is predominantly contaminated with volatile organic compounds: VOC's. In this typical case, as already stated before, the chlorinated solvents trichloroethylene (PCE), tetrachloroethylene (TCE), cis 1,2-dichloroethylene (DCE) and vinylchloride (VC) are the most abundant. These substances are mostly used as degreasing fluids for cleaning metal machines or dry-cleaning for instance. Vinylchloride is also used for making plastics.

Generally, VOC's have a low absolute solubility in water. They have a relative density which is higher than water. Also they have a low adsorption coefficient, which make them very mobile in the subsurface. Lastly, they are known to have a high vapour pressure.

Although slowly, VOCs will dissolve into the groundwater and can be a contaminant source for a long time. Because the density is higher than water these VOCs are considered DNAPL (Dense Non-Aqueous Phase Liquids) in its pure form and will sink to the bottom by the force of gravity. Except VC, which has a lower density than water.

Because of the low vapour pressure, VOC tend to evaporate in the unsaturated zone and in this way cause contamination in the gaseous phase. [12]

Below, some general properties are given of the four VOC's that are of interest (Table 0-1).

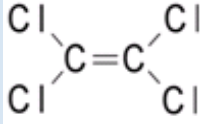
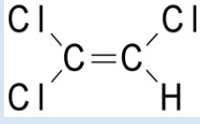
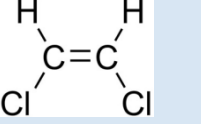
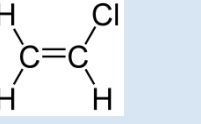
| [15] | Tetrachloroethylene | Trichloroethylene | Cis-1,2-dichloroethylene | Vinyl chloride |
|-----------------------------------|---|---|--|---|
| |  |  |  |  |
| Molecular formula | C ₂ Cl ₄ | C ₂ HCl ₃ | C ₂ H ₂ Cl ₂ | C ₂ H ₃ Cl |
| Molar mass (g/mole) | 165.83 | 131.39 | 96.95 | 62.5 |
| Density (g/cm³) | 1.622 | 1.46 | 1.28 | 0.911 |
| Solubility (g/L) [8] | 0.15 | 1.1 | 0.8 | 1,1 |
| Koc [21] | 240 | 110 | 72 | 33 |
| Intervention value (µg/L) | 40 | 500 | 20 | 5 |

Table 0-1 Properties of VOC's

Biodegradation of VOC's

Biodegradation of VOC takes place in the dissolved phase as a consequence of the metabolism of micro-organisms. The rate of degradation depends on the redox conditions in the subsurface. Aerobic degradation isn't possible for PCE. TCE, DCE and VC can degrade aerobically. VC by oxidative and co-metabolic dechlorination. The latter process is also applicable to TCE and DCE.

With oxidative dechlorination bacteria use the VOC as electron donor and use oxygen as acceptor. In co-metabolic dechlorination, bacteria, that grow on methane, ethane, butane and propane and use them as electron donor, use TCE, DCE or VC as an electron acceptor. This is

also the case with the anaerobic reductive dechlorination, where the VOC is also the (intermediate) electron acceptor. The degradation constant for the different processes, for the VOC that are of interest in this thesis, are given below (Table 0-2). [12]

| [14] | Tetrachloroethylene | Trichloroethylene | Cis-1,2-dichloroethylene | Vinyl chloride |
|---------------------------------|---------------------|-------------------|--------------------------|----------------|
| O₂ | - | - | - | 0.087 |
| Co-metabolic | - | 0.948 | 0.885 | 1.73 |
| Reductive Dechlorination | 0.010 | 0.003 | 0.002 | 0.003 |

Table 0-2 Degradation coefficients of VOC's (d⁻¹) under different conditions

VOC sequential degradation

The reaction product in the PCE, or TCE, or DCE degradation reaction is the next VOC in the degradation chain as pictured below (Figure 0-1).

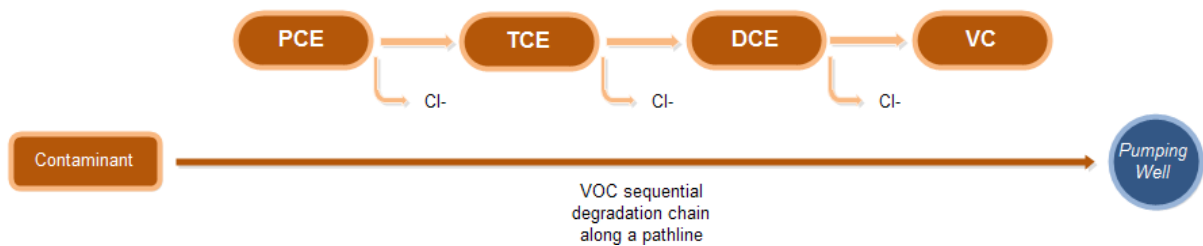


Figure 0-1 Sequential degradation of chlorinated solvents

Appendix B: ATEs systems (Utrecht)

| Location | Number of wells | Depth (m - NAP) | X | Y | Permitted quantity of water to be pumped (m ³ /u) |
|----------------------------|-----------------|----------------------------|--------|--------|--|
| Fire department Utrecht | 1 | -28 tot -33 en -47 tot -55 | 132365 | 456730 | 15 |
| Cap Gemini | 2 | -20 tot -60 | 134550 | 453100 | 120 |
| Cendris | 2 | -19 tot -39 | 131800 | 458100 | 65 |
| Centraal College | 1 | -25 tot -30 en -39 tot -44 | 137530 | 454960 | 20 |
| Corio | 3 | -20 tot -40 | 136250 | 456050 | 270 |
| Creative Valley | 1 | -26 tot -36 en -45 tot -54 | 133720 | 453835 | 25 |
| Daimler Chrysler | 1 | -20 tot -60 | 133700 | 453130 | 135 |
| Danone | 3 | -20,5 tot -47,5 | 140500 | 455700 | 240 |
| Diakonessenhuis | 1 | -22,5 tot -52,5 | 138000 | 454800 | 110 |
| Ekris | 1 | -25 tot -45 | 131550 | 458300 | 14 |
| Fortis | 6 | -18 tot -45 | 139000 | 456200 | 250 |
| Hoogstraat | 1 | -18 tot -26 en -45 tot -53 | 138480 | 455500 | 20 |
| HTS | 1 | -13 tot -23 en -30 tot -38 | 135795 | 457065 | 40 |
| Huize Transwijk | 1 | -30 tot -60 | 135350 | 454035 | 54 |
| Jaarbeurs | 11 | -15 tot -50 | 135600 | 455300 | 1700 |
| Office location Rijsweerd | 2 | -28 tot -48 | 138600 | 455850 | 180 |
| KPN Papendorp | 1 | -25 tot -50 | 133580 | 453500 | 100 |
| Kromhout Kazerne | 6 | -18 tot -48 | 138755 | 454790 | 456 |
| Kropman | 1 | -26 tot -50 | 133984 | 453130 | 15 |
| Marnix Academie | 1 | -19 tot -34 | 137600 | 457300 | 38 |
| Mesos Medisch Centrum | 3 | -20 tot -40 | 132375 | 457280 | 340 |
| Msolutions | 1 | -20 tot -50 | 133880 | 453550 | 20 |
| Nieuw Welgelegen | 3 | -13 tot -23 en -43 tot -53 | 135270 | 454790 | 45 |
| OPG | 2 | -20 tot -40 | 132715 | 457190 | 160 |
| Police station Kroonstraat | 3 | -11 tot -47 | 136140 | 456300 | 180 |
| Provincial Office | 1 | -15 tot -35 | 138700 | 456100 | 60 |
| Rabobank | 5 | -20 tot -47 | 135950 | 455350 | 350 |
| Red Swan | 3 | -19 tot -39 | 133400 | 458500 | 99 |
| Sportpark Zuilen | 1 | -20 tot -30 | 132950 | 459395 | 26 |
| Triple Q | 1 | -25 tot -60 | 134030 | 453050 | 50 |
| University Medical Center | 4 | -15 tot -50 | 140800 | 455500 | 300 |
| University Medical Center | 3 | -16 tot -40 | 140800 | 455700 | 260 |
| Utrecht University | 4 | -20 tot -50 | 139800 | 455500 | 340 |
| Nursing home Terwijde | 1 | -20 tot -28 en -40 tot -48 | 132161 | 456940 | 15 |
| Wartburg | 1 | -34 tot -59 | 134380 | 454750 | 25 |
| Westraven | 2 | -19 tot -54 | 135440 | 452300 | 170 |

Table 0-1 Location of ATEs systems (Arcadis)

| X | Y | Flow rate (m ³ /d) | Top | Bottom |
|----------|----------|-------------------------------|---------|---------|
| 145550 | 455687.5 | -155.64 | 1.72 | -8.75 |
| 144850 | 455887.5 | -153.86 | 1.61 | -8.69 |
| 142150 | 460250 | -201.97 | 1 | -11.26 |
| 137187.5 | 456987.5 | -887.08 | -14.28 | -42.24 |
| 134537.5 | 457037.5 | -543.51 | -2.02 | -13.4 |
| 145350 | 456687.5 | -11535.2 | -37.35 | -100.33 |
| 143450 | 460350 | -2834.99 | -18.36 | -120.26 |
| 142650 | 458387.5 | -13045.9 | -52.32 | -104.42 |
| 141550 | 452350 | -6836.88 | -63.3 | -153 |
| 137887.5 | 459987.5 | -17270 | -57.54 | -146.94 |
| 137187.5 | 446350 | -12191.1 | -76.97 | -139.87 |
| 136287.5 | 448850 | -126.41 | -83 | -136.01 |
| 133350 | 447450 | -6350.85 | -63.12 | -104.02 |
| 131250 | 457487.5 | -10347.4 | -67.26 | -157.46 |
| 129850 | 455187.5 | -4384.72 | -87.94 | -126.71 |
| 138650 | 450650 | -305.1 | -72.46 | -113.56 |
| 142450 | 452650 | -162.28 | -131.39 | -154.89 |
| 142350 | 452650 | -2514.49 | -66.69 | -124.49 |
| 138850 | 456987.5 | -57.92 | -53.39 | -92.19 |
| 137537.5 | 457087.5 | 6.89 | -50.5 | -87.37 |
| 137487.5 | 457087.5 | -42.3 | -53.39 | -89.36 |
| 135087.5 | 449750 | -159.56 | -61.61 | -130.41 |
| 133450 | 458087.5 | -123.31 | -62.85 | -98.64 |
| 132750 | 459087.5 | -108.38 | -62.03 | -96.83 |
| 132250 | 458087.5 | -748.92 | -57.74 | -156.94 |
| 131650 | 460075 | -194.18 | -56.37 | -87.67 |

Table 0-2 Industrial extractions (Deltares)

| X | Y | Flow rate (m ³ /d) | Top | Bottom |
|----------|----------|-------------------------------|--------|--------|
| 143650 | 456037.5 | 1086.85 | -18.1 | -97.11 |
| 143550 | 455987.5 | -1087.9 | -17.43 | -96.67 |
| 141650 | 447550 | 1610.73 | -18.18 | -51.45 |
| 141550 | 447550 | -1611.55 | -17.79 | -51.39 |
| 140850 | 455687.5 | 1529.23 | -13.7 | -41.57 |
| 140750 | 455687.5 | -1531.18 | -13.08 | -96.57 |
| 140850 | 455487.5 | 4170.59 | -0.97 | -43.23 |
| 140750 | 455487.5 | -4172.35 | -1.19 | -43.45 |
| 138750 | 456087.5 | 199.64 | -0.11 | -35.59 |
| 138650 | 456087.5 | -200.03 | 0.03 | -35.65 |
| 135937.5 | 453887.5 | 2722.06 | -17.5 | -48.98 |
| 135887.5 | 453887.5 | -2731.78 | -17.42 | -48.8 |
| 135637.5 | 455287.5 | 1162.97 | -0.32 | -47.25 |
| 135587.5 | 455287.5 | -1168.61 | -0.3 | -47.22 |
| 134587.5 | 453087.5 | 1498.77 | -18.04 | -47.06 |
| 134537.5 | 453087.5 | -1500.28 | -17.96 | -47.23 |
| 133750 | 453137.5 | 682.55 | -19.02 | -51.27 |
| 133650 | 453137.5 | -683.58 | -19.51 | -51.49 |
| 131850 | 458087.5 | 542.8 | -3.18 | -45.19 |
| 131750 | 458087.5 | -542.8 | -3.85 | -45.81 |
| 131750 | 453787.5 | 420.05 | -4.27 | -55.45 |
| 131650 | 453787.5 | -420.35 | -3.91 | -55.81 |
| 136587.5 | 455537.5 | 34.27 | -11.14 | -35.22 |
| 136537.5 | 455537.5 | -34.27 | -11.36 | -35.83 |

Table 0-3 ATES systems continuous throughout the year (Deltares)

| X | Y | Flow rate (m ³ /d) | | Top | Bottom |
|----------|----------|-------------------------------|--------|--------|--------|
| | | summer | winter | | |
| 136062.5 | 456312.5 | 356 | -356 | -0.53 | -39.17 |
| 136112.5 | 456312.5 | 356 | -356 | -0.55 | -38.64 |
| 136137.5 | 456312.5 | 356 | -356 | -0.48 | -38.35 |
| 136162.5 | 456312.5 | 356 | -356 | -0.49 | -38.08 |
| 136087.5 | 456237.5 | -356 | 356 | -0.59 | -39.08 |
| 136112.5 | 456237.5 | -356 | 356 | -0.69 | -38.85 |
| 136137.5 | 456212.5 | -356 | 356 | -0.82 | -39 |
| 136162.5 | 456212.5 | -356 | 356 | -0.8 | -38.91 |
| 136287.5 | 456087.5 | -1972.6 | 1972.6 | -13.26 | -39.53 |
| 136287.5 | 456062.5 | -986.3 | 986.3 | -13.07 | -39.39 |
| 136362.5 | 455912.5 | 986.3 | -986.3 | -13.2 | -40.78 |
| 136387.5 | 455912.5 | 986.3 | -986.3 | -13.29 | -40.71 |
| 136362.5 | 455887.5 | 986.3 | -986.3 | -13.19 | -40.81 |
| 135987.5 | 455487.5 | 816 | -816 | -15.13 | -43.58 |
| 136012.5 | 455462.5 | 816 | -816 | -15.06 | -43.34 |
| 135862.5 | 455387.5 | -1632 | 1632 | -16 | -47.34 |
| 136062.5 | 455387.5 | -816 | 816 | -14.69 | -42.12 |
| 136062.5 | 455362.5 | -816 | 816 | -14.85 | -42.39 |
| 135912.5 | 455287.5 | 816 | -816 | -16.29 | -47.22 |
| 135912.5 | 455262.5 | 816 | -816 | -16.31 | -47.26 |
| 136137.5 | 455262.5 | -816 | 816 | -14.26 | -42.11 |
| 135987.5 | 455162.5 | 816 | -816 | -16.1 | -45.52 |

Table 0-4 ATES systems that have different flow rates in summer and winter (Deltares)

Appendix C: Exceedance of intervention values.

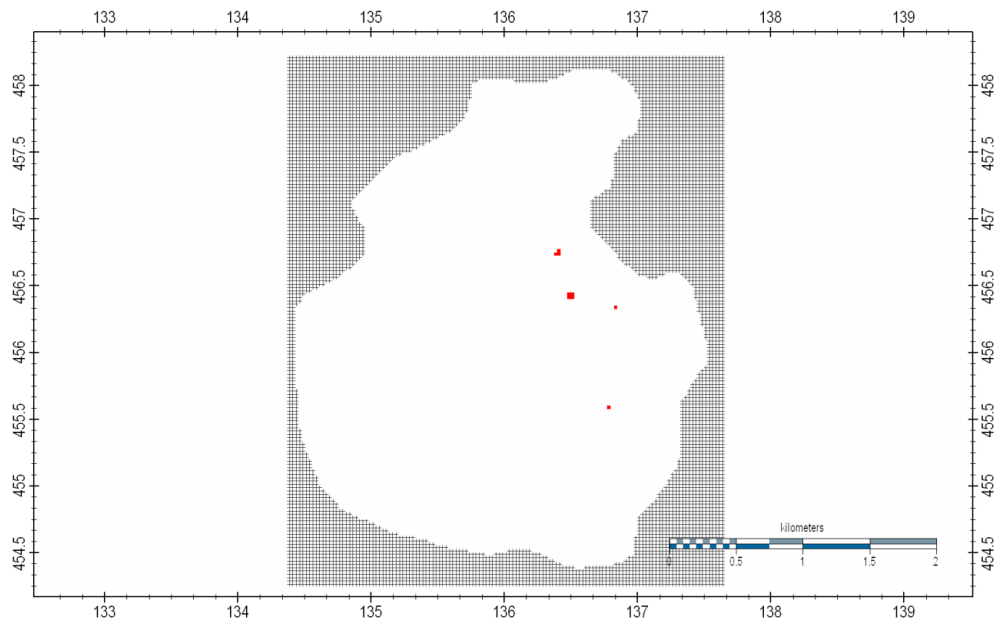


Figure 0-1 Location where the concentrations of PCE is higher than the intervention value in 2018 until 2258

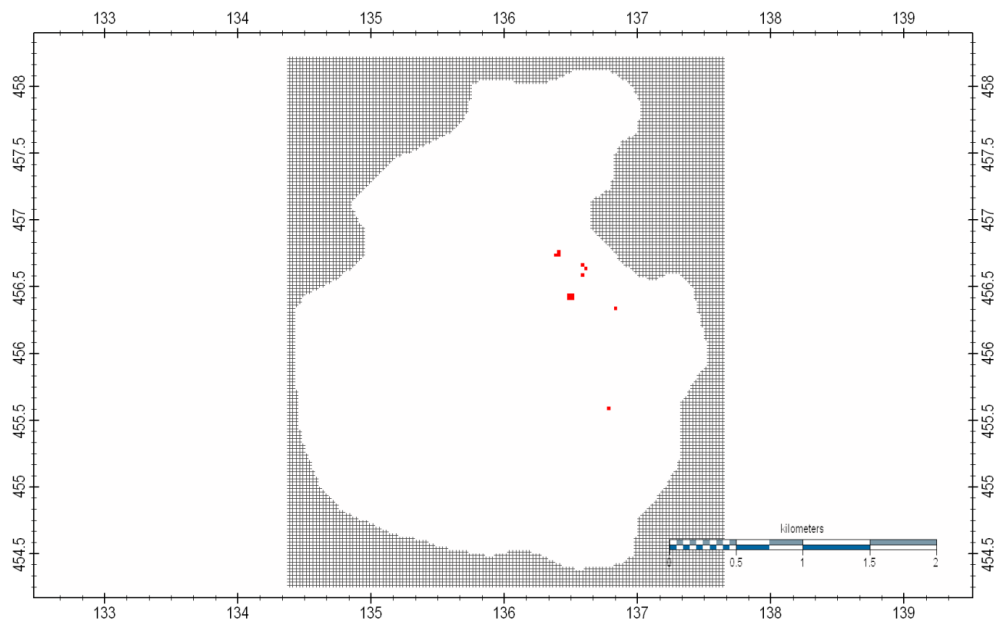


Figure 0-2 Location where the concentrations of TCE is higher than the intervention value in 2018

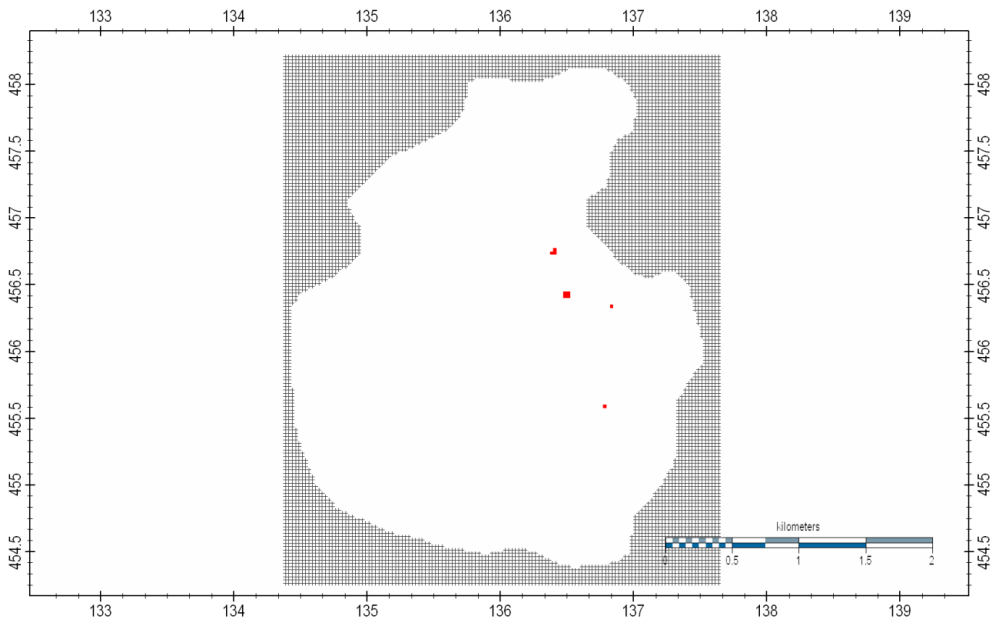


Figure 0-3 Location where the concentrations of TCE is higher than the intervention value in 2038 until 2258

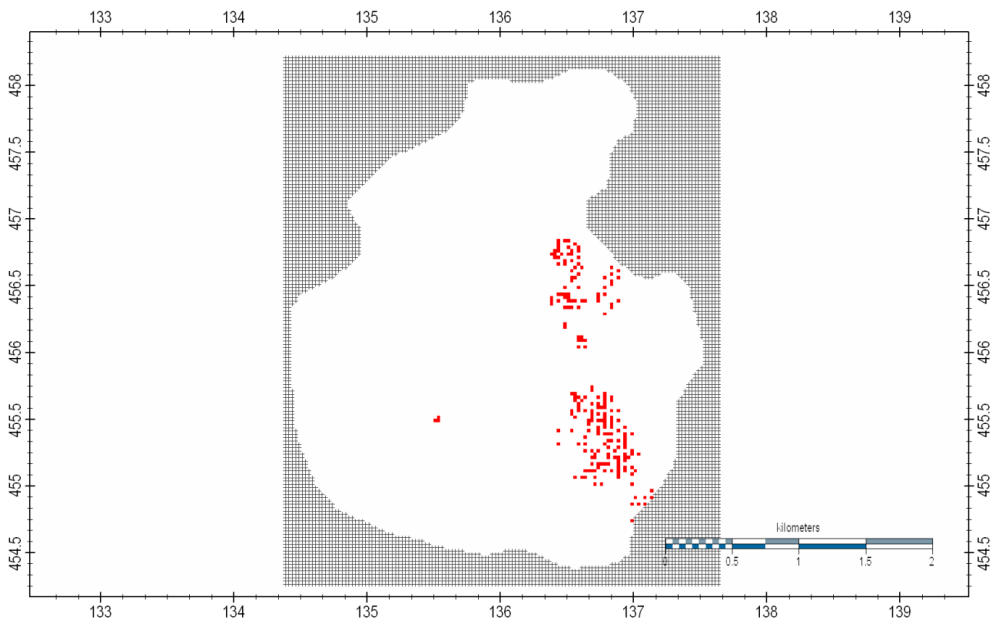


Figure 0-4 Location where the concentrations of DCE is higher than the intervention value in 2018

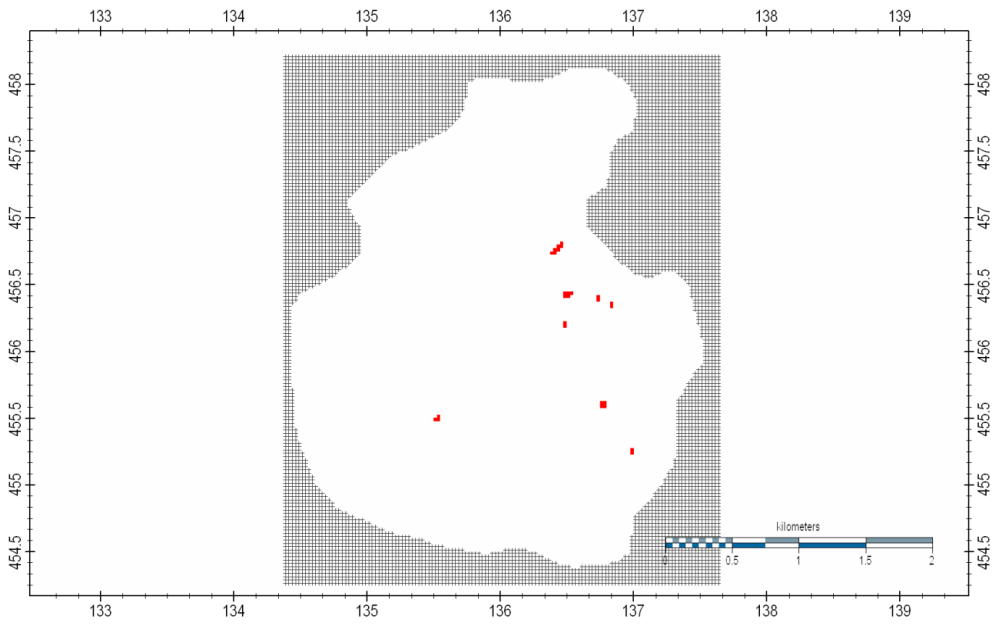


Figure 0-5 Location where the concentrations of DCE is higher than the intervention value in 2038 until 2258

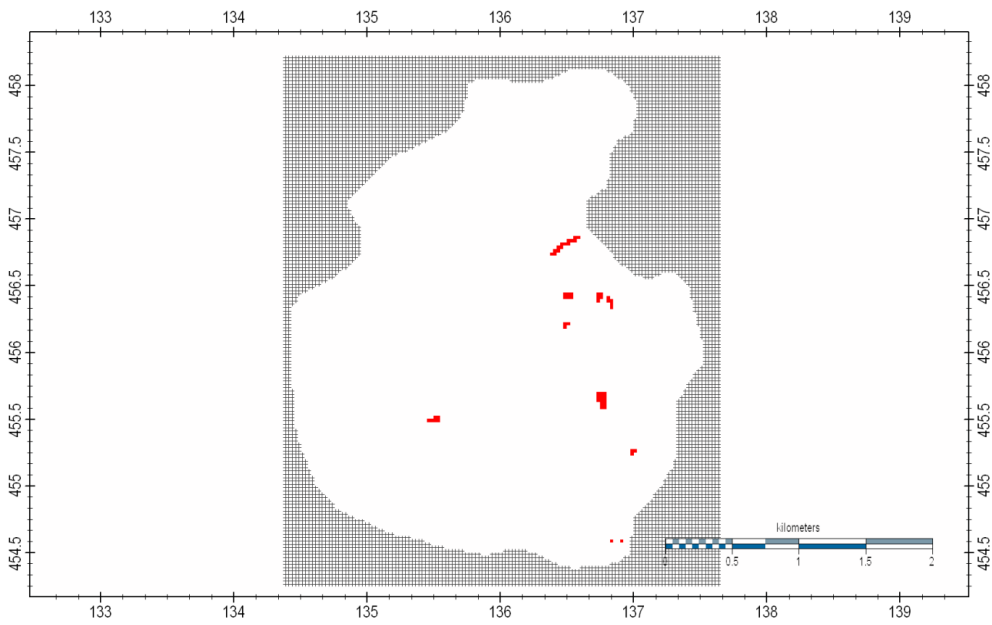


Figure 0-6 Location where the concentrations of VC is higher than the intervention value in 2208 until 2258