Technology models

Generic guideline

Target audience: Scientists, Consultancies & authorities

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Project website address: aquarehab.vito.be

Abbreviations

GRI	groundwater river interaction zone
CAH	chlorinated aliphatic hydrocarbon
DSS	decision support system
TCA	tri-chloro-ethane
TCE	tri-chloro-ethene
DCE	di-chloro-ethene
VC	vinyl chloride
VOC	volatile organic compounds
MCM	mixing cell model
TVOC	total volatile organic compounds
DOC	dissolved organic carbon
TIC	total inorganic carbon
BGU	Ben Gurion University

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1 Introduction

Technology models are reactive transport models that allow the user to simulate (1) the fate of chemicals in the subsurface and (2) the effect of an in-situ technology for groundwater remediation. In the Aquarehab project, models were developed for technologies related to (i) smart carriers, (ii) reactive barriers, (iii) injectable micro-scale Fe, (iv) groundwater-river interaction zones, and (v) wetlands.

This document describes generic guidelines for setting up, evaluating and upscaling of field scale reactive transport models for a number of innovative remediation technologies.

- The first chapter describes the general information with regard to technology models, i.e., development stage, applicability, input requirements, costs associated to licenses and the setup of a model, and availability of the model.
- The following chapters illustrates approaches using example cases to setup a technology model, i.e., the conceptual model, model calibration and evaluation, reaction networks, hydrologic models, reactive transport models. Furthermore attention is paid to evaluate and extract parsimonious model structures from more complex models, for use in river basin or groundwater management.

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2 Fact sheets technology models

2.1 Technology models

The effectiveness of groundwater remediation technologies depend on numerous processes such as advection with groundwater flow, dispersion, reactions and transformations in the subsurface.

Technology models are reactive transport models that can be used:

- to model the impacts of remediation technologies on water quality at the field scale,
- to design innovative remediation technologies, and
- to upscale the model results to the management scale for a groundwater body or river catchment.

2.2 Development stage

The development stage of the model is defined as to what extent the model is explored, tested and evaluated with measurement data, and to what extent it can be used in a management context. We call a model:

- **Emerging** : model, evaluated with data from lab or pilot experiments
- **Transferable** : model, evaluated with field data
- **Available** : model, evaluated with field data from multiple sites and available for practical applications (simplified version available)

The acceptability of the model is defined as to what extent a field evaluation is performed:

- **Moderate** : field evaluation is lacking, new data need to be collected for process understanding
- **Good** : field evaluation on 1 site, more data need to be collected for robustness checking
- **High** : field evaluation on more than 1 site

Table 1: Development stage of technology models

Technology Model	Code used	Model development stage	Model acceptability
Drainflow	MCM	Available	Good
Smart carriers (pilot)	Hydrus-1D	Emerging	Moderate
Reactive (multi)barriers	MIN3P/PHAST	Available	High
Injectable iron	PHREEQC MNM-1D	Emerging	Moderate
Groundwater-river interaction zone	HP1	Transferable	Good
Wetlands	FEFLOW	Available	High

Drainflow refers to a specific problem investigated in Aquarehab for a set of drainage ditches draining contaminated (process) water from a site in a dry area. The MCM model used for this purpose allows to attribute water to certain source zones in the area and to explain water flow based on chemical composition of the drainage water. The model is available and is evaluated for a specific site in Israel, but can be applied to other cases where chemical composition data in the drains or rivers and groundwater are available. The model for smart carriers is only applied to a pilot case study. It is considered emerging since data on the performance of the technology itself are emerging and scarce.

For **reactive (multi)barriers**, reactive transport models are capable to simulate contaminant degradation and the key processes needed to predict the long term efficiency of the technology are available. Nevertheless, these models are characterized by an elevated number of model parameters and require an extensive amount of field and lab data. For column-scale geochemical modelling PHAST and MIN3P models may be used. These models simulate kinetic reactions (such as contaminant degradation) and equilibrium reactions (such as carbonate equilibriums in groundwater). Compared to PHAST, MIN3P has a rigorous numerical implementation and is more efficient. The use of these models in full scale applications is limited by the long runtimes and the need of a detailed measurement campaign, which includes the measurements of geochemical species (such as TIC, Ca^{2+}, pH and oxygen). At field scale RT3D may be used, which neglects geochemical processes. In most of the PRB sites is likely that monitoring data are available for the first period of barrier operation and neglecting the geochemical deactivation of the reactive material might be a reasonable simplification. For long term predictions the medium deactivation must be taken into account, for example modelling with a geochemical model only the portion of the site that includes the barrier. For technology applications using injection of iron, the same reaction network as for the reactive barriers is developed in PHREEQC, but a coupling with particle transport is lacking at this stage. Therefore, the technology model is considered to be emerging and further data need to be collected for field evaluation.

Wetlands can be modelled using codes that simulate groundwater flow and solute transport in 2 or 3 dimensions, such as FeFlow. FeFlow is a finite element code that allows for a flexible grid setup including irregular river boundaries. FeFlow simulates 2D variable-saturated steady-state flow and multi-species transport, and includes redox-zone dependent sequential first-order degradation of agrochemical compounds and metabolites. FeFlow has been evaluated on a number of wetlands in the Odense catchment and is considered to be available.

Models that simulate CAH removal in groundwater-river interaction zones are well established for simulating transformations under lab and pilot tests, and are considered to be transferable. The HP1 code e.g. allows to easily implement a sequence of zones where reaction rates change along a groundwater-river flow path. The model has been evaluated at one site in Belgium. The number of suitable sites to evaluate the model performance is small and further evaluation is necessary.

2.3 Applicability

The applicability of a model refers to the suitability of the field model to perform an impact assessment of a technology for specific substances. The following classification is used:

- **Low**: the model can be applied only to a limited extent for the specific substance since the technology is emerging, field data are lacking and process understanding is limited
- **Moderate**: the model can be applied moderately for the specific substances since process understanding is good, but field data are scarce
- **Good**: the model can be applied well for the specific substances since process understanding is good and field data are available
- **High**: the model can be applied to a great extent for the specific substances since process understanding is high and field data are available in detail

The critical success factors that determine the applicability of the model, are related to the model parameters that show the largest influence on the model output and are shown in Table 2. The substances listed are the ones that were modelled in the Aquarehab project.

Table 2: Applicability of technology models and critical success factors

Technology Model	Applicability	Substances	Critical success factors
Drainflow	Good	Mixture of substances	Chemical composition groundwater
Smart carriers (pilot)	Low	Pesticides	Degradation rate constants
Reactive (multi)barriers	High	CAHs, BTEX, nitrate	Degradation rate constants, corrosion parameters (Fe)
Injectable iron (pilot)	Moderate	CAHs	particle transport, rate constants, corrosion (Fe), reactivity (Fe)
Groundwater-river interaction zone	Good	CAHs	Degradation rate constants, hydrological conditions
Wetlands	Good	Nitrate, pesticides	Degradation Rate constants, extent of flooded area, presence of peat layers, flow residence time

The drainflow model can be applied to assess the sources and pathways of a mixture of chemicals when information on chemical composition of groundwater (inorganic constituents) is available. For the other technologies, in general site specific degradation constants are needed to model their performance. For the technologies related to Fe, the corrosion rates of the iron are very important to estimate the lifetime of the technology.

2.4 MODELLING COSTS

Estimated costs related to the modelling, are license costs (if any), operational cost (range) to setup a model for a given site given all criteria for applicability are fulfilled, and maintenance costs (updates). Costs associated to the technology models developed in Aquarehab, are shown in Table 3.

Table 3: Expected costs of modelling for various technologies

Technology Model	Costs	Explanation
Drainflow	License: free	MCM is available from the developers at BGU
Smart carrier (pilot)	License: free Setup: ~1 personmonth for a pilot case	Hydrus-1D is freely available
Reactive (multi)barriers	License: free PHAST MIN3P License fee: VISUAL MODFLOW 1,600-5,500 US$ Setup: ~1-3 personmonths	PHAST is freely available MIN3P is not freely downloadable and the model executable must be asked directly to the developer (Prof. Uli Mayer) Graphical interface require a license (e.g. VISUAL MODFLOW) or can be freely available (e.g. Model Muse, USGS). Depending on the level of complexity of the (multi)barrier site a skilled person might be hired to analyze the available data and prepare and calibrate a model able to perform predictions.
Injectable iron	License: free PHREEQC Setup: 1~3 personmonths MNM1D (Tosco et al., 2010)	PHREEQC is freely available and downloadable MNM1D is available upon request
Groundwater-river interaction zone	License: free HP1 PHREEQC Setup: ~1-3 personmonths	The model code of HP1 and PHREEQC is freely available. As such, the setup of a GRI model is solely determined by capital costs. A rule of thumb is 50:50 – model setup:model run. Maintenance costs are not included in the estimated range. These could amount to 20-50% of the former depending on the eventual added complexity or reporting requirements.
Wetlands	License: FeFlow ~7.000 Euros Setup: ~1-6 personmonths	License estimate is for Feflow (www.dhigroup.com) Setup includes (a) setting up the model (1 month), calibration (1-2 month), and running/validating the model (1-2 month). Model runs take on average a few days on a new PC. These are minimum requirements.

2.5 INPUT AND OUTPUT (I/O)

Required input and output of the technology models are shown in Table 4.

Table 4: Input /output of technology models

Technology Model	Code used	Model input	Model output
Drainflow	MCM	Hydraulic parameters Chemical composition	Mixing regime Source tracking
Smart carrier	Hydrus 1D	Soil hydraulic properties, first order degradation	Evolution of contaminant concentrations in drain (conc vs distance) and in outflow (conc time series)
Reactive (multi)barriers	Column scale: PHAST/MIN3P Field scale: RT3D	Topography information and soil information, groundwater flow field, contaminant and inorganic concentrations, degradation rates, corrosion rates,	Evolution of contaminant plume and predictions of the remediation efficiency of the reactive barrier.
Injectable iron	PHREEQC	Fe corrosion rates, thermodynamic constants, contaminant concentrations, degradation rates	Degradation of contaminants , corrosion of Fe
Groundwater-river interaction zone	HP1	Soil hydraulic properties and parameters Solute transport definitions and parameters Hydraulic and solute boundary conditions	Water flow and solute transport in the modelled flow path in time
Wetlands	Feflow	Hydrogeological parameters Flooding conditions or hydroperiods Rate parameters and redox zonation	Flow distribution and residence time Plume migration Water and mass budgets

2.6 Availability of the technology models

Table 5 gives information related to the availability of the codes used for the AQUAREHAB technology models. Example input files for the various technologies may be made available upon request by the authors via the AQUAREHAB website (aquarehab.vito.be), however taking confidentiality of the data into account.

Table 5: Availability of technology models

Technology Model	**Code used**	**Code availability**	**Link**
Drainflow	MCM	Free	http://aquarehab.vito.be
Smart carriers (pilot)	Hydrus-1D	Free	http://www.pc-progress.com/en/Default.aspx?hydrus-1d
Reactive (multi)barriers	MIN3P/PHAST	Free	http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/ http://water.usgs.gov/nrp/gwsoftware/ModelMuse/ModelMuse.html http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/ http://bioprocess.pnnl.gov/rt3d.downloads.htm
Injectable iron	PHREEQC MNM-1D	Free	http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/ Tosco T. et al., 2010
Groundwater-river interaction zone	HP1	Free	http://www.pc-progress.com/en/Default.aspx?hydrus-1d
Wetlands	FEFLOW	Commercial	http://www.feflow.info/

2.7 Generic character of the technology models

The codes used in developing the technology models contain generic descriptions of the reactive transport process of a contaminant plume that can be used in multiple applications. The table below illustrates the algorithms used to describe the reactive transport process and to what type of technology they can be applied. E.g. a degradation process can be described using a first-order decay algorithm, which is implemented in various codes (e.g. Hydrus-1D, HP1, Feflow, RT3D, …), and is applicable for a number of technologies (e.g. wetland, groundwater-river interaction zone, smart carrier in drain).

Table 6: Characteristics of the AQUAREHAB technology models.

Process	Algorithm	Available in code	Applicable technology	Demonstrated Aquarehab
Biological degradation	Single + sequential first order with temperature dependence	Almost all: Hydrus, HP1, FeFlow, MIN3P, PHAST, MODFLOW-RT3D	Wetland Reactive zone (multibarrier) Groundwater river interaction zone Smart carrier	FeFlow PHAST HP1 Hydrus-1D
Chemical degradation	Single first order	Almost all: Hydrus, HP1, FeFlow, MIN3P, PHAST, MODFLOW-RT3D	Reactive barrier	PHREEQC PHAST MIN3P
Iron corrosion	Linear Exponential	PHREEQC, PHAST, MIN3P	Zerovalent iron reactive barrier	PHREEQC, PHAST, MIN3P
Geochemistry	Aqueous speciation Sorption Precipitation	PHREEQC, PHAST, MIN3P	Zerovalent iron reactive barrier	PHREEQC, PHAST, MIN3P
Variably saturated flow	Richards' equation	Hydrus, HP1, MIN3P, FeFlow	Wetlands	FeFlow
Saturated flow	Darcy equation	MODFLOW, HP1, PHAST, MIN3P, FeFlow	Wetlands Reactive zone (multibarrier) Groundwater river interaction zone	FeFlow MODFLOW-RT3D HP1

3 SETUP OF A TECHNOLOGY MODEL

3.1 INTRODUCTION

The setup of a model for groundwater remediation is following the general principles of good modeling practice (Freeze and Cherry, 1979; Anderson and Woessner, 1992; Bedient et al., 1994). Prior to initiating a conceptual modeling process, the following questions must be answered:

- Is the model to be used for predictive purposes, research purposes, or screening/management purposes?
- What problem is to be solved using the model?
- Is modeling the most appropriate methodology for evaluating the problem?
- What degree of model sophistication is needed?
- What level of confidence is associated with the field data and results from the model?
- What are the benefits and costs of the modeling effort?

Responses to these questions will allow the modeler to determine the nature of the modeling effort and establish characteristics of the conceptual model. It is of no use to establish a sophisticated model when only a few aquifer parameters are available. If steady flow is adequate, then the expense of developing a transient model may be excessive. A conceptual model should take into account the outcome of the cost-benefit analysis of the modeling.

3.2 CONCEPTUAL MODEL

Two types of conceptual models can be distinguished: a field based conceptual model (conceptual site model) and a science based conceptual model (conceptual simulation model).

3.2.1 Conceptual site model

A conceptual site model provides a representation of the groundwater flow and transport system that exists under field conditions. The nature of the field based conceptual model defines the dimensionality of the groundwater model and the design of any discretization grid used in numerical models. Construction of a field based conceptual model starts with a thorough understanding of the geology and hydrology of the area to be modeled, heterogeneous nature of the aquifer, the anisotropic nature of the aquifer, whether or not flow occurs through fractures or porous sand or gravel, the nature of initial and boundary conditions, existing measurements, contours, location of receptors, buildings, pavements, source zones, historical information, … An example of a field based conceptual model is shown in Figure 1.

Example 1: Field based conceptual model for a TCE+TCA contaminated site

The aim was to delineate the plume and the source areas. In 2003-2005 an extensive monitoring campaign was performed. After 2005 the monitoring efforts were focused only on the green piezometers. A number of sources were delineated: Source 1 (TCA, TCE): 1967-1996, Source 2 (TCA, TCE): 1970-1992, Source 3 (TCE): 1965-1975, Source 4 (PCE,TCE): 1957-1994, Source 5 (TCA): 1966-1996. From the observations, it could be concluded that some important source zones were lacking. Source zone determination is critical for reactive transport modeling studies.

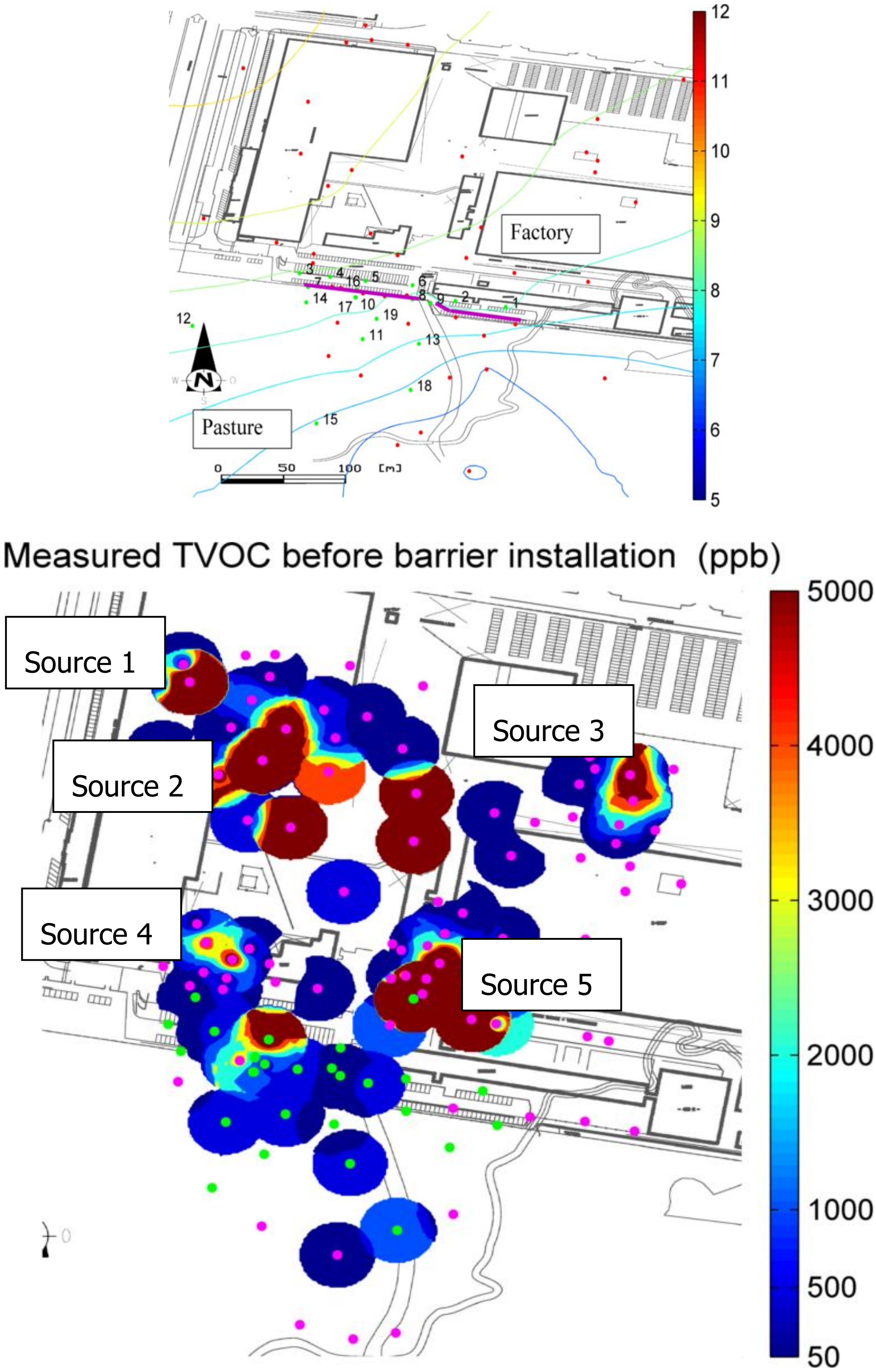


Figure 1: Conceptual site model for a TCE contaminated site

3.2.2 Conceptual simulation model

A conceptual simulation model is a model representation of the site, containing the model domain, the grid size, the boundary conditions, internal boundaries, aquifer heterogeneity and layering. An example of conceptual simulation models is given in Figure 2 for a TCE+TCA contaminated site and in Figure 3 for a wetland.

Example 2: Conceptual hydrological simulation model for TCE + TCA contaminated site

In this example the model is oriented 15° counter-clockwise with respect to the local coordinate system to keep the east and west boundaries perpendicular to the average head contours lines, such that these boundaries can be modelled as no flow boundary conditions. The north and south boundaries of the model were specified as general head boundaries. In the unpaved areas a groundwater recharge equal to the precipitation minus the evaporation was imposed. Finally, drain boundary conditions were imposed downstream in the pasture. These drains are necessary to close the water mass balance and are also supported by field inspections. The bigger drains at the end of the pasture (7 m wide by 1 m deep) carries water only for a part of the year and the measured water depth does not exceed 0.5 m. The other small drain in the middle of the unpaved area corresponds to an observed features of the site (a small canal at the right hand site of a road).

The model grid is refined where reactive transport was simulated, coinciding with the area where more measurements were collected and containing the iron reactive barrier. The yellow dots represent the locations of hydraulic conductivity estimations. In this case 127 hydraulic conductivities, 127 drainable porosity and 3 drain conductances were estimated on 420 groundwater measurements. More unknowns were estimated in the active transport area, where a refined description of hydraulic conductivity was required.

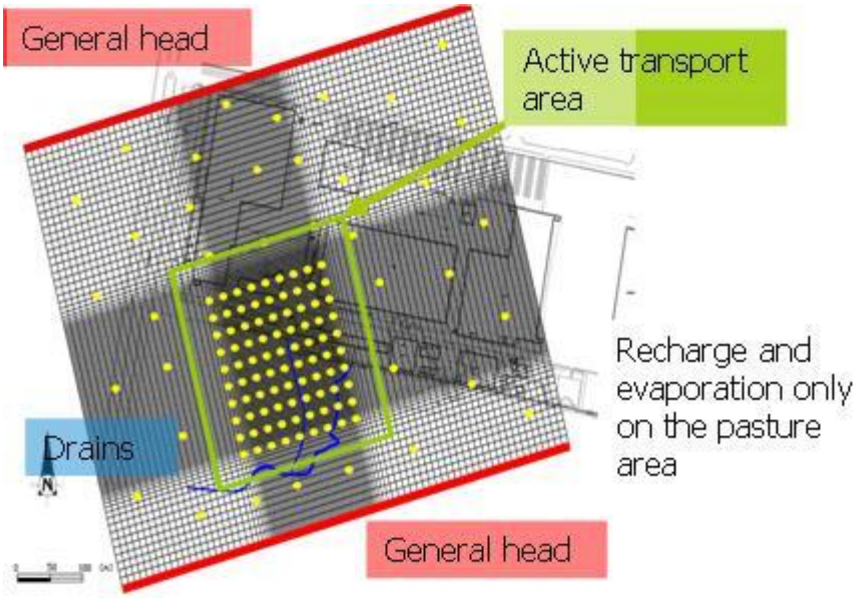


Figure 2: Conceptual hydrological model for a (multi) barrier site

Example 3: Conceptual hydrological model for a wetland

The riparian zone slopes gently from around 24.0 m at the river bank to approximately 25 m near the track separating the riparian zone from the nearby Christmas tree plantation and agricultural fields. Much of the area is flooded about 1/3 of the year due to river restoration. During periods with heavy rainfall the area is completely flooded. 51 shallow wells (10 cm screen depths from approx. 1.4 to 8 meters) have been installed manually and two deep wells were established with a 100 cm screens at depths of 15-16 and 17-18 meters, respectively. Geophysical explorations (Multi-Electrode Profiling) indicate that a (semi-permeable) clay layer is present about 10 m below land surface. Geologically the site can be described as consisting of two layers, an upper 1 m thick silty organic-rich layer and an approximately 9 m thick sand aquifer. The hydraulic conductivity of the sand aquifer is approximately K=10 m/day (at least in the top part of the aquifer). During summer time (with no flooding) the water table slopes gently from around 23.5 m near the river to about 24.75 m at the perimeter of the riparian zone. The wetland system is characterized by a distinct change in redox conditions 10-40 m into the wetland relative to the wetland perimeter. Here both oxygen and nitrate is found.

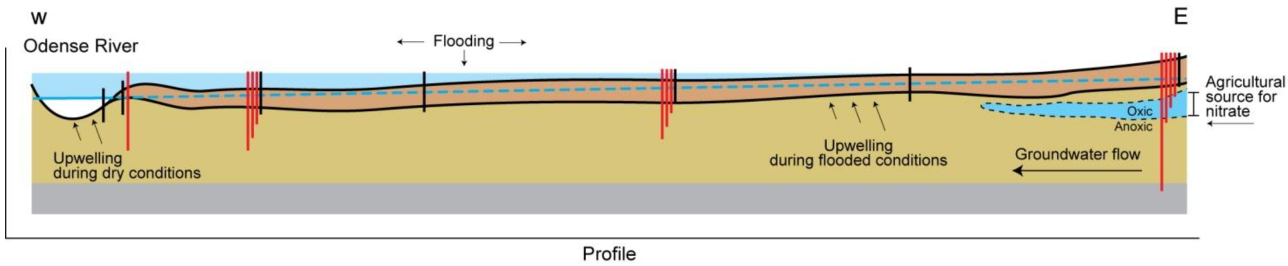


Figure 3: Conceptual model of a wetland field site. The section sketches basic observations from field investigations with a simple three layer model; an impermeable clay layer (grey), a sand aquifer (light brown) and an overlying peat layer (brown). Piezometers along the transect (black and red bars), flooding (light blue), hydraulic head (dashed blue line), oxic zone (dark blue) and source for diffuse nitrate from agriculture are shown as well.

3.3 HYDROLOGICAL MODEL

The first step in modeling contaminant transport is to calibrate the hydrological model for the site using data from observation wells. Site specific information about boundary conditions (constant head, variable head, atmospheric, flux), hydraulic conductivity, piezometry, meteorological conditions, recharge, use of geophysics to reveal spatial heterogeneity, all part of the conceptual site model, is implemented in the model to simulate groundwater flow.

<u>Example 4: Calibration of a hydrological model for TCE + TCA contaminated site</u>

The hydraulic parameters may be calibrated on groundwater head data. The result of such a calibration is summarized in Figure 4. In Figure 4(a) the cross plot of observed against simulated head shows a good match. The RMSE of the calibration step was 0.154 m, which was specified as the level of the measurement and structural noise. This good fit was achievable as a result of the flexible parameterization of the hydraulic conductivity (Figure 4(b)) and specific yield.

The simulated groundwater levels for several piezometers are shown in Figure 3. As can be seen, the piezometers located in a pasture area (V2PB305, V2PB402 and V2PB404) show larger fluctuations compared to the piezometer located in a paved area (V2PB104), due to the direct effect of precipitation on the pasture area. The model simulates fairly well the validation data (green asterisks) for the pasture piezometers whereas a worse match was obtained for the paved area piezometer.

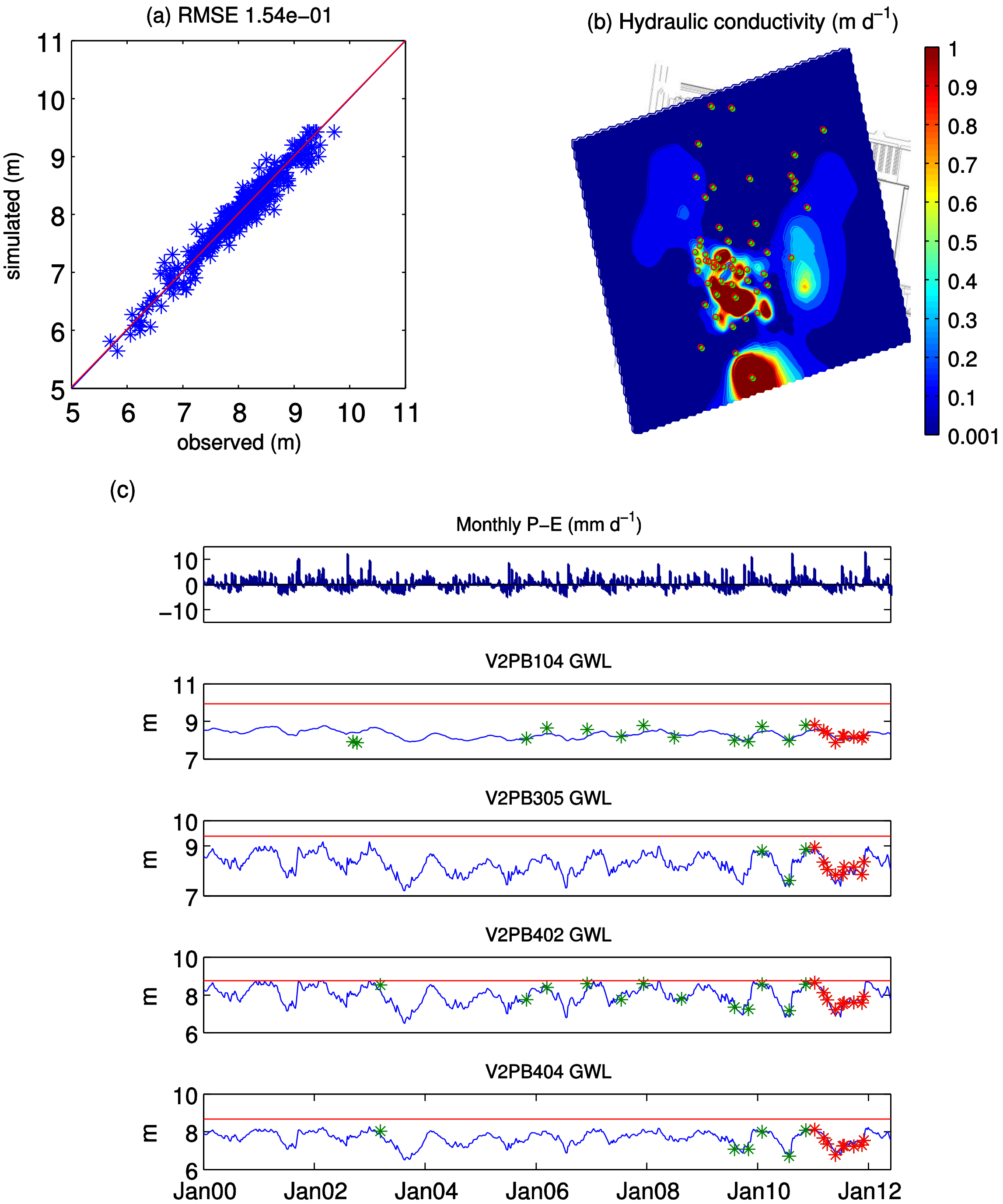


Figure 4: Flow model results. (a) Cross plot of observed against simulated groundwater levels. (b) Hydraulic conductivity field estimated on the groundwater level measurements. (c) Flow model results: simulated groundwater levels (solid blue line), measurements used to calibrate the model (red asterisks) and measurements used as validation dataset (green asterisks). The solid red line indicates the ground level in each piezometer.

3.4 Reaction network

An important step in field site modeling involves the setup of a reaction network containing the relevant chemical reactions (e.g. sorption, mineral precipitation, aqueous speciation) and biological transformations (e.g. degradation kinetics) in the system. A reaction network can be evaluated based on dedicated batch or column experiments in the lab.

Example 5: Reaction network setup for CAH removal in Fe-PRB + NA

For the (multi)barrier site each reactive zone has a particular reaction network. The reaction network setup must rely on literature information, data analysis and lab experiments. In this example case, a reactive zone consists of a 30 cm thick iron barrier (built with a mixture of 20% iron and 80 % sand in weight) and a natural attenuation zone represented by the pasture itself.
For the iron barrier the removal of CAH is assumed to proceed directly to ethene, with little formations of toxic intermediates (such as VC). As an example the PCE degradation by zero valent iron is here reported:

$$C_2Cl_4 + 3.61Fe^0 + 3.61H^+ \rightarrow 3.61Fe^{2+} + 0.13C_2HCl_3 + 0.87C_2H_4 + 3.61Cl^-$$

Similar stoichiometries are reported for TCE, cis-DCE and VC [*Arnold and Roberts*, 2000].

In the natural attenuation zone, biodegradation usually generates intermediates and ethane (non toxic byproduct) is produced only at the end of the degradation chain. The degradation chains might be quite complex and must be determined by the analysis of the available data. For this example, the biodegradation chain reported in Figure 5 was used. The choice was supported by literature studies [*Rifai et al.*; *Wiedemeier*, 1998] and by field data (area with high 1,1,1-TCA concentrations also shows high DCA, cis-DCE and VC concentrations).

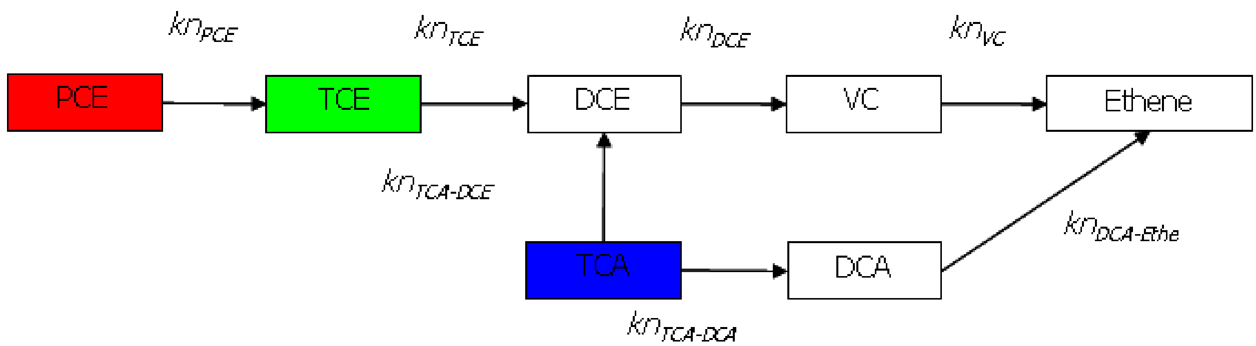


Figure 5: Biodegradation network in a natural attenuation zone

Besides the degradation network an appropriate rate model must be selected for each reaction. For the iron barrier a mixed order rate model was chosen [*Wüst et al.*, 1999]:

$$\frac{d[VOC]}{dt} = -k_{VOC} S \frac{[VOC]}{K_{1/2} + [VOC]} \qquad \textbf{Eq. 1}$$

where k_{VOC} is the rate coefficient of contaminant degradation per unit of iron reactive surface area (mol m^{-2} s^{-1}), S is the iron reactive surface area per unit water volume (m^2 L^{-1}), $K_{1/2}$ is the half-saturation constant (mol L^{-1}) and VOC is the contaminant concentration (mol L^{-1}) . In this model the reactive surface area S decreases as carbonate minerals precipitate into the barrier.

For the natural attenuation part a first order rate model was chosen to simulate the degradation of each compound of the chain.

$$\frac{d[VOC]}{dt} = -kn_{VOC}[VOC] \qquad \textbf{Eq. 2}$$

Where k_{VOC} is the rate coefficient of contaminant degradation by natural attenuation (also indicated in Figure 5).

Example 6: Reaction network setup for CAH removal in a GRI through aquifer biostimulation and removal in river sediment

The design of a remediation approach for a chlorinated solvent plume discharging to a river requires a good approximation of the reactions *in situ* by a numerical model that can simulate new boundary conditions. Therefore, the driving variables of the reactions should be included in the model code as much as possible. This requires intensive monitoring with lab-scale experiments. And a thorough correlation analysis of the results. The Monod kinetics with eventual limiting factors can describe microbial growth. But the parameters describing the maximal degradation rate and microbial growth are strongly correlated and, as such, difficult to determine. Furthermore, the assumed linear relationship between the degradation rate and microbial numbers can be questioned (Roling 2007). Therefore, the obtained data could be better simulated using less elaborate kinetics such as Michaelis-Menten or even first-order. These kinetics lump the driving variables to a larger extent and are less prone to the problem of 'equifinality' in model calibration. The setup of a reaction network should consider these three kinetics and evaluate the simulation results of lab-scale or monitoring data, taking into account the limitations of lumped kinetics for a scenario-analysis.

The mathematical model of the sequential first-order degradation for chlorinated ethenes is expressed as follows:

$$RATE_n = -k_n c_n + k_{n+1} c_{n+1} \qquad \textbf{Eq. 3}$$

with k_n [d^{-1}] the first-order degradation constant and c_n [µM] as the aqueous concentration of compound *n*, or of the parent compound *n+1*. Degradation rates for the Michaelis-Menten kinetics can be calculated by extending the first-order degradation constant with:

$$k_n = \frac{k_{max,n}}{\left(K_{s,n}\left(1+\frac{c_{n+1}}{I_{n+1}}+\frac{c_{n+2}}{I_{n+2}}\right)+c_n\right)} \qquad \textbf{Eq. 4}$$

with $k_{max,n}$ [µmol d^{-1}] as the maximum utilization rate, $K_{s,n}$ [µM] the half velocity constant of compound *n*, and c_n, c_{n+1}, $and\ c_{n+2}$ [µM] the aqueous concentration of compound *n* and its parent compounds, and I_{n+1} and I_{n+2} [µM] the competitive inhibition constants. The Monod kinetics include the cell numbers of dechlorinating species *x* as X_x [cells L^{-1}]. It requires an adaptation of the Michaelis-Menten kinetics by:

$$k_n = \frac{k_{max,n} X_x}{\left(K_{s,n}\left(1+\frac{c_{n+1}}{I_{n+1}}+\frac{c_{n+2}}{I_{n+2}}\right)+c_n\right)} \qquad \textbf{Eq. 5}$$

with $k_{max,n}$ [µmol cell^{-1} d^{-1}] as the species specific maximum utilization rate. Microbial growth is determined by equation (4) with Y_x [cells µmol^{-1}] as the yield coefficient and d_x [d^{-1}] as the decay rate of species *x*:

$$\frac{dX_x}{dt} = \sum(Y_x RATE_n) - X_x d_x \qquad \textbf{Eq. 6}$$

3.5 Reactive transport model

In a reactive transport model, the reaction network (3.4) is coupled to the hydrological model (3.3), simulating the transport of an aqueous component in the groundwater. Usually, computer codes that simulate reactive transport are available in the public or the commercial domain. Examples are FEFLOW (Diersch, 2005), PHAST (Parkhurst et al., 2004), MIN3P (Mayer et al., 2013), HP1 (Jacques and Šimůnek, 2005).

<u>Example 7: Reactive transport model for a wetland</u>

The wetland-aquifer systems have been modelled using a reactive transport model in FeFlow (Diersch, 2005). The model has the following main characteristics;

1. 2D variable-saturated steady-state flow and multi-species transport
2. Redox-zone dependent sequential first-order degradation of agrochemical compounds and metabolites

The sequential degradation model is formulated in the following manner, where it is assumed that denitrification occurs in steps; NO3->NO2->½N2, with each step governed by a first-order reaction;

$$\begin{aligned}
r_{NO3}(x,z) &= \frac{dC_{NO3}}{dt} = -k_{NO3}(x,z)C_{NO3} \\
r_{NO2}(x,z) &= \frac{dC_{NO2}}{dt} = +k_{NO3}(x,z)C_{NO3} - k_{NO2}C_{NO2} \\
r_{N2}(x,z) &= \frac{dC_{N2}}{dt} = +\tfrac{1}{2}k_{NO2}C_{NO2}
\end{aligned} \qquad \textbf{Eq. 7}$$

where k_i (i=NO_3 or NO_2) are the degradation rates that are allowed to vary in space (*x,z*).

<u>Example 8: Reactive transport model for CAH removal in Fe-PRB + NA</u>

In PHAST the chemical reactions are assumed not to be affected by the flow field. Therefore PHAST first solves the groundwater flow at each time step and then the advection-dispersion-reactions equations for each chemical species involved in the simulation. The user must specify the reaction network and the reaction rates in a separate .chem file. This file is divided in blocks, where each blocks begins with a PHREEQC keyword. The reaction rates are specified under the RATES keyword using BASIC statements. The stoichiometries are specified under the KINETIC keyword. For further details see the PHAST and PHREEQC user manual (section 6).

Unlike PHAST, MIN3P accounts for the effect of chemical reactions on the flow field, such as the decrease of porosity caused by mineral precipitation. In MIN3P the groundwater flow and the transport equations are solved simultaneously. As in PHAST the stoichiometry of the chemical reactions can be specified in a separate file. However, only a limited number of reaction rates are available, since they are hardly coded into the model. For further details about MIN3P features, ask prof Uli Mayer (section 6).

For field applications RT3D might be used. The model assumes the flow field not to be affected by chemical reactions and uses the flow field calculated by a preliminary MODFLOW simulation. By splitting the simulation in two parts the user can use the capabilities and the packages developed in MODFLOW to simulate the real groundwater flow dynamics.

In RT3D the reaction rates and stochiometries must be defined in a separate reaction module file. The module complies to fortran standards and is used by the model as a fortran subroutine. The module can be compiled as a dynamic linked library before being used by RT3D. Another option is to compile the module together with the whole source code, which also works under UNIX systems. The value of the rate coefficients are then read from the .rct file, which must be written accordingly to the defined module. For further details about the RT3D capabilities see the user manual (references are reported on section 6).

<u>Example 9: Reactive transport model for CAH removal in the groundwater-river interaction zone</u>

The CAH degradation in the sequence of aquifer and hyporheic zone can be explicitly simulated using the numerical model HP1 (Parkhurst & Appelo 1999; Jacques and Šimůnek 2005; Jacques et al. 2006; Šimůnek et al. 2006, 2008). It is a combination of Hydrus-1D that simulates flow and transport, and PHREEQC that simulates the reaction network. The graphical user interface (GUI) of Hydrus-1D allows an easy setup of physical variables in the modelled domain together with the applied boundary conditions. The reaction network is first elaborated in PHREEQC for microcosm experiments. The relevant keywords with the related input are subsequently transferred to Hydrus using the PHREEQC definitions in the GUI of Hydrus-1D. One should take care that the input in the geochemical model relates to the spatial discretization of the domain by Hydrus-1D. Therefore, it is advisable to define the relevant keywords for different regions in the modelled domain using the subkeyword '-material X' with X pointing to the material number that can be defined in the graphical editor of the GUI. HP1 uses the operator-splitting approach with no iterations during one time step (a non-iterative sequential modeling approach) to relate the reaction network to the solute transport defined in Hydrus-1D.

4 TECHNOLOGY MODEL EVALUATION

4.1 INTRODUCTION

Before a technology model can be used in scenario analysis or design calculations for field applications, its performance needs to be assessed by comparing modelled concentrations to measured concentrations at the field scale. This means that the calibrated model is used to predict groundwater concentrations for a time period different from the period for which the model is calibrated. In the following sections we present a number of technology models and how they were evaluated using field data (4.2) and how they can be used in designing the technology (4.3) for a specific field application.

4.2 TECHNOLOGY MODEL EVALUATION

Example 10: Field evaluation of the reactive transport model for CAH removal in Fe-PRB + NA

A calibrated flow field was used for the transport model. The simulations starts in June 2003 from the average pre-barrier concentration measurements. The model simulates the contaminants shown in Figure 1 (6 contaminants), the degradation of contaminants by the barrier and by natural attenuation and the sorption and release of contaminants from the sources areas (indicated in Figure 6(a) by numbers). The dispersion, degradation and source release parameters were calibrated on all concentration measurements available after the barrier installation (1956 measurements for the period 2005-2012). The results are summarized in Figure 6. In Figure 6(a) the average total contaminant concentration measured after the barrier installation is mapped with the inverse distance square method. The corresponding model results are reported in Figure 6(b). As can be seen from the simulation results, the total contaminant concentration in the source 1 remains too high compared to the measurements. The left part of the barrier (indicated with a purple line in Figure 6(a) and Figure 6(b)) is too much contaminated compared to the measurement map. The pollution in the pasture area is underestimated, even adding additional source of contamination (the fourth source of contamination in Figure 6(a)).

The transport model was able to reproduce the main direction of plume migration in the pasture and the effect of barrier installation on the piezometer close to the barrier. This can also be seen for the piezometer V2PB303 of the Figure 6(c). The underestimation of contaminant concentrations on the pasture area is evident for the piezometers V2PB404 and V2PB504.

The main difficulty encountered on the modelling of real concentrations was the quantification of the source release parameters and the exact localization sources, since little information was available from the historical records. This is a general and important limitation for all field modelling related to contaminated sites. To improve the model fit it a joint estimation of flow and transport parameters might be required.

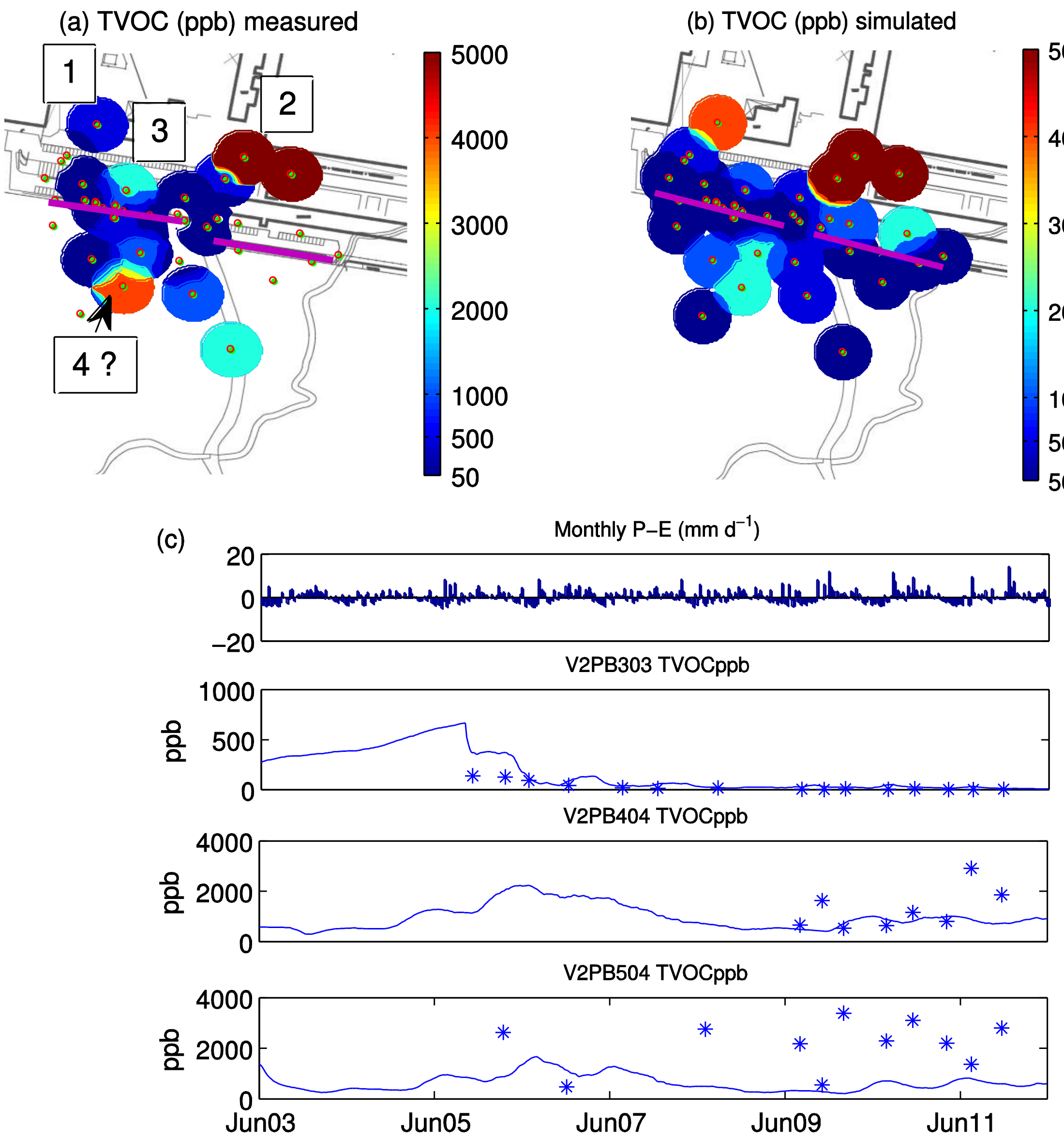


Figure 6: (a) Average total concentration measured after the barrier installation (2005-2012). (b) Average simulated total concentration, interpolated with the inverse distance square interpolation method as done for the measured concentrations. (c) Simulated concentrations (solid blue line) and measured concentrations (blue asterisks).

Example 11: Field evaluation of the reactive transport model for a wetland

The model was evaluated/calibrated based on the following field data;

- Hydraulic head data during dry and wet periods
- Presence/absence of nitrate
- Lab-derived denitrification rates

For example, Figure 7 shows two possible scenarios: (1) using only lab-derived parameters based on a zonation with four rates (with high rates in the peat layer and very low rate in the sand) and (2) calibrating the denitrification rate in the sand. Scenario 2 matches best the observations with a disappearance of nitrate between two set of wells (Figure 8). The lab-derived denitrification rates were in principle directly transferable to the field with the following remarks: (1) in the highly-reactive peat layer we have no observations of nitrate and will here assume that nitrate concentrations are zero. Thus, in the simulations the denitrification rates only needed to be so high as to remove nitrate quickly. This makes a one-to-one comparison with lab-derived rates difficult, only one can say that both lab- and model rates were high, (2) the rates were not determined more than about 1 m into the top of the sand aquifer. These were much lower than the rates in the peat. It is believed that this rate is still due to some DOC leaching/diffusing into the sand from the peat. Furthermore, it was hypothesised that the rest of the deeper sand essentially was inert (low rate). However, the simulation results indicate that some denitrification must occur in the deeper sand as well, and it is speculated that another denitrification process with pyrite maybe on-going.

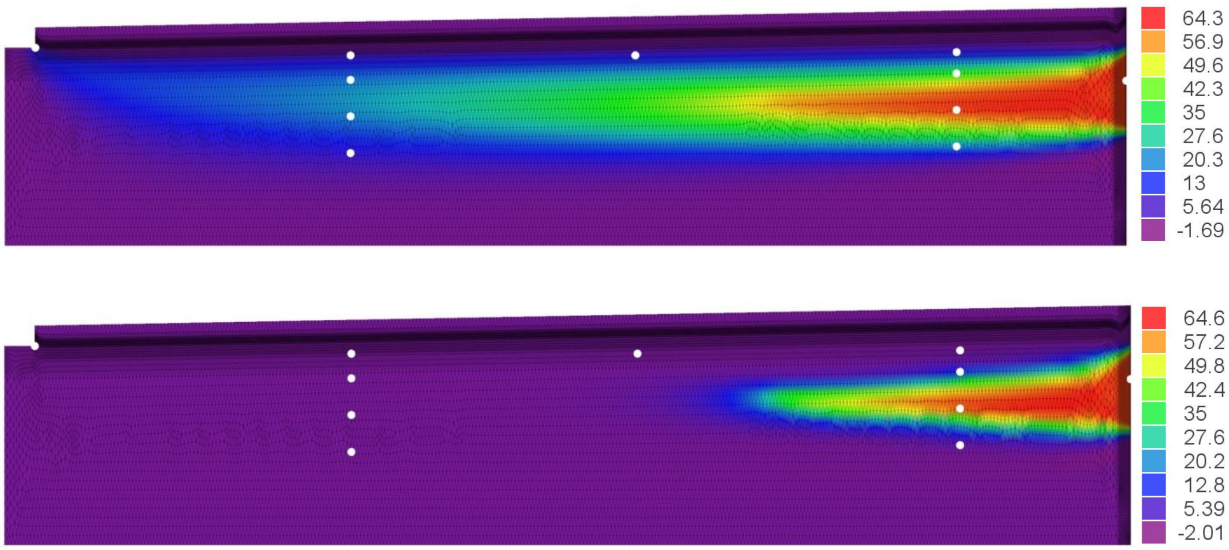


Figure 7: Feflow modelled scenario 1 (top) and 2 (bottom). Nitrate is in mg/L and the figure is with 3x vertical exaggeration. White circles are well screens.

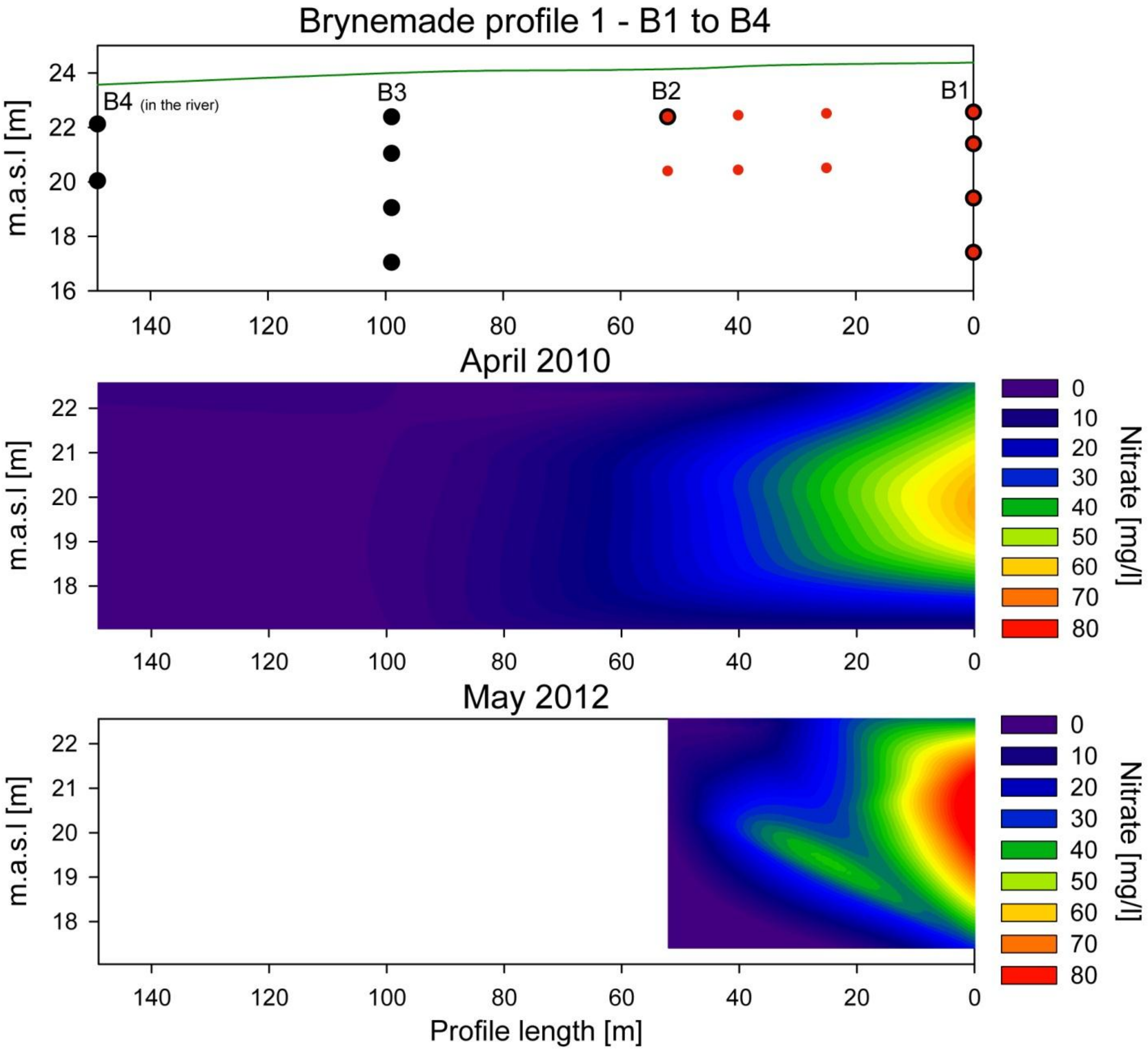


Figure 8: Measured nitrate profiles at Brynemade. Profile 1 – B1 to B4 (top), measured nitrate April 2010 in existing piezometers (black dots) (middle) and measured nitrate profile May 2012 with temporarily wells for identifying local nitrate boundary (red dots) (bottom). Nitrate is in mg/L.

<u>Example 12: Field evaluation of the reactive transport model for CAH removal in the groundwater-river interaction zone</u>

A site-scale model in Hydrus-2D/3D of the Zenne site, Belgium, indicated that groundwater CAH plumes of DCE and specifically VC were entering the hyporheic zone at concentrations above the intervention limits. Therefore, a model was developed to describe the groundwater-river interactions in the hyporheic zone and to estimate the attenuation before the groundwater discharges in the Zenne river. The flux exchange between the groundwater and surface water across the stream bed interface was initially estimated by using a two-dimensional , finite difference variably saturated , groundwater flow and heat transport model (VS2DH) (Healy and Ronan, 1996). While a first-order model in PHREEQC containing advective-dispersive solute transport with first order degradation was developed to represent the degradation of VC in the Zenne river sediment. These two approaches were finally combined in the HP1 model to facilitate data management and processing using only one software tool for the simulation of the processes near/in the hyporheic zone (see Figure 9).

A flowline of 11.9 m was selected from a monitoring well next to the river up to the river sediment since HP1 can only simulate 1D reactive transport. This should not markedly influence the solute transport as it proceeds along the flowline with minimal lateral dispersion. But it could have an effect on the simulation of heat transport as the flowline has a parabolic shape circumventing a steel wall next the river bank. Water flow was simulated using the difference in pressure head between the monitoring well and the river as the upstream boundary condition. The downstream BC was set to a pressure head of zero. Figure 10 shows that the lab-derived first order rate constants adequately simulate the CAH degradation *in situ*. The concentration of ethene (ETH) is overestimated due to its large volatility or because it is scavenged by other microorganisms. The temperature profile along the 1D flowline could be approximated by increasing the thermal conductivity of the aquifer by half compared to the previous 2D simulations using VS2DH. However, results of a 2D simulation were deemed superior compared to 1D for heat transport in this specific case.

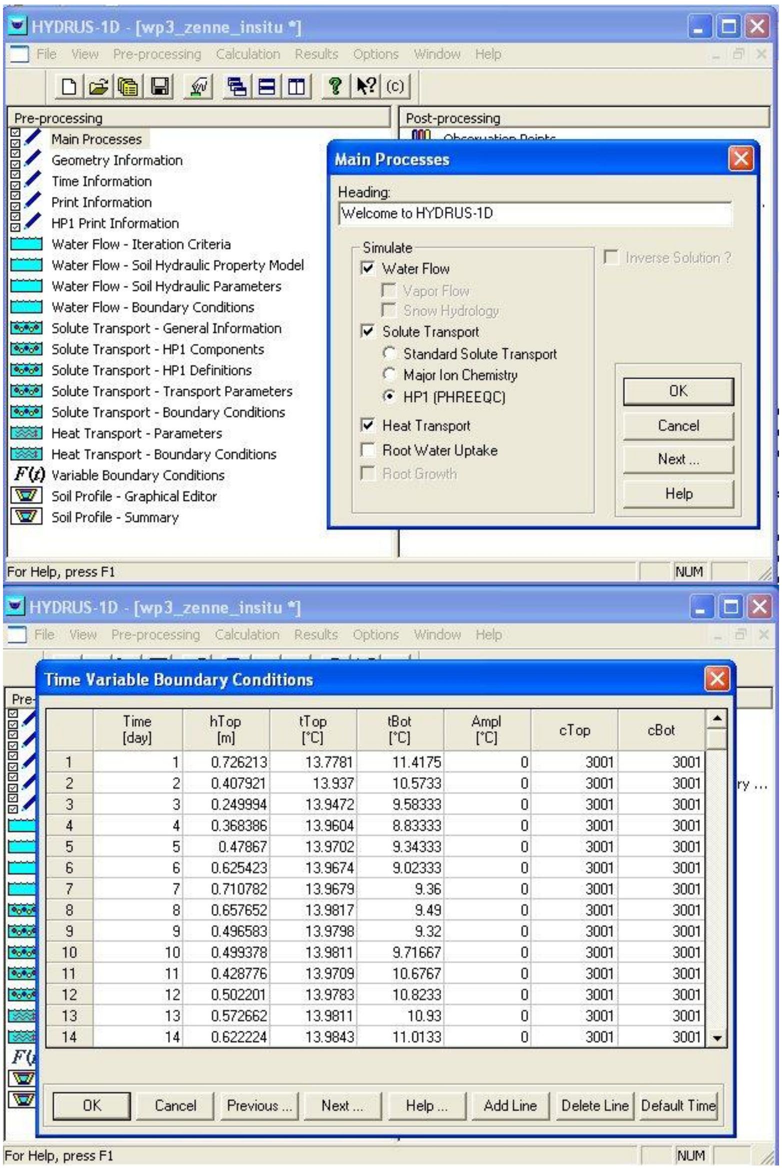


Figure 9: The graphical user interface of HP1 illustrating the possible simulations (top) and the time variable boundary conditions for pressure heads, temperature and concentrations at the boundaries of the 1D domain (bottom).

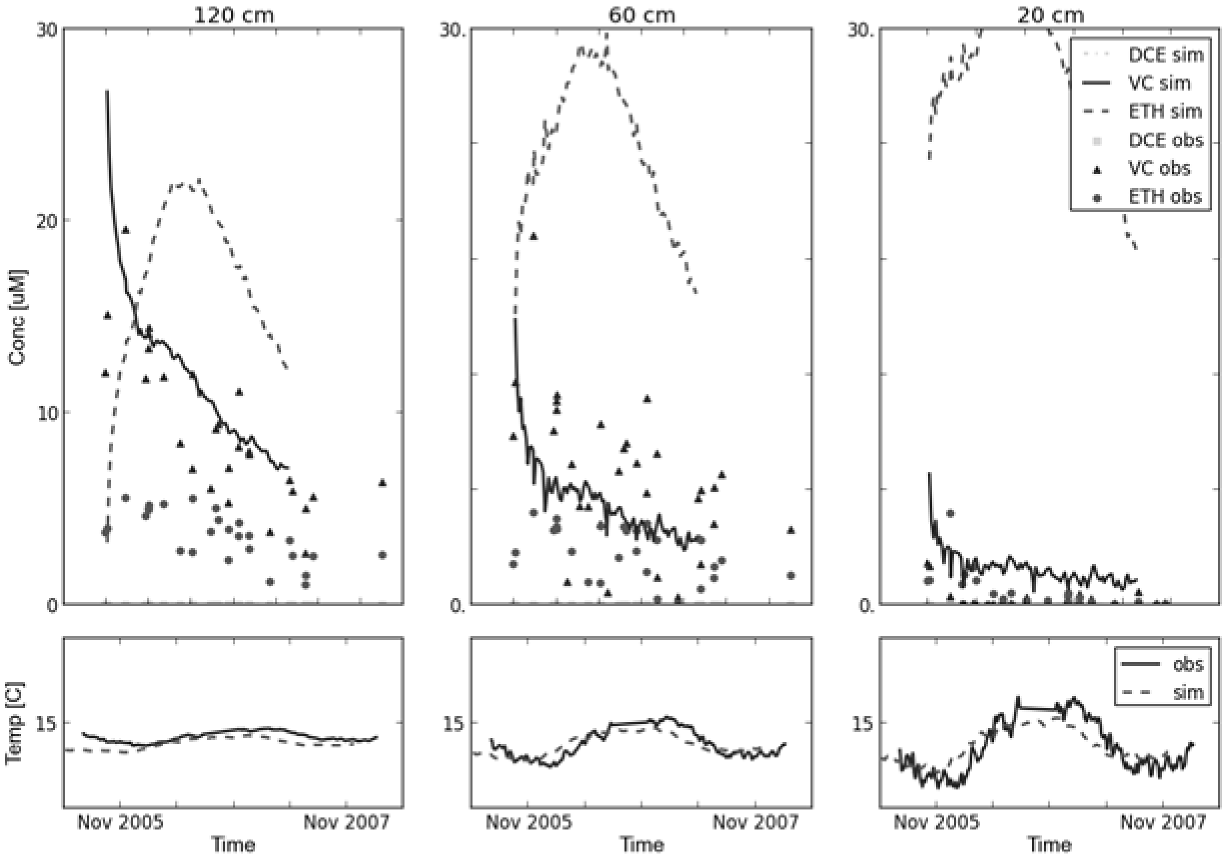


Figure 10: the top graphs show the observed and simulated concentrations of CAHs in the sediment at the Zenne site, Belgium, at 20, 60 and 120 cm depth using HP1. The bottom graphs show the observed and simulated temperatures at the respective locations in time.

4.3 USE OF MODEL RESULTS

After calibration and field evaluation the technology models can be used to run scenarios to evaluate the performance of the technology under varying conditions and to design the technology. In some applications, field models can be used to select optimal placement of monitoring wells.

Example 13: Field model for CAH removal in Fe-PRB + NA

An example on how the model can help in design the reactive barrier is reported in Figure 11. The model parameters were calibrated on the contaminant and inorganic concentrations measured in a column experiment that resembles the site A installation (both for the material used to fill the column and for the concentrations of organic and inorganic species in the influent). Therefore, the predictions provided by the model cannot be generalized to other PRB sites.

As can be seen from the Figure 11, the efficiency of the barrier depends on the inflow rates. At low inflow rates (Figure 11(a)) the barrier is able to degrade the contaminants completely close to the column influent. After 30 years the mineral front has advanced only 4 cm. At higher groundwater velocity (2 m y^{-1}) the barrier is still reactive after 30 years, although the mineral front has advanced more into the column. Figure 11(a) and Figure 11(b) should be the more representative of the site A, were effective groundwater velocity at the barrier influent should not exceed 2 m y^{-1}.

At 10 m y^{-1} (Figure 11(c)) the contaminant breakthrough is expected after 15 years. It can also be noticed that once the reactive surface becomes significantly depleted the decrease in contaminant degradation slows down, as results of the lower mineral precipitation rate at the end of the barrier lifetime.

The results of this numerical experiment show that the model can provide useful information to design the barrier (for example the thickness required to completely degrade the influent contamination for a designed number of years). However these predictions require a good knowledge of the inflow rates and detailed lab measurements to calibrate the model parameters.

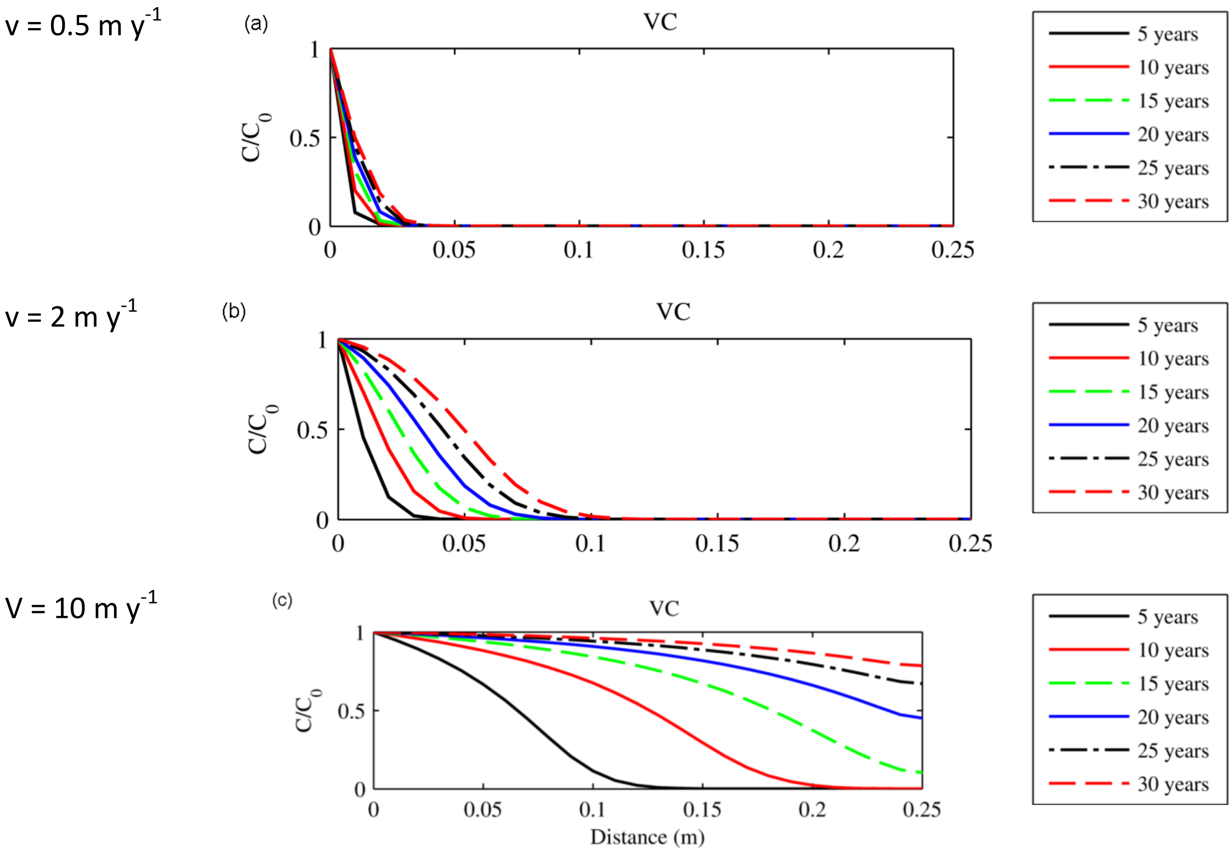


Figure 11: VC concentration profiles predicted by the model under different inflow rates. (a) effective groundwater velocity of 0.5 m y^{-1} (b) effective groundwater velocity of 2 m y^{-1} and (c) effective groundwater velocity of 10 m y^{-1}.

The prediction provided by numerical model should be verified with site observations. Reactivity tests of the field site barrier material were performed to assess if the barrier performance declined 7 years after its installation. The results of the reactivity test indicate that the barrier reactivity has not declined. This result agrees with Figure 11(a) and Figure 11(b), which do not indicate a substantial reactivity decline after 7 years.

Example 14: Use of the model for a wetland

Early model results guided the installation of wells, i.e., the phase 2 of well installations were based on field data and simulation results. For example, it was clear that (1) two deeper wells were needed in order to complement the geophysical surveys and locating the bottom of the aquifer, (2) nested wells were needed to show any vertical gradient and lower limit of nitrate plume, and (3) more wells were needed to better delimit the nitrate plume extension. For example, Figure XX shows how extra wells were used to more accurately capture the horizontal and vertical distribution of nitrate between wells B1 and B2 (that were installed in phase 1)

Furthermore, model results indicate the possibility of designing river restoration projects to optimize nitrate removal in wetlands. More intense and longer flooding of wetlands or riparian areas will increase denitrification by forcing incoming nitrate up through the highly-reactive peat layer instead of migrating directly through the less-reactive sand aquifer directly to the stream. For example, the simulation results show that an up to 47% increase in nitrate removal can happen under the most favourable case (where the sand aquifer has a low hydraulic conductivity and low denitrification rate) if the restoration project goes from having no flooding at all to flooding the riparian zone consistently at observed maximum flood for 75% of the year.

Example 15: Use of the model for CAH removal in the groundwater-river interaction zone

The HP1 model was used to perform a scenario analysis of remedial options at the Zenne site, Belgium. A CAH polluted groundwater plume discharges in the Zenne river and three remedial options were discerned: no action (= natural attenuation), biostimulation in the aquifer and the application of a capping material (e.g. straw) on top of the sediment. The results presented below make use of constants that were derived in lab-scale experiments or numerical evaluations and were not validated in the field. The starting concentrations of *cis*-DCE and VC were set to 600 and 1560 µg/L, concentrations that were encountered at the upstream monitoring well.

Results in Figure 10 show the need for a good parameterization of the flow in the aquifer as it has a large influence on the CAH concentrations that reach the hyporheic zone. The model output indicates a better performance of biostimulation in the aquifer than the capping layer. The performance of biostimulation is also less influenced by the magnitude of the water flow due to the longer residence time in the biostimulated zone than in the capping layer. The presented results were derived from a simplified conceptual model with a homogeneous aquifer, a steady-state flow, lab-scale CAH degradation parameters and worst-case boundary conditions for the mass transport. However, field data show smaller concentrations of CAHs in the sediment and indicate the importance of a good delineation of the boundary conditions (see 4.2, example 12). As such, the application of a capping layer should only be considered if the boundary conditions can be estimated to a large extent or as a final polishing step after the implementation of a zone with biostimulation in the aquifer.

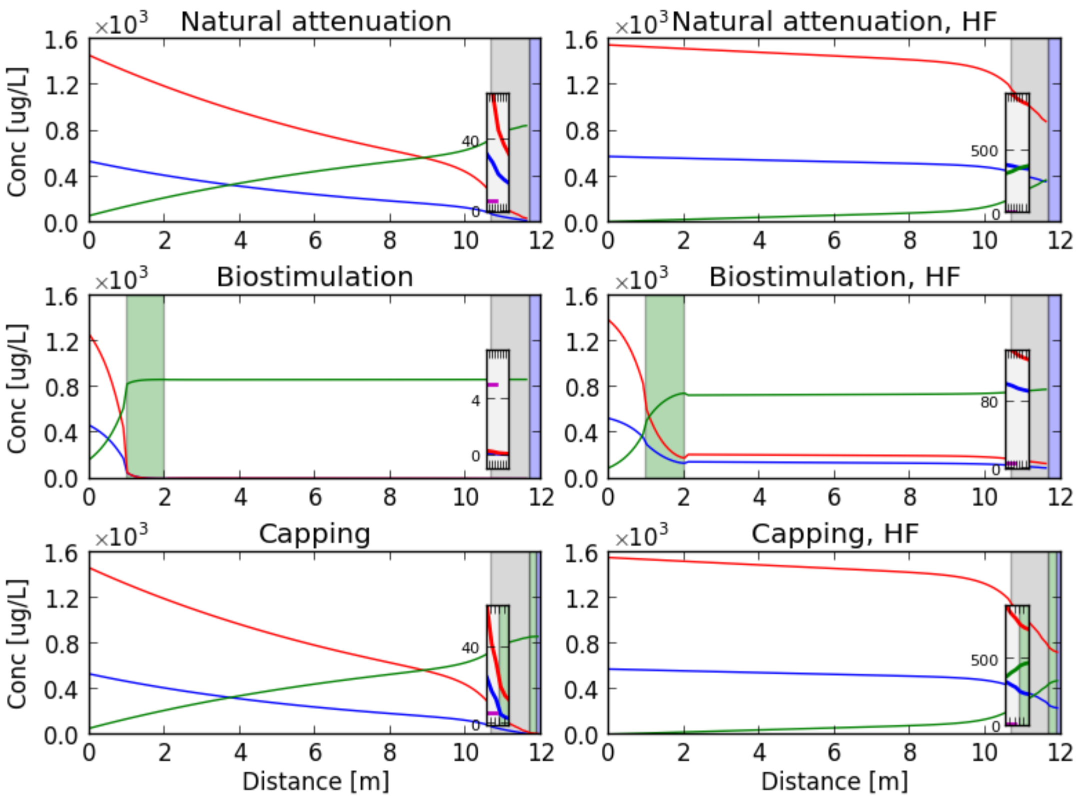


Figure 9: A scenario analysis of measures at the Zenne site, Belgium. The left graphs show the model output for the ambient groundwater velocity of 5 cm/day. The graphs at the right hand side show the situation for a hypothetical groundwater velocity of 50 cm/day (High Flow). The graphs show the concentrations of *cis*-DCE (blue), VC (red) and ethene (green). The inserts show the concentrations at the top of the sediment before the groundwater discharges in the river with the legal threshold for VC indicated by the dashed line. The green zone indicates the bioactive zone in the aquifer or the capping material, the sediment is indicated in gray and the river in blue.

5 TECHNOLOGY MODEL IMPLEMENTATION IN WATER MANAGEMENT DECISION SUPPORT

5.1 INTRODUCTION

The implementation of reactive transport models in catchment scale water management and rehabilitation, is not straightforward and limited by data availability and computational effort. Reactive transport models require process understanding at the microscopic scale and extensive parameterisation, which is not feasible at the catchment level. One way to upscale reactive transport models to the catchment scale is to derive simplified model structures from the more complex ones. The performance of these simplified model structures are verified with the complex model structures. The reduced model outputs can be plugged into decision support tools (for more information on setup of a DSS see Aquarehab generic guideline 6.6) under the form of databases for each technology containing detailed information on removal efficiency, applicability, lifetime and implementation rate, with its dependence on site specific characteristics.

5.2 INTEGRATION OF TECHNOLOGY MODELS IN DSS SCENARIOS

A certain measure can be implemented in the database structure of a DSS by specifying its *applicability*, *efficiency, lifetime* and *implementation* rate. For example, buffer strips and wetlands act on the nitrogen loads that enter the river network. These measures can be distributed based on geographical data or expert knowledge about the technology. Buffer strips and wetlands can only be applied on waterways with additional restrictions due to current land use. E.g., the *applicability* of these technologies is defined as the percentage of the smallest class of waterways compared to the total length of waterways in the respective catchments, i.e., the applicability is specific for each catchment. The *lifetime* or *efficiency* for a specific technology is calculated with a simplified reactive transport model (see 5.3). The *implementation rate* is user defined and reflects a manager’s decision to implement a certain technology.

The effect of a measure that acts on e.g. the nitrogen load attaining the surface water (e.g. buffer strips, wetlands and connection of unconnected households) can be directly calculated from the multiplication of the three terms above and the load *i* in the respective subcatchment:

$$effect = ImpGr \times Eff \times App \times Load_i \qquad \textbf{Eq. 8}$$

As an example, the measures with regard to N considered in a DSS are shown in Table 7.

The user defined efficiency (e.g. wetlands) can be calculated using the simplified technology models. The way to set up simplified models is described in the following sections.

Table 7: The measures considered in Aquarehab for nitrogen in the Scheldt river basin (implementation rates are predefined for the scenario calculations)

Measure	Implementation rate	Removal Efficiency	Applicability
Cattle reduction	[0,0.17,0.26,0.35]	1	1
Fertilizer reduction	[0,0.05,0.1]	1	1
Buffer strips	[0,0.1,0.5]	1 (u.d.)*	d.**
Connection of unconnected households to WWTPs	[0,0.25,0.5,1]	1	1
Wetlands	[0,0.1,0.2]	1 (u.d.)*	d.**

*u.d. the user can define efficiencies based on additional data or expert knowledge

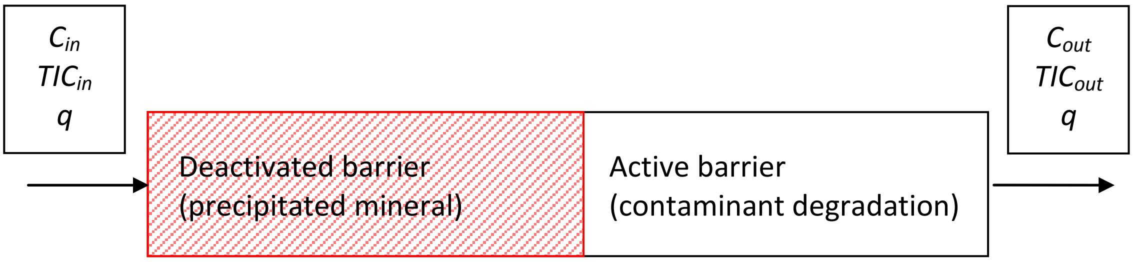
** d. The applicability is distributed per subcatchment as the percentage of smallest class rivers

5.3 Reactive transport model reduction

Example 16: Fe- PRB lifespan calculator

The estimation of the barrier longevity based on the collection of lab data and the calibration of a reactive transport model is complex. Moreover, the deactivation process might not be modelled as occurring in the real site conditions. For example, the model might not describe the formation of silica complexes that hinder access of contaminants to the iron surface. Such a process was proven to be important for the deactivation of iron-sand PRBs [*Kohn and Lynn Roberts*, 2006]. A simpler approach to estimate the barrier longevity is reported in Figure 12. The simplified model assumes that a mineral front develops in the PRB under low flow velocities (field conditions) and that before the front all the reactive surface area is depleted. Hence, only behind the deactivation front contaminants are actively degraded. The mineral front advances with the aging of the barrier according to the formula reported in Figure 12. The numerical input required by the formula is described in the Figure 12 caption. Assuming a constant velocity of the front, the barrier longevity can be calculated dividing the barrier thickness by the front velocity. Site specific parameters include the Darcy velocity, the TIC concentration of the influent groundwater, the porosity of the barrier medium and the reactive surface area. The average volume of carbonate minerals can be assumed equal to 5.6E-5 $m^3_{mineral}$ mol^{-1} whereas the thickness of the mineral covering can be assumed equal to 3.1E-8 $m^3_{\ mineral}$ $m^{-2}_{\ reactive\ surface}$. The thickness value was estimated from the column experiment and should be confirmed by other lab tests.

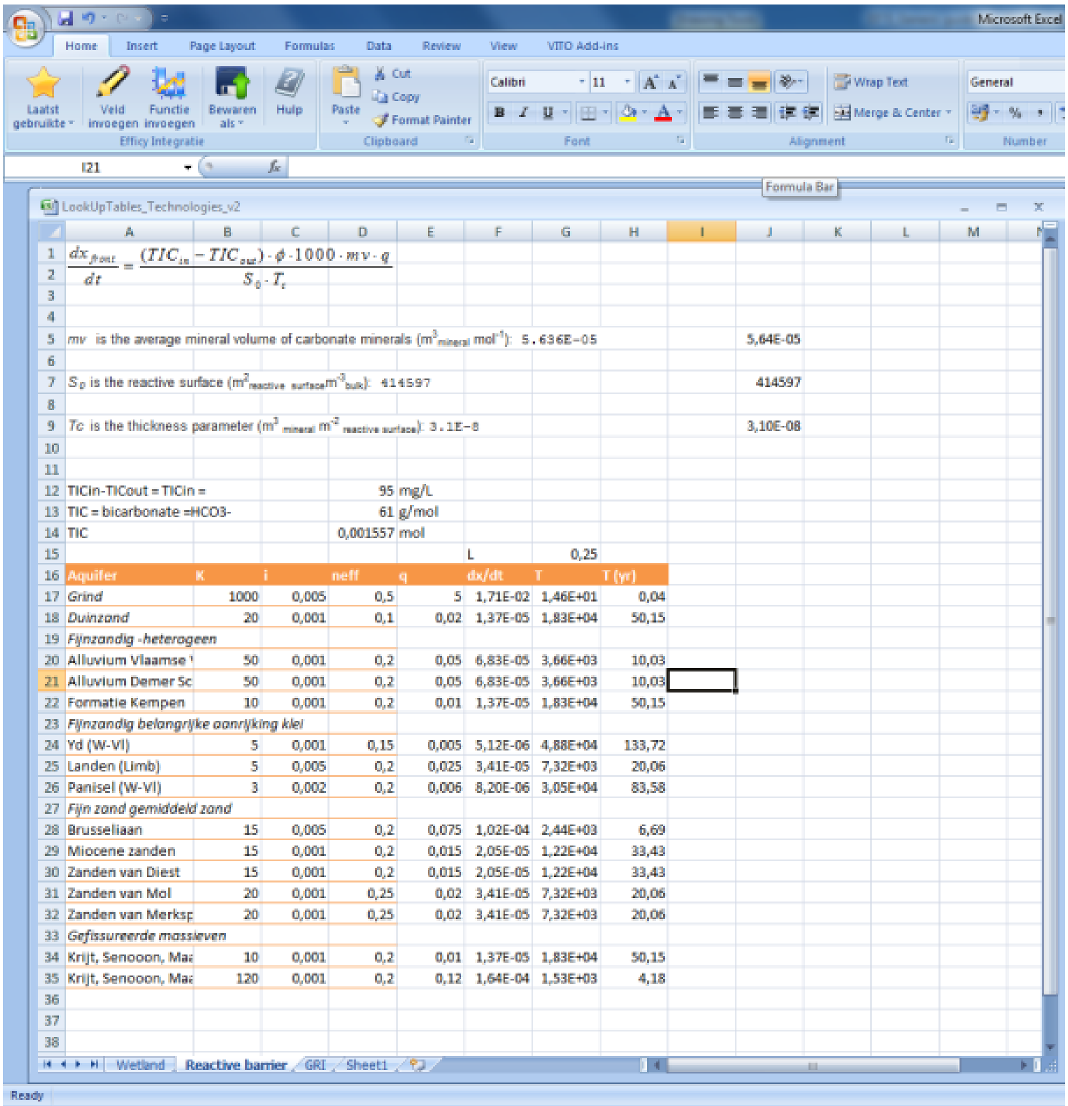
The reduced model is available as an excel spreadsheet for a standard set of parameters (Figure 13).



x_{front}

$$\frac{dx_{front}}{dt} = \frac{(TIC_{in} - TIC_{out}) \cdot \phi \cdot 1000 \cdot mv \cdot q}{S_0 \cdot T_c} \qquad \text{Eq. 9}$$

Figure 12: Simplified model conceptualization. *C* is the contaminant concentration (mol L^{-1}), *TIC* is the total inorganic carbon concentration (mol L^{-1}), *q* is the darcy velocity (m_{bulk} s^{-1}), ϕ is the porosity (-), *mv* is the average mineral volume of carbonate minerals ($m^3_{mineral}$ mol^{-1}), S_0 is the reactive surface ($m^2_{reactive\ surface}$ m^{-3}_{bulk}) and *Tc* is the thickness parameter ($m^3_{mineral}$ $m^{-2}_{reactive\ surface}$).



LookUpTables_Technologies_v2

$$\frac{dx_{front}}{dt} = \frac{(TIC_{in} - TIC_{out}) \cdot \phi \cdot 1000 \cdot mv \cdot q}{S_0 \cdot T_c}$$

mv is the average mineral volume of carbonate minerals ($m^3_{mineral}$ mol^{-1}): 5.636E-05 — 5,64E-05

S_0 is the reactive surface ($m^2_{reactive\ surface}$ m^{-3}_{bulk}): 414597 — 414597

Tc is the thickness parameter ($m^3_{mineral}$ $m^{-2}_{reactive\ surface}$): 3.1E-8 — 3,10E-08

TICin-TICout = TICin =			95	mg/L			
TIC = bicarbonate =HCO3-			61	g/mol			
TIC			0,001557	mol			
					L	0,25	
Aquifer	**K**	**i**	**neff**	**q**	**dx/dt**	**T**	**T (yr)**
Grind	1000	0,005	0,5	5	1,71E-02	1,46E+01	0,04
Duinzand	20	0,001	0,1	0,02	1,37E-05	1,83E+04	50,15
Fijnzandig -heterogeen							
Alluvium Vlaamse '	50	0,001	0,2	0,05	6,83E-05	3,66E+03	10,03
Alluvium Demer Sc	50	0,001	0,2	0,05	6,83E-05	3,66E+03	10,03
Formatie Kempen	10	0,001	0,2	0,01	1,37E-05	1,83E+04	50,15
Fijnzandig belangrijke aanrijking klei							
Yd (W-Vl)	5	0,001	0,15	0,005	5,12E-06	4,88E+04	133,72
Landen (Limb)	5	0,005	0,2	0,025	3,41E-05	7,32E+03	20,06
Panisel (W-Vl)	3	0,002	0,2	0,006	8,20E-06	3,05E+04	83,58
Fijn zand gemiddeld zand							
Brusseliaan	15	0,005	0,2	0,075	1,02E-04	2,44E+03	6,69
Miocene zanden	15	0,001	0,2	0,015	2,05E-05	1,22E+04	33,43
Zanden van Diest	15	0,001	0,2	0,015	2,05E-05	1,22E+04	33,43
Zanden van Mol	20	0,001	0,25	0,02	3,41E-05	7,32E+03	20,06
Zanden van Merksp	20	0,001	0,25	0,02	3,41E-05	7,32E+03	20,06
Gefissureerde massieven							
Krijt, Senooon, Maa	10	0,001	0,2	0,01	1,37E-05	1,83E+04	50,15
Krijt, Senooon, Maa	120	0,001	0,2	0,12	1,64E-04	1,53E+03	4,18

Wetland | Reactive barrier | GRI | Sheet1

Figure 13: Screenshot of the PRB lifespan calculator, illustrating the lifetime of a 0.25m Fe-barrier for a number of Belgian phreatic aquifer types with characteristic hydraulic properties

Example 17: Wetland plug flow reactor

The steady-state relative concentration of a plug flow wetland reactor with a flow residence time of τ_G and first-order decay (with rate λ) is;

$$C_r = \frac{C}{C_0}\exp(-\lambda\tau_G) \qquad \textbf{Eq. 10}$$

where C_0 is the concentration of water entering the wetland. The efficiency of a wetland in reducing mass can also be expressed by a mass reduction ($M=1-C_r$) according to the so-called Damkohler number (D) defined as;

$$D = \frac{\tau_G}{\tau_R} \qquad \textbf{Eq. 11}$$

i.e, the ratio of the flow residence time and a characteristic reaction time scale (τ_R) here given as the half-life of the reaction, or;

$$\tau_R = \frac{\ln(2)}{\lambda} \qquad \textbf{Eq. 12}$$

Thus, when D is large (slow groundwater flow), mass reduction is high and vice versa.
From above the Damkolher number may be written as;

$$D = \frac{L/v}{\tau_R} = \frac{L * n/(K * i)}{\tau_R} \qquad \textbf{Eq. 13}$$

Which encapsulates some of the primary factors controlling removal of nitrate (and pesticides) in wetlands, i.e., length of wetland (L), hydraulic conductivity (K), porosity (n), and hydraulic gradient (i).

This represents a worst-case scenario in the sense that other processes will increase removal (as demonstrated by the numerical model); (1) the presence of a peat layer and (2) flooding causing flow dynamics forcing more groundwater to discharge vertically up through the reactive peat layer.

The reduced model is available as an excel spreadsheet for a standard set of parameters.

Exemple 18: Groundwater – river tanks in series reactor

A simplified model for the sequence of aquifer and hyporheic compartments is to consider mixed tanks in series. Since the removal processes in each separate compartment can be described using first order kinetics, the model for tanks in series can be expressed by using the Damköhler number approach (Green, 2012):

$$C_n = \frac{C_0}{(1+D_i)^n} \qquad \textbf{Eq. 14}$$

Where C_n is the concentration leaving tank *n*, C_0 is the concentration entering the series of tanks, D_i is the Damköhler number for tank *i* (from Eq. 5), *n* is the number of tanks.

$$C_r = \frac{C_n}{C_0} \qquad \textbf{Eq. 15}$$

Any layer with its specific Damköhler number can be included in the analysis.

The reduced model is available as an excel spreadsheet for a standard set of parameters.

5.4 IMPLEMENTATION OF REDUCED MODELS IN DECISION SUPPORT

Reduced models for the wetlands and the groundwater river interaction zones can be used to calculate removal efficiencies defined as the reduction of a contaminant concentration (concentration leaving the treated zone versus concentration entering the treated zone). The removal efficiencies serve as user defined values in the measures database that can be implemented in decision support.

Removal efficiency for wetlands can be calculated using the plugflow reactor model from the following wetland characteristics:

- Total width
- Width of aerobic zone
- Average hydraulic conductivity
- Porosity
- Hydraulic gradient
- Degradation rates in aquifer and peat layers

The removal efficiency of a groundwater river interaction zone can be calculated using the tanks-in-series tool from:

- Thickness of aquifer
- Thickness of sediment layer
- Thickness of a capping technology
- Hydraulic conductivity in aquifer
- Hydraulic conductivity in sediment
- Porosity
- Hydraulic gradient
- First order reaction rates in aquifer, sediment and capping material

Hydrogeological characteristics (apart from the width of the aerobic zone for wetlands) are generally available from surveys and hydrogeological data. Degradation rates need to be estimated from experiments with material from the site or inverse modeling using observed concentrations. If no data are available, ranges in literature values need to be used.

The Fe-PRB lifespan calculator can be used to estimate the lifetime of a barrier limited by reactivity loss due to mineral precipitation, using the following parameters:

- Aquifer hydraulic conductivity
- Aquifer porosity
- Hydraulic gradient
- Groundwater composition , i.e., total inorganic carbon
- Mineral volume of carbonate minerals
- Reactive surface area of the material used
- Mineral thickness parameter

Aquifer properties are generally available from geological surveys. Data on groundwater composition are generally less available and should be varied in the analysis. Data on mineral volume and mineral thickness need to be abstracted from literature. The reactive surface area needs to be defined by the provider of the material.

6 DESCRIPTION OF CODES FOR SPECIFIC TECHNOLOGIES

HP1 – Coupled Hydrus-1D and PHREEQC model

The HP1 code is fully incorporated into the HYDRUS-1D software package which can be downloaded from the link below. The user manual and notes on how to use HP1 can be found on this website:

- http://www.pc-progress.com/en/Default.aspx?hydrus-1d [available on-line, 03/05/2013]
- In addition, users can have a look at the website of HP1 specifically for benchmark problems, applications and other relevant information: http://www.sckcen.be/hp1/ [available on-line, 03/05/2013]

FeFlow

Feflow 6.0 was used to simulate 2D flow and reactive transport. Feflow is a commercially available from http://www.feflow.info/

MIN3P

MIN3P is a geochemical model, particularly suited for lab-scale applications under simple flow conditions. Contact Prof. Uli Mayer, umayer@eos.ubc.ca for a copy of the model and source code.

MODFLOW – PHAST

- Model Muse, is a free MODFLOW and PHAST interface, http://water.usgs.gov/nrp/gwsoftware/ModelMuse/ModelMuse.html
- PHAST is a PHREEQC based geochemical model with an internal flow solver, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/

PHREEQC

PHREEQC models geochemical process and 1D contaminant transport. On line guide and download instructions can be found at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

PHT3D

PHT3D is a PHREEQC based geochemical model which uses as flow input the MODFLOW output, http://www.pht3d.org/pht3d_exe.html

RT3D

RT3D is a customizable reactive transport model which uses as flow input the MODFLOW output, http://bioprocess.pnnl.gov/rt3d.downloads.htm

MCM
The MCM is available from the developer at BGU and at the AQUAREHAB website.

Plugflow reactor model for wetlands
The plugflow wetland reactor model has been implemented in Excel and is available at the AQUAREHAB website.

Tanks in series model for groundwater river interaction zones
The tanks in series model has been implemented in Excel and is available at the AQUAREHAB website.

lifespan calculator for permeable reactive barriers
The PRB lifespan calculator has been implemented in Excel and is available at the AQUAREHAB website.

7 GENERAL CONCLUSIONS

Based on the lessons learned in the Aquarehab project, the following general conclusions can be drawn:

- A thorough schematisation of the subsurface is needed for site modeling, since the subsurface is heterogeneous in nature, which can affect performance of the technology and the model (see description of multibarrier site and wetland sites)
- The determination of source zones and their history is crucial, since source term is important driver for observed concentrations in groundwater and design of the technology (see description of multibarrier site)
- Parameterisation of field models is an issue for the practical application of the models by consultants since a lot of parameters need to be estimated for technology performance assessment
- Reasonable approximations are obtained with reduced models for performing first screening calculations of the performance for some in situ technologies, still the data availability may be an issue
- For uptake in decision support and water management groundwater body scale and river basin scale, field models cannot be used directly given the great level of detail in process description and amount of parameters needed, and simplified versions of the models such as the PRB lifespan calculator, the wetland plugflow reactor or the tanks-in-series type of models need to be provided

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VITO NV (Belgium)	Piet Seuntjens piet.seuntjens@vito.be Pieter-Jan Haest	Coordination modelling group and general aspects Hydrus Model smart carriers HP1 model groundwater-river interaction zone
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University of Copenhagen (Denmark)	Jannick Jensen Peter Engesgaard pe@geol.ku.dk	Wetland model
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