# Multibarrier

## Generic guideline

Target audience: Scientists, Consultancies, contractors, authorities, feasibility test labs

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# 1 INTRODUCTION

The multibarrier technology is an innovative in-situ technology to improve the quality of groundwater. Multibarriers consist of a combination of permeable reactive barriers (PRBs) and reactive zones (RZ), in which different pollutant removal processes are combined.

This document intends to provide general information about this technology, and its application area and boundary conditions for authorities, consultants and site owners. Further, information is enclosed for supporting consultants, authorities and scientists to evaluate the feasibility and the impact of the technology to rehabilitate degraded waters, as well as for designing, implementing and monitoring multibarriers.

The document was composed within the frame of the FP7 project AQUAREHAB (GA 226565), and comprises outcomes and lessons learned during this project and the MULTIBARDEM LIFE project (LIFE06 ENV/B/000359).

DISCLAIMER: Although the information described in this document is believed to be reliable and accurate, the guideline does not offer warranties of any kind.

# 2 GENERAL PRINCIPLES OF THE MULTIBARRIER TECHNOLOGY

## 2.1 CONCEPT

A multibarrier is a sustainable in-situ passive solution to contain and treat contaminated groundwater. It consists of a tailor-made combination of different types of permeable reactive barriers and reactive zones in which different pollutant removal processes are active. The groundwater flows through the system during which the pollutants are degraded or immobilized. As such multibarriers prevent further spreading of the pollution to the downstream area.

Groundwater is the main source of drinking water in Europe. Contaminated groundwater is one of the major concerns for the European society in the beginning of the 21st century. Especially the Water framework Directive (and its daughter Directive on groundwater) states that the water and groundwater quality must be improved before the year 2015. Recently, *in-situ* treatment is becoming more interesting for aquifer treatment as the technology is developing and becoming more reliable and accepted.

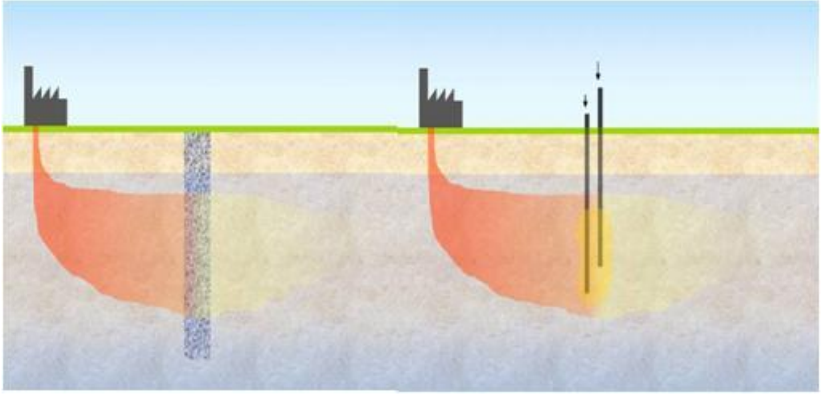


**Figure 1: Schematic representation of a permeable reactive barrier (LEFT) and reactive zone (right).**

A very attractive *in-situ* concept on the one hand is the "**Permeable Reactive Barrier (PRB)**", a technology in which a trench is made perpendicular to the groundwater flow. This trench is filled with a coarse material in which a pollutant removal process (biological, chemical reduction, sorption, ...) is induced to remediate the passing groundwater. On the other hand "**reactive zone**s **(RZ)**" represent a promising in-situ remediation technology, where, locally, pollutant removal processes are induced by injection of slurries/liquids containing reactive products or degradation stimulating products (without excavation).

Mostly, PRBs and RZs are designed to abate specific pollutants. However, at many sites the polluted groundwater contains a mixture of a variety of both organic and inorganic contaminants. The abatement of pollutant mixtures may not be possible with a simple barrier/zone which is based on removal of the pollutants by either physico-chemical or biological processes. However, complex pollutant mixtures might be treated using a combination of different reactive barriers/zones. Such a combination is defined as a **Multifunctional Permeable Barrier** (MULTIBARRIER). The multibarrier approach is a tailor made technology and requests the efficient synergistic interaction and compatibility of different pollutant removal processes, often of microbial and physico-chemical key-components of the system. An example of a multibarrier is given in Figure 2.

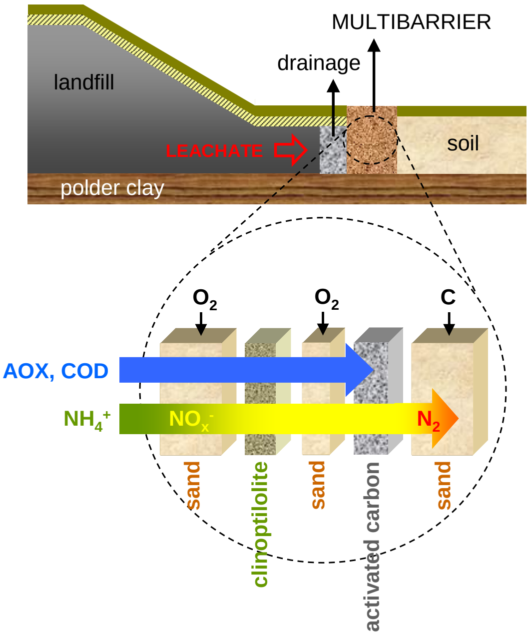


**Figure 2: Example of a multibarrier system (LIFE-project MULTIBARDEM).**
**Multibarrier concept that was successfully designed for the semi-passive removal of ammonium, AOX, COD and toxicity from landfill leachate. The MULTIBARRIER consists of (1) a nitrifying zone, (2) a sorption zone with clinoptilolite, (3) a second nitrifying zone, (4) a zone with granular activated carbon (GAC) for the removal of AOX and COD by sorption, and (5) a denitrifying zone.**

## 2.2 TARGETED SUBSTANCES & REACTION MECHANISMS

Table 1 provides an overview of some substances that can be targeted by the multibarrier technology along with potential emissions sources of the different substances. In principle, multibarriers can deal with all compounds that can be degraded biologically or chemically, or that can be retained by certain materials like sorbents.

The multibarrier technology is especially useful for mixtures of pollutants or for pollutants that require different steps to be degraded.

**Table 1 Examples of substances that can be tackled by the MULTIBARRIER technology.**

| Targeted substances | | Emission sources | Potential pollutant removal processes |
|---|---|---|---|
| Class | Specific substance | | |
| CAHs (chlorinated aliphatic hydrocarbons) | Trichloroethene (TCE)<br>Tetrachloroethene (PCE)<br>Cis-dichloroethene (cDCE)<br>Vinylchloride (VC)<br>Chlorinated ethanes<br>… | Drycleaner activities, degreasing activities, ... | • Chemical reduction via zerovalent iron (see DL4.3 part A)<br>• Biodegradation-anaerobic (see DL4.3 part B)<br>• Sorption<br>• ... |
| BTEX | Benzene, Toluene, ethylbenzene & xylenes | Petrochemical industry<br>Petrol gas filling stations | • Biodegradation – aerobic<br>• Sorption<br>• ... |
| Inorganics | Ammonium | Landfill leachate | • Biologically: nitrification – denitrification<br>• Ion exchange<br>• ... |
| Oxygenates | Methyl-tert-butyl ether (MTBE)<br>Tert-butyl alcohol (TBA)<br>... | Petrol gas<br>Petrochemical industry | • Biodegradation – aerobic<br>• ... |
| Metals | Nickel, zinc, .. | Metal industry | • Sorption<br>• Bioprecipitation processes<br>• ... |
| ... | | | |
| Mixed pollutions | Mixtures of pollutants mentioned above | Industrial sites<br>Overlapping groundwater plumes | combination of the above mentioned processes |

## 2.3 DEVELOPMENT STAGE OF THE TECHNOLOGY

Within technology development, the following stages can be defined:

- A technology is very emerging when it is at the research stage (not even implemented in other sectors).
- It is emerging when it is implemented in another sector and is being developed in the concerned sector (but it is no at the pilot plant trial stage yet).
- It is becoming transferable when it is at the pilot plant trial stage in the concerned sector.
- It is transferable when it is at the full scale trial stage in the concerned sector.
- It is available when it is commercially available and in use in the concerned sector.

The multibarrier technology is transferable as:

- The technology has been studies on lab scale for a variety of pollutant mixtures.
- Pilots were performed (for instance LIFE project MULTIBARDEM)
- Steps to full scales are made

As the multibarrier technology is a combination of different types of barriers and reactive zones, it is a more complex than single barriers or zones. As such, the acceptability in Europe is expected to be a bit lower than for single barriers & zones. The latter ones are well accepted in a number of countries, although in practice more conventional methods like pump&treat are still used more frequently.

Some examples of multibarrier systems studied at lab and pilot scale are given in Table 2.

**Table 2 . Examples of multibarriers**

| *Site* | *Landfill*<br>*Belgium* | *Landfill*<br>*Belgium* | *Industrial site*<br>*Belgium* | *Landfill*<br>*Belgium* | *Landfill*<br>*Belgium* |
|---|---|---|---|---|---|
| *Scale & Multibarrier type* | lab-study<br>sequential multibarrier | lab-study<br>mixed multibarrier | lab-study<br>sequential multibarrier | Lab<br>sequential multibarrier | Lab scale<br>Mixed multibarrier |
| *Installation date* | | | | 2008 | 2008 |
| *Pollutants* | *Chlorinated ethenes*<br>*BTEX*<br>*metals* | *Chlorinated ethenes*<br>*BTEX*<br>*metals* | Chlorinated ethenes<br>MTBE<br>BTEX | ammonium,<br>AOX, COD | Ammonium |
| *Pollutant removal mechanisms* | | | A. ZVI-part: removal of chlorinated comp.<br>B. buffer<br>C. Inoculated aerobic biobarrier : MTBE & BTEX removal | aerobic biobarrier<br>anoxic biobarrier<br>ion ex-change part<br>aerobic biobarrier<br>sorption barrier | Clinoptilolite (ion exchange)<br>Biological nitrification & denitrification |
| *Composition filling material* | *ZVI, filter sand* | *ZVI, filter sand* | ZVI, filter sand/aquifer mixture | Filter sand, zeolite, GAC | Clinoptililite & sand |
| *Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)* | | | | | |
| *Location monitoring wells* | | | | *Upstream & downstream multibarrier; Between and in different multibarrier compartments* | |
| *Installation costs* | | | | | |
| *Information source* | *Dries et al., 2003*<br>*Van Nooten et al., 2007* | *Dries, 2004.* | *Bastiaens et al., 2007*<br>*Bastiaens et al.,2008* | *Van Nooten et al., 2008 & 2010*<br>*MULTIBARDEM LIFE project* | *Van Nooten et al., 2011* |

**Table 2 . Examples of multibarriers (cont.)**

| *Site* | *Industrial site*<br>*Austria* | *Landfill*<br>*Belgium* | *Landfill*<br>*Belgium* | *Portadown gaswork*<br>*Ireland* |
|---|---|---|---|---|
| *Scale & Multibarrier type* | *Lab & pilot* | pilot<br>sequential horizontal multibarrier | Pilot<br>Sequential vertical multibarrier | Full scale<br>Sequential anaerobic aerobic biodegradation and GAC |
| *Installation date* | *2008* | 2008 | 2009 | |
| *Pollutants* | *Chlorinated ethenes & ethanes* | ammonium,<br>AOX, COD | ammonium,<br>AOX, COD | BTEXN, PAH, cyanide, ammonium |
| *Pollutant removal mechanisms* | *Aerobic and anaerobic biodegradation* | Nitrification & denitrification<br>ion exchange & sorption | Nitrification & denitrification & sorption | Air to promote aerobic biodegradation, sorption |
| *Composition filling material* | The molasse pulse dosing grape stems | Filter sand, clinoptilolite, GAC, | Filter sand & GAC | GAC, sand |
| *Dimensions of the barrier (L: length; T: Thickness; D: depth; H: height)* | | *L = 2.4 m; T =9 m; h = 2.4 m* | L = 4 m; D = 1.2 m | Funnel= L = 175 + 70 m, Diameter = 6-8 m |
| *Installation method* | *Funnel & gate*<br>*reactive zones* | *Gate installed in container* | Gate installed in subsurface vessel | 6 reactive vessels in series (2 anaerobic, 2 aerobic, 2 GAC) |
| *Location monitoring wells* | | *Upstream & downstream multibarrier; Between and in different multibarrier compartments* | *Upstream & downstream multibarrier; Between and in different multibarrier compartments* | Influent, effluent, between and within each vessel |
| *Costs of filling material* | | 8900 euro | 2000 euro | |
| *Installation costs* | | | | |
| *Totale costs* | | 126050 euro | 28887 euro | |
| *Information source* | *Pümpel et al. (not published)*<br>*MULTIBARDEM LIFE* | *Bastiaens et al.,2008*<br>*MULTIBARDEM LIFE* | *MULTIBARDEM LIFE* | *SEREBAR demo project*<br>*ES&T 2007* |
| | | | | |

NA = Not available;

# 3 APPLICABILITY AND BOUNDARY CONDITIONS OF THE MULTIBARRIER TECHNOLOGY

The applicability area and boundary conditions (depth of the impervious layer, depth of the phreatic aquifer, composition of the groundwater, depth of the groundwater plume, groundwater flow, porosity aquifer, hydraulic conductivity, ...) of the multibarrier technology are determined by:

- The applicability and boundary conditions of the single barriers (or reactive zones) that are comprised within the multibarrier, and
- The type of PRBs or reactive zones that needs to be combined.
- The mixed pollutants present

For zerovalent iron barriers and biobarriers, examples of single barriers, the applicability area and boundary conditions are described in DL4.3A and DL4.3.B, respectively.

In principle, multibarriers are applicable for all compounds and locations where single barriers/zones are appropriate. However, a number of additional aspects should be taken into account when considering a multibarrier technology:

- The impact of **co-pollutants** in the groundwater on an envisioned removal process needs to evaluated and taken into account when designing multibarriers
    - Example of positive effects (to be used in multibardems):
        - Presence of Ni in groundwater when envisioning ZVI-barrier for removal of chlorinated ethenes. Cementation of Ni (as $Ni^0$) on ZVI increases its reactivity.
        - Co-metabolic effects in biobarriers: for instance BTEX-compounds can serve as electron donor for biological reductive dehalogenation
    - Examples of negative effects (to be avoided by adapting the multibarrier concept)
        - High metal concentration can negatively impact biobarriers and bioreactive zones.
        - Nitrate in groundwater when envisioning a ZVI-application for chlorinated ethenes. Nitrate is a competitor for electrons and reduces the reactivity of ZVI over time.
        - Preferential substrate use in biobarriers
- **Different pollutant removal processes** within a multibarrier need to be compatible.
    - Examples of non-compatible removal processes (to be physically separated) are:
        - Aerobic and anaerobic processes
        - Aerobic biobarriers and ZVI-barriers: the zerovalent iron will corrode fast when oxygen is present.
        - Sorption barriers and biobarriers
    - Example of removal processes that have a positive interacting effect:
        - ZVI-reactive zone and anaerobic biological processes (biodegradation, biological metal precipitation, ...).

# 4 PERFORMANCE OF THE MULTIBARRIER TECHNOLOGY

The **abatement rate** can be defined as the substance concentration after the technology implementation divided by the substance concentration before implementation of the technology.

The multibarrier-technology aims at an abatement rate close to 100%, which means that flux reduction rate in the multibarrier for the pollutants is almost 100%. The local regulatory limits are determining for the exact targeted abatement rates that need to be taken into account during the barrier design. Note that generally, the multibarrier does not affect the pollution concentration upstream and does not deal with the pollution that is already downstream of the barrier. The barrier does prevent spreading of the upstream pollutants to the downstream located area.

**Efficiency drivers** are (1) the degradation/removal rates of the different pollutants and their breakdown products, (2) the groundwater flow velocity, (3) the thickness of the barrier (flow through path) and (4) the inactivation of the multibarrier over time (permeability & reactivity).

**Longevity of the multibarrier technology:** In most cases, it is needed that the technology is operational for several years up to decades. Practically, there may be needs for additional investments during these long times for some multibarrier types. The longevity is depending on the barrier type:

- ZVI-barriers: 10-30 years (expected & deduced from field data)
- Bio-barriers: years
- Sorption barriers: months to years (depending on contaminant loading)
- Multibarriers: months to years

# 5 COST OF THE MULTIBARRIER TECHNOLOGY

Cost drivers for the multibarrier technology comprise (1) the dimensions of the barrier (depth, length and thickness), (2) the price of the filling materials, (3) the local situation on the site (accessibility, surroundings buildings, underground constructions, type of subsurface ...), and (4) the local labour costs (country dependent), and (5) the costs of the tailor made design and feasibility test.

In general, it may be assumed that site characterization, design and contingency planning costs will be higher for a multibarrier than for P&T.

Construction costs depend highly on the type of multibarrier installed (reactive barriers vs reactive zones), and may be either higher or lower than for P&T. Therefore, multibarriers can be cost-efficient compared to P&T systems, and are more likely to be so for long-running remediations. However, much depends on the long term performance of multibarriers, and potential need for replacement of reactive materials. This remains as yet a major unknown (Horckmans et al., 2009).

Operational costs of multibarriers are normally lower than those associated with traditional groundwater remediation techniques such as P&T (pump&treat). Due to its passive nature, electricity and maintenance costs should be very low. Operational costs for reactive zones may be higher than for reactive barriers due to the required addition of nutrients, oxygen or other and higher energy use (Horckmans et al., 2009).

Monitoring costs for multibarriers may be higher than for traditional systems. PRB performance has been shown to decline with time (ITRC, 2005). Due to the large heterogeneity of in situ conditions, laboratory tests and in-situ measurements will never be able to completely predict multibarrier performance in the field. Therefore, continuous monitoring of hydrological, geochemical and microbiological performance is necessary. Regulatory monitoring requirements for these novel techniques will most likely also be higher than for traditional, "proven", methods such as P&T. This is for example the case in Flanders, where monitoring requirements for ZVI-barriers are prescribed by the Flemish Waste Agency (OVAM, 2005). The required number of monitoring wells is much higher than that usually placed for P&T installations (Horckmans et al., 2009).

Cost estimation for specific multibarrier configurations are given in Table 2.

# 6 GENERIC APPROACH TO DETERMINE APPLICABILITY OF THE MULTIBARRIER TECHNOLOGY AT A SPECIFIC SITE OR AREA

For a successful application of the multibarrier technologies, the following stepped approach is recommended:

## 6.1 STEP 1: SITE CHARACTERISATION

A site characterisation is required for checking the application and boundary conditions associated with the technology (see section 3). The site characterisation comprises:

- Identification of the type and concentration of pollution that is present
- Evaluation of groundwater chemical data including conductivity, pH, redox potential, temperature, oxygen content as well as inorganic parameters such as Ca, Fe, K, Mg, Na, Si, Cl, $SO_4$, $NO_3$, alkalinity, TOC and DOC.
- Determination of the location of the pollution (soil, groundwater, depth, ...)
- Collection of information on the geology (type of layer, permeability, ...)
- Collection of hydrological data (groundwater flow direction, groundwater flow velocity, ...)
- Evaluation of the accessibility of the site

## 6.2 STEP 2: SELECTION OF POLLUTANT REMOVAL PROCESSES

For each of the present pollutants that need to be reduced in concentration, effective pollutant removal processes need to be identified (Table 3). In some cases small lab scale feasibility tests can have benefits. Next, a combination of pollutant removal processes needs to be selected that can jointly cope with the present (mixed) pollution.

Table 3. Generic example of pollutant-removal process matrix.

| | Removal process 1 | Removal process 2 | Removal process 3 | Removal process 4 |
|---|---|---|---|---|
| Pollutant A | x | | | |
| Pollutant B | | x | x | |
| Pollutant C | | x | | x |
| … | | | | |

In first instance, a theoretical approach can be used to combine the selected pollutant removal processes in a multibarrier configuration. Here a distinction can be made between sequential multibarriers (pollutant removal processes are physically separated) and mixed multibarrier systems (Figure 3).

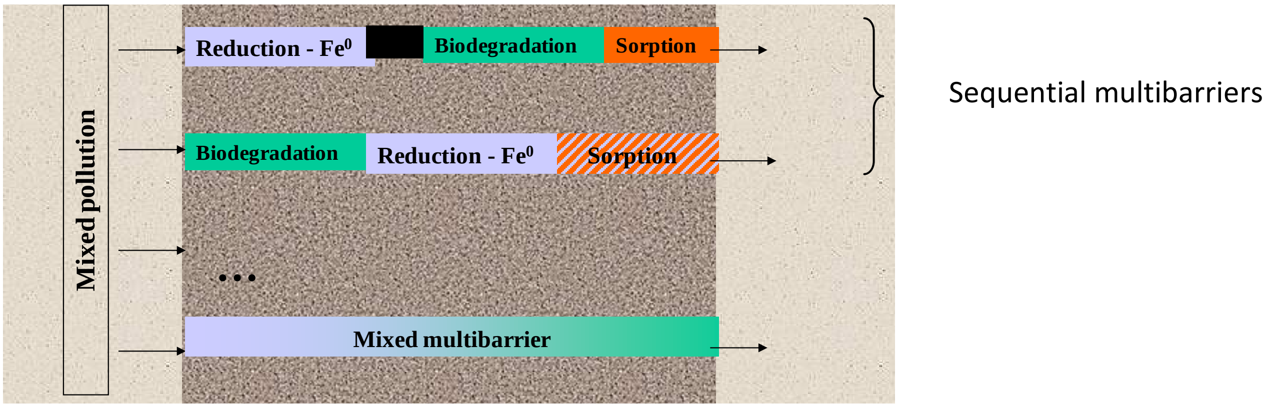


Figure 3. Examples of sequential and mixed multibarrier configurations.

## 6.3 STEP 3: FEASIBILITY TEST AT LAB SCALE

It is strongly advised to verify the multibarrier concept also via a lab scale feasibility test, preferably a column test. Here the multibarrier is simulated at labscale using groundwater and aquifer material from the site (examples see Figure 4). Aims of the test are:

- To evaluate the performance of each multibarrier compartment
- Evaluate the impact of co-pollutants and the interaction between the different removal processes.
- Deduce degradation/removal rates and other parameters that are needed for the design of a larger scale multibarrier system.

**Example 1:** Multibarrier concept tested for the semi-passive removal of ammonium, AOX, COD and toxicity from landfill leachate (Figure 4). The MULTIBARRIER that was evaluated consisted of (1) a nitrifying zone, (2) a sorption zone with clinoptilolite, (3) a second nitrifying zone, (4) a zone with granular activated carbon (GAC) for the removal of AOX and COD by sorption, and (5) a denitrifying zone (Figure 2).

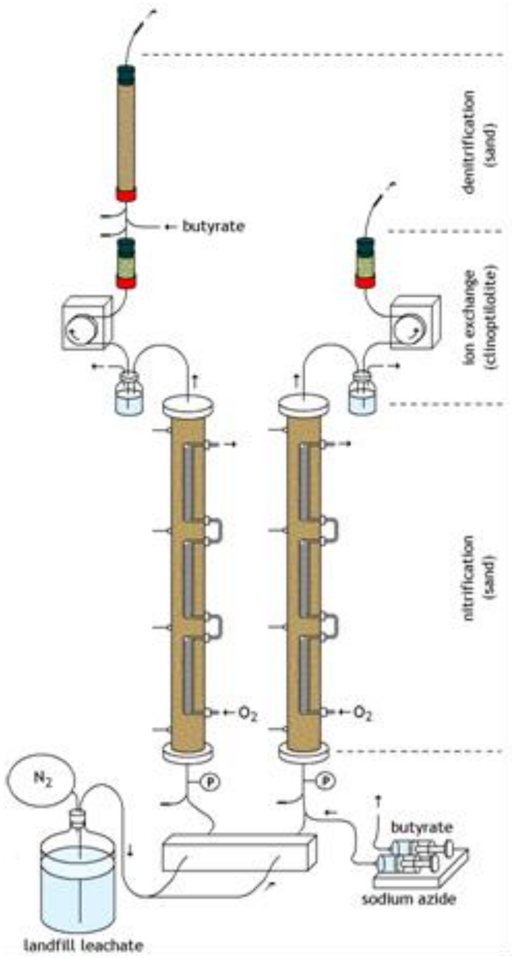


**Figure 4. Schematic overview of the sequential laboratory-scale multibarrier system, comprising a viable column train and a column train poisoned with sodium azide.** (SOURCE: MULTIBARDEM)

**Compartment 1: Aerobic zone – nitrification**
**Compartment 2: Ion exchange**
**Compartment 3: Anoxic zone – denitrification**

**Example 2**: A laboratory feasibility study has been performed based on batch and column tests to evaluate the potential for a multibarrier for the remediation of contaminated groundwater at a former manufactured gas plant site. The conclusions were the following (Gemoets J, 2004):

- BTEXN, phenols, NSO-heterocyclics, free cyanide and thiocyanate can be treated by aerobic bioremediation (biobarrier);
- Sorption materials were identified which are highly effective for removal of complex cyanides, SCN and NSO compounds;
- Zerovalent iron could effectively remove complex cyanide and thiocyanate; formation of free cyanide should be monitored;
- A multifunctional permeable reactive barrier may be a good treatment alternative for contaminated groundwater of MGP sites.

## 6.4 STEP 4: DESIGN & DIMENSIONING OF PILOT/FULL SCALE

PRB-barriers can be installed as continuous barriers or funnel-and-gate systems. For the latter, permeable barrier parts (gates) are altered with impermeable barrier parts (funnels) that have the function to funnel the groundwater through the gate (Figure 5). For multibarriers, the funnel & gate concept may have advantages as a multibarrier concept often allows a more easy installation and better control of a multibarrier.

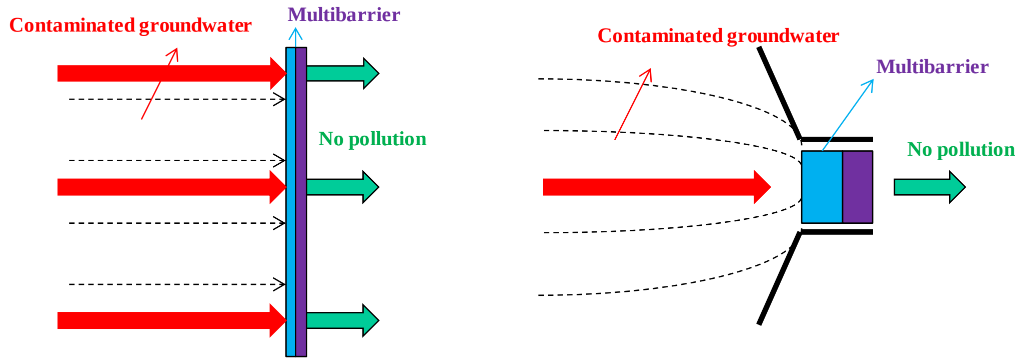


**Figure 5 Schematic representation of a continuous (left) and funnel & gate (right) PRB concept**

Within a gate several removable cartridges may be present in which different processes may be stimulated (Figure 6).

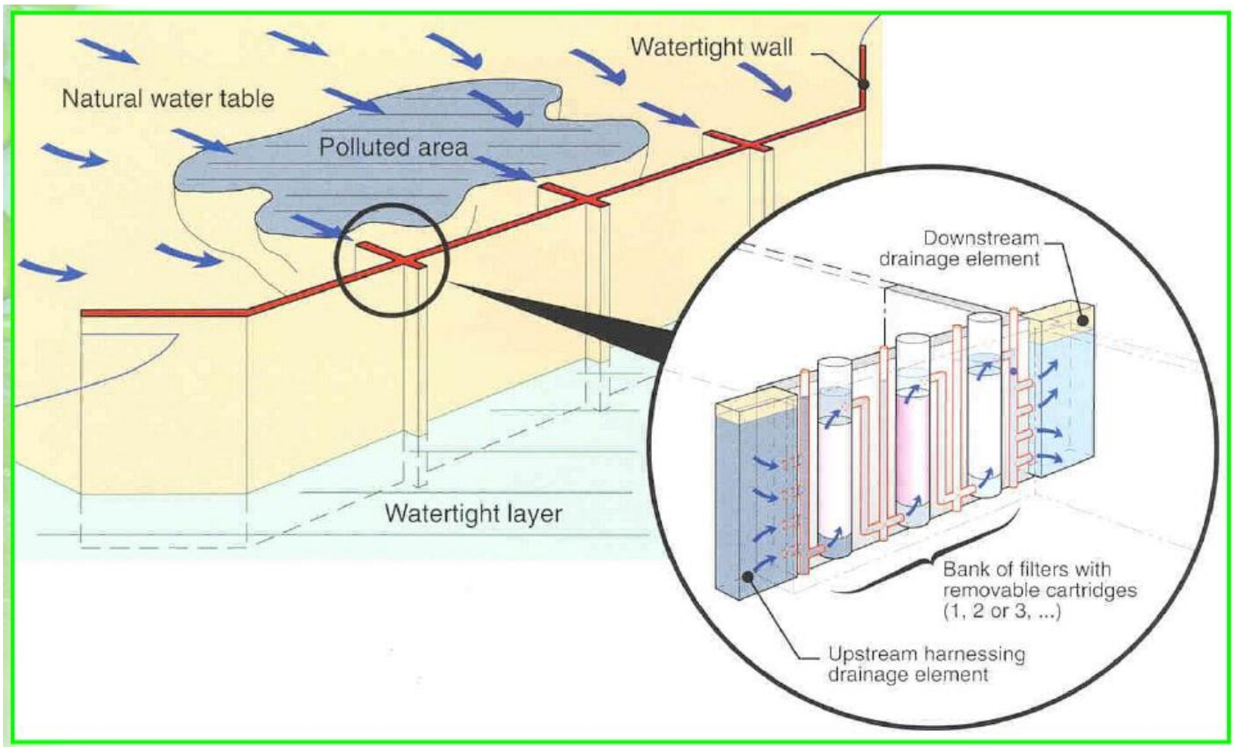


**Figure 6 Removable cartridges in a funnel and gate reactive barrier (after SolEnvironment)**

For an envisioned installation location at the site and the selected barrier type, the required length and depth of the barrier to catch the groundwater contamination plume are determine based on the collected field information.

Next, a minimal thickness of each multibarrier compartment can be calculated based on (1) the expected pollutant concentration in the influent of the barrier, (2) the groundwater flow velocity, (3) pollutant degradation rates deduced from feasibility test result and (4) the regulatory limits. Once the dimensions are determined, the required amount of filling material can be calculated as illustrated in Figure 7.

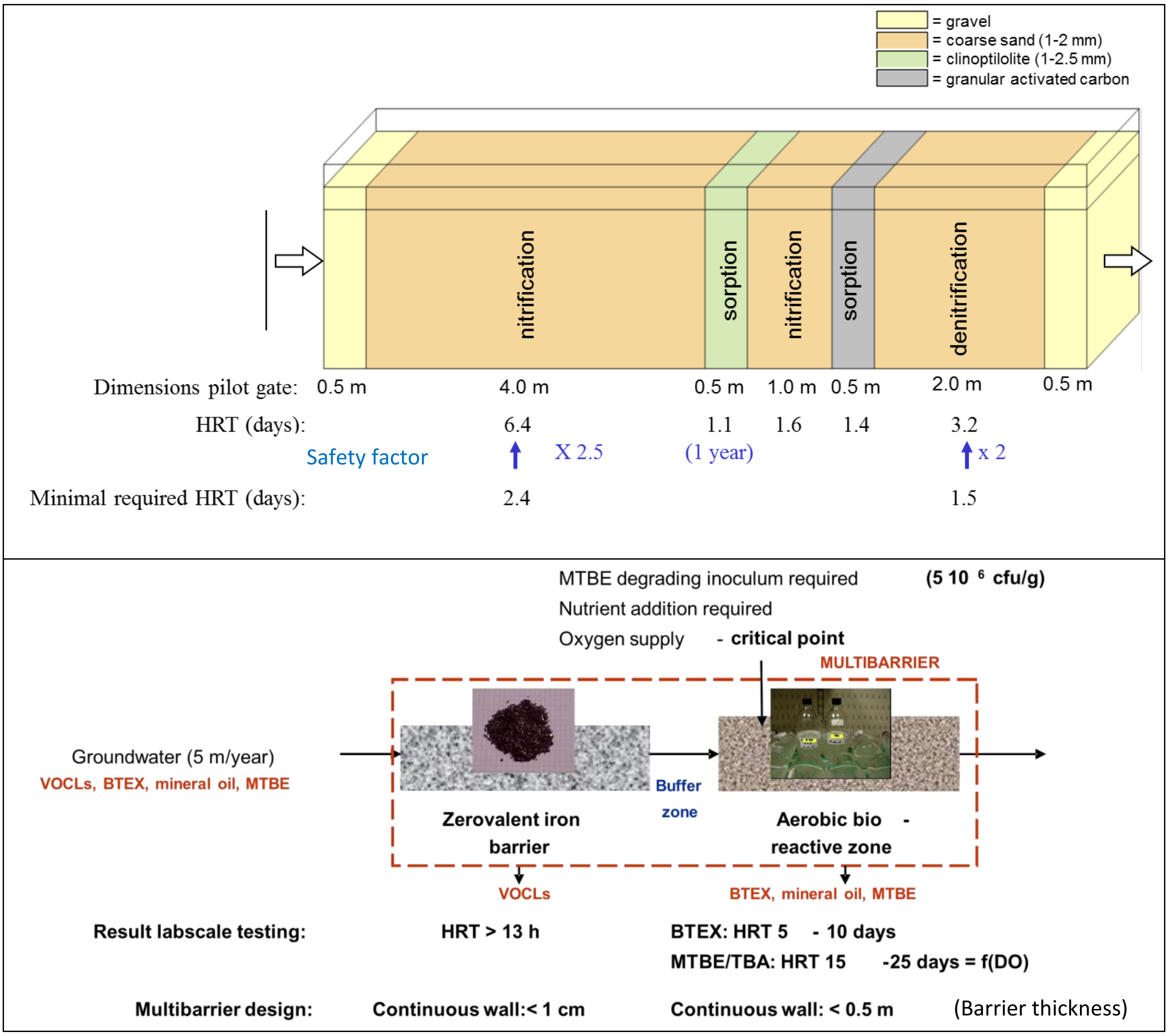


**Figure 7. Illustrations of multibarrier designs. (top) multibarrier design of the system depictured in Figure 2; (bottom) multibarrier design for a groundwater containing chlorinated compounds, BTEX, mineral oil and MTBE – The multibarrier concept comprises a zerovalent iron barrier for removal of the chlorinated compounds (VOCls) and an incolated bioreactive zone for aerobic removal of the BTEX, oil and MTBE -**

During the design phase, numerical modelling can be a help, as explained more detailed in section 7.

## 6.5 STEP 5: IMPLEMENTATION OF THE MULTIBARRIER TECHNOLOGY

This step comprises the installation of the multibarrier conform to the design parameters. Different implementation methods have been described and used.

- For reactive barriers, similar construction methods may be used as for single barriers (see DL4.3. Part A.2)., such as excavation, continuous trenching and vertical hydrofracturing.
- Stability measures during excavation can consist of sheet piling, secant walls, casings or more novel techniques using biodegradable slurry. The exact method used will depend on site characteristics. Some of these stability measures (such as sheet piling or secant walls) can be

quite expensive. Filling of the multibarrier system can consist of direct filling (in open excavations), prior filling in containers that are then placed into the excavation or step by step filling in different chambers.

- Construction of reactive zones is limited to the installation of the injection systems. Installation costs for reactive zones are therefore likely to be lower than for reactive barriers. Additional costs may be associated with the injected material.

Some images of the construction of a reactive barrier constructed for research purposes within the MULTIBARDEM LIFE-project are given Figure 8.

**Figure 8. Construction of a MULTIBARRIER at pilot scale in a container system, which is a similar process as filling a gate.**

## 6.6 STEP 6: MONITORING PERFORMANCE & CORRECTIVE ACTIONS

A post installation monitoring aims at following the performance of the multibarrier, where reduced pollutant concentrations downstream of the multibarrier are envisioned. Generally, permanent groundwater monitoring wells are installed upstream and downstream of the different multibarrier compartments and are sampled during the whole operation time. Beside chemical parameters, other parameters such as the groundwater levels before and behind the barrier are to be followed. For multibarriers, the installation of monitoring wells in between different sequential multibarrier parts is recommended.

Parameters recommended to be followed over time the performance may comprise (depending on multibarrier type):

- Groundwater level
- Groundwater velocity through the barrier
- Field parameters: pH, redox potential (ORP),dissolved oxygen, electrical conductivity (EC), temperature
- Organic analyses: pollutants of interest & potential breakdown products of concern

- Inorganic analyses like Calcium, Iron, Chloride, Magnesium, Alkalinity, Silicon in solution, Manganese, Nitrate and ammonium (when nitrate is present), phosphate, sulfate
- Microbiological parameters
- Etc.

Details on monitoring principles and associated recommendations are described in the generic guidelines for ZVI-barriers and biobarriers that were also composed within the AQUAREHAB project.

## 6.7 STEP 7: SITE CLOSURE

Generally, parts of the multibarriers are expected to remain in the subsurface once the site is closed. Multibarrier compartments which contain sorbed pollutants need to be regenerated or replaced to avoid release of the compound via desorption.

For more details on the different steps the reader is referred to the generic guidelines that were composed for ZVI-barriers and bioreactive zones that can both be part of a Multibarrier.

# 7 THE USE OF HP1 IN THE EXPERIMENTAL DESIGN OF MULTIBARRIERS – EXAMPLES FROM AQUAREHAB

## 7.1 INTRODUCTION

The implementation of an *in situ* groundwater remediation technology requires substantial knowledge on the behaviour of the groundwater system and the interaction with the given technology. Therefore, it is considered good practice to use the following steps: (1) site characterization, (2) selection of suitable pollutant removal mechanism, (3) lab scale test to verify the feasibility and derive design parameters, (4) design & dimensioning of a pilot/full scale, (5) implementation of the technology in the field, (6) monitoring and adjustments when needed, and (7) site closure. Practitioners tend to rely on expert knowledge to estimate the interaction of the groundwater system with the given technology, necessary in steps 2 to 6. This can prove effective for skilled practitioners and well established technologies. But for innovative technologies the multitude of reactions that can take place require special attention in the experimental design.

The coupled Hydrus-1D and PHREEQC model (HP1) can prove effective in different steps of the experimental design from the start of the conceptual model to the definition of boundary conditions and objectives for the actual experiments, as well as for the design of full scale multifunctional permeable reactive barriers. The concurrent simulation of flow, heat and mass transport allows to evaluate the uncertainties of the hydrological regime, the lab-scale constants and the potential effects of buffering or sorption capacities on the reactive barrier's performance. The use of HP1 is illustrated using a pilot test of a multifunctional reactive barrier treating landfill effluents at a site in Flanders, Belgium.

## 7.2 THE TEST CASE CONSIDERED WITHIN AQUAREHAB

A multi-barrier was constructed in the MULTIBARDEM project (LIFE06 ENV/B/000359) to treat the leachate from a landfill near Antwerp, Belgium. The leachate contains a large amount of contaminants at variable concentrations. E.g.: halogenated hydrocarbons (AOX) at 0.08 to 2.2 mg/L, ammonium at 2 to 1200 mg/L, BTEX at 72 to 475 mg/L and a chemical oxygen demand (COD) of 10 to 460 mg/L.

The multi-barrier system consists of 5 compartments to treat the various contaminants by denitrification, sorption and nitrification (Figure 9).

Two compartments contain oxygen diffusers to allow for nitrification and are separated by a clinoptinolite that sorbs peak amounts of ammonium. A compartment with granulated activated carbon (GAC) sorbs the AOX and COD. Butyrate is added to the final compartment to achieve anaerobic conditions and allow for denitrification to remove nitrates from the flow-through.

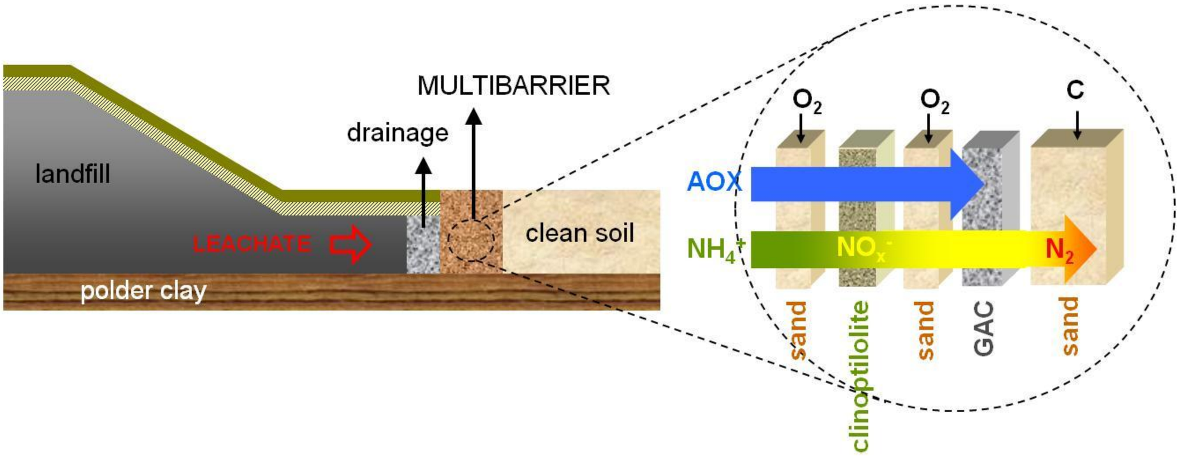


**Figure 9: The multi-barrier at site O to treat ammonium, AOX and COD of landfill effluent.**

The reactions in the different compartments were previously characterized in lab-scale experiments and were used to dimension the pilot-scale reactive barrier (Van Nooten et al., 2008, 2010). The two years of monitoring data were used in this study to evaluate how the HP1 model could have furthered the successful deployment of the pilot test by highlighting points of attention in the experimental design using lab-scale data (steps 3-6).

## 7.3 THE HP1 PROGRAM

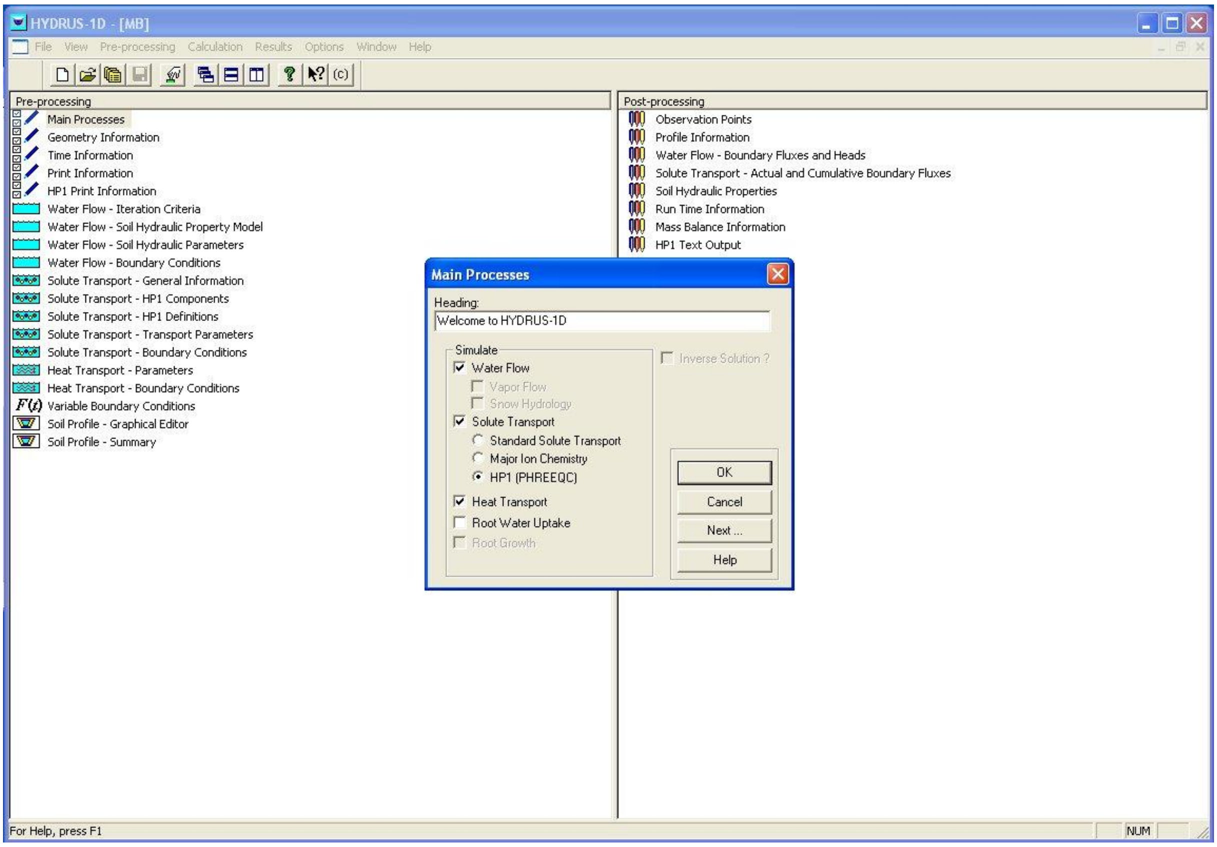
The HP1 program (acronym for HYDRUS1D-PHREEQC) is a significant expansion of the individual Hydrus-1D (Simunek et al., 2008) and PHREEQC (Appelo et al., 1998) programs. It contains modules to solve transient water flow, transport of multiple components, biogeochemical reactions and heat transport in one-dimensional variably saturated porous media. The versatility of the software to check for parameters related to the various governing processes in mass transport through porous media (water flow, mass transport and biogeochemical reactions) makes it an attractive option in the experimental design of multi-barriers. The water flow and mass transport is governed by Hydrus, while the biogeochemical reactions are calculated by PHREEQC and both programs are coupled in a split-operator approach.

HP1 comes with the graphical user interface provided in Hydrus. As such, the user only needs to define the studied domain with the appropriate boundary conditions and governing processes. The model calculations and required user manipulations are comprehensively elaborated in the manuals of Hydrus and HP1 (Jacques & Šimůnek, 2005; Jacques & Simunek, 2009a, 2009b; Simunek, Sejna, Saito, Sakai, & van Genuchten, 2013). The application of HP1 for the test case described above is provided with special attention to the inputs for the PHREEQC part of the program.

### 7.3.1 Inputs

The user needs to create a new project using the graphical user interface (Figure 10). The options can be changed at any time but take into account that this could cause a deletion of existing outputs. Not all screens will be exemplified below. But it is worthwhile noting that the appropriate units are defined in the geometry and time information screens (Figure 11). In addition, the user should define the number of time-variable boundary conditions, i.e. the number of times that one of the boundary conditions for flow, mass or heat transport changes. If options are not clear one can press “help” to enter the electronic manual with concise information of each screen.

In this example, the barrier was homogenously discretized at 5 cm and 5 different materials were defined for the different compartments. These were characterized by their measured porosities but were given equal hydraulic conductivities of 7.2 m/day since no additional data were available. This also applied for the solute transport with a homogeneous dispersivity of 0.4 m, and for the heat transport parameters that were derived from the default values for sand in the HP1 program. The monitoring data yielded 47 time-variable boundary conditions in the barrier over a time-span of 719 days.

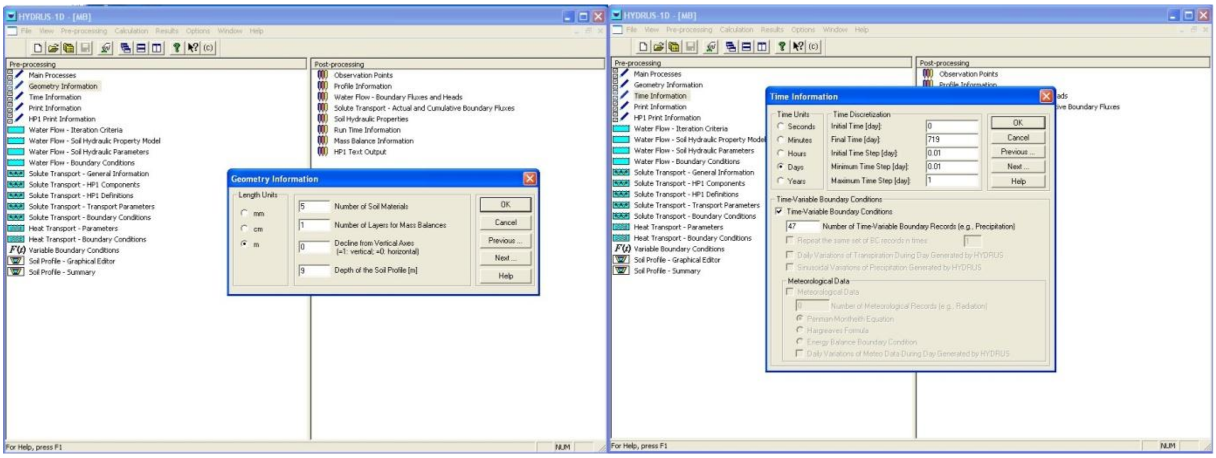


Heading: Welcome to HYDRUS-1D

Simulate
- ☑ Water Flow
  - ☐ Vapor Flow
  - ☐ Snow Hydrology
- ☑ Solute Transport
  - ○ Standard Solute Transport
  - ○ Major Ion Chemistry
  - ● HP1 (PHREEQC)
- ☑ Heat Transport
- ☐ Root Water Uptake
- ☐ Root Growth

☐ Inverse Solution ?

**Figure 10: the graphical user interface of HP1 with the definition of a new project.**



Geometry Information

Length Units: ○ mm ○ cm ● m

5 Number of Soil Materials
1 Number of Layers for Mass Balances
0 Decline from Vertical Axes (=1: vertical; =0: horizontal)
9 Depth of the Soil Profile [m]

Time Information

Time Units: ○ Seconds ○ Minutes ○ Hours ● Days ○ Years

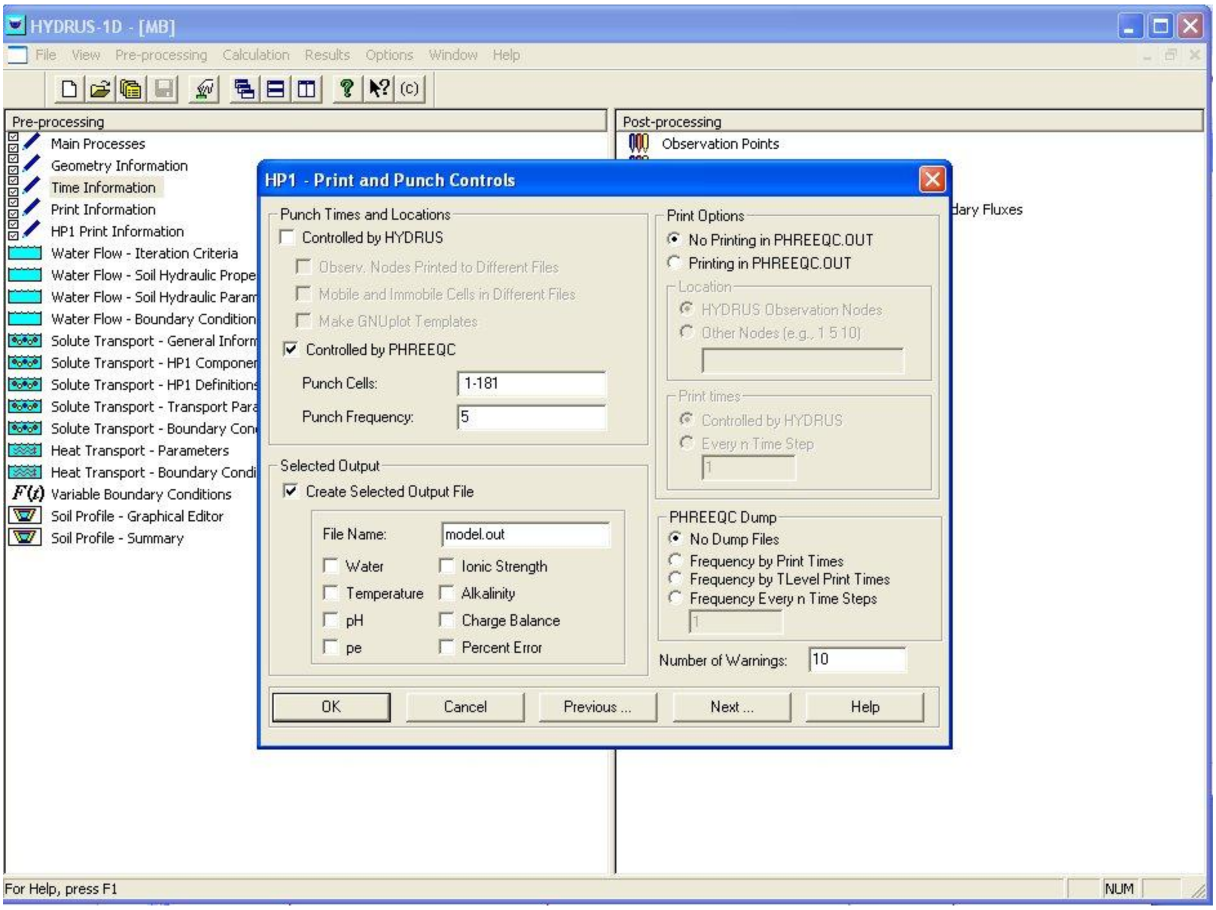
Time Discretization
Initial Time [day]: 0
Final Time [day]: 719
Initial Time Step [day]: 0.01
Minimum Time Step [day]: 0.01
Maximum Time Step [day]: 1

Time-Variable Boundary Conditions
☑ Time-Variable Boundary Conditions
47 Number of Time-Variable Boundary Records (e.g., Precipitation)
☐ Repeat the same set of BC records n times 1
☐ Daily Variations of Transpiration During Day Generated by HYDRUS
☐ Sinusoidal Variations of Precipitation Generated by HYDRUS

Meteorological Data
☐ Meteorological Data
0 Number of Meteorological Records (e.g., Radiation)
● Penman-Montheith Equation
○ Hargreaves Formula
○ Energy Balance Boundary Condition
☐ Daily Variations of Meteo Data During Day Generated by HYDRUS

**Figure 11: the definition of the geometry information (left) and the time information (right)**

Users familiar with Hydrus will prefer the output to be printed in that format. But for users that are more familiar with PHREEQC, the user interface provides the option to obtain the output of the mass transport calculations as defined in PHREEQC (Figure 12). Mind that you manually take into account or correct for the number of cells that is defined by the discretization in a later stage and the output frequency that is related to the time discretization.



HP1 - Print and Punch Controls

Punch Times and Locations
☐ Controlled by HYDRUS
☐ Observ. Nodes Printed to Different Files
☐ Mobile and Immobile Cells in Different Files
☐ Make GNUplot Templates
☑ Controlled by PHREEQC
Punch Cells: 1-181
Punch Frequency: 5

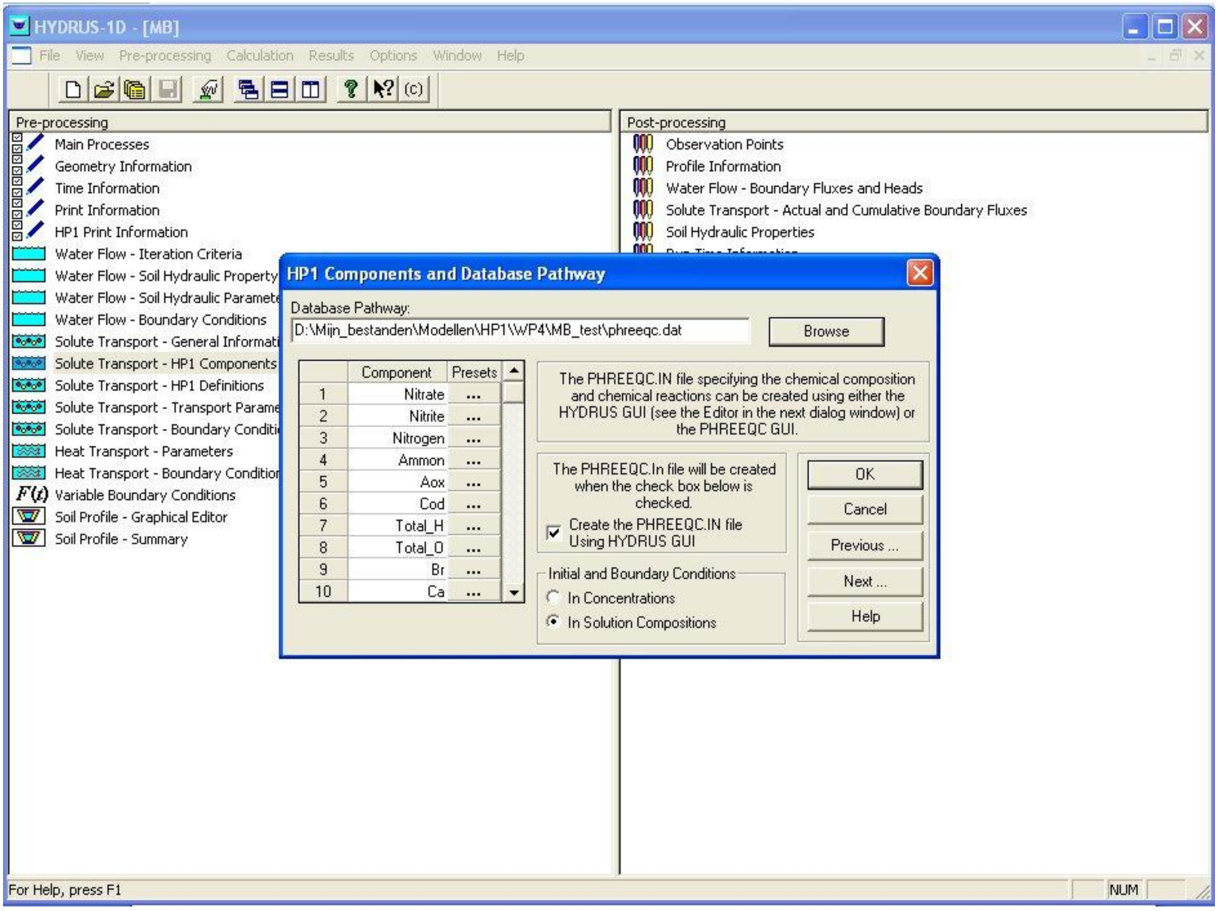
Selected Output
☑ Create Selected Output File
File Name: model.out
☐ Water ☐ Ionic Strength
☐ Temperature ☐ Alkalinity
☐ pH ☐ Charge Balance
☐ pe ☐ Percent Error

Print Options
● No Printing in PHREEQC.OUT
○ Printing in PHREEQC.OUT
Location
● HYDRUS Observation Nodes
○ Other Nodes (e.g., 1 5 10)
Print times
● Controlled by HYDRUS
○ Every n Time Step
1

PHREEQC Dump
● No Dump Files
○ Frequency by Print Times
○ Frequency by TLevel Print Times
○ Frequency Every n Time Steps
1
Number of Warnings: 10

**Figure 12: the user can opt for output in the format of Hydrus, GNUplot or as defined in PHREEQC.**

The solute transport is defined in PHREEQC and up to 18 substances can be described simultaneously (Figure 13). The code actually transports up to 20 components but one should always define Total_H and Total_O for the PHREEQC model to work correctly. The remaining components should be defined in the database or by the HP1 definitions (see further). The easiest interaction with PHREEQC is obtained by letting the Hydrus GUI take care of the changes between cells and nodes and the correct assignment of boundary conditions and material properties.



Database Pathway: D:\Mijn_bestanden\Modellen\HP1\WP4\MB_test\phreeqc.dat

| | Component | Presets |
|---|---|---|
| 1 | Nitrate | ... |
| 2 | Nitrite | ... |
| 3 | Nitrogen | ... |
| 4 | Ammon | ... |
| 5 | Aox | ... |
| 6 | Cod | ... |
| 7 | Total_H | ... |
| 8 | Total_O | ... |
| 9 | Br | ... |
| 10 | Ca | ... |

The PHREEQC.IN file specifying the chemical composition and chemical reactions can be created using either the HYDRUS GUI (see the Editor in the next dialog window) or the PHREEQC GUI.

The PHREEQC.In file will be created when the check box below is checked.

☑ Create the PHREEQC.IN file Using HYDRUS GUI

Initial and Boundary Conditions

○ In Concentrations

● In Solution Compositions

**Figure 13: the pathway to the PHREEQC database and the components that are discerned in PHREEQC for this model.**

The HP1 definitions are the core of PHREEQC in the HP1 model (Figure 14). The first option with the additions to the thermodynamic database allows to add new substances and reactions with the same keyword datablocks as in PHREEQC. In this example, microbial reactions were approximated by 1st order kinetics adjusted for temperature dependant degradation as described by the Arrhenius equation assuming that the reaction rate is halved with a temperature decrease of 10°C:

$$\frac{\partial C}{\partial t} = k_{T1} \times EXP\left(\frac{-E_a}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]\right) \times C$$

With C the modelled compound, $k_{t1}$ the reaction rate at lab temperature $T_1$, $E_a$ the activation energy, R the gas constant and $T_2$ the ambient temperature in that modelled period. The nitrification rates were determined at 2.67 to 2.82 day$^{-1}$ and the denitrification rate at 17.7 day$^{-1}$. Sorption of COD and AOX on the GAC was described as a first order kinetics with an assumed maximal sorption capacity of 10 g/L:

$$\frac{\partial C}{\partial t} = k \times C \times \left(1 - \frac{C_{COD,s} + C_{AOX,s}}{10}\right)$$

With C the concentration of COD or AOX in the aqueous phase and $C_{x,s}$ the relative sorbed concentration on the GAC. The sorption constant was similar for both compounds and was found to be 1.94 day$^{-1}$. The clinoptinolite was characterised as an ion exchanger with a capacity of 0.358 eq/L.

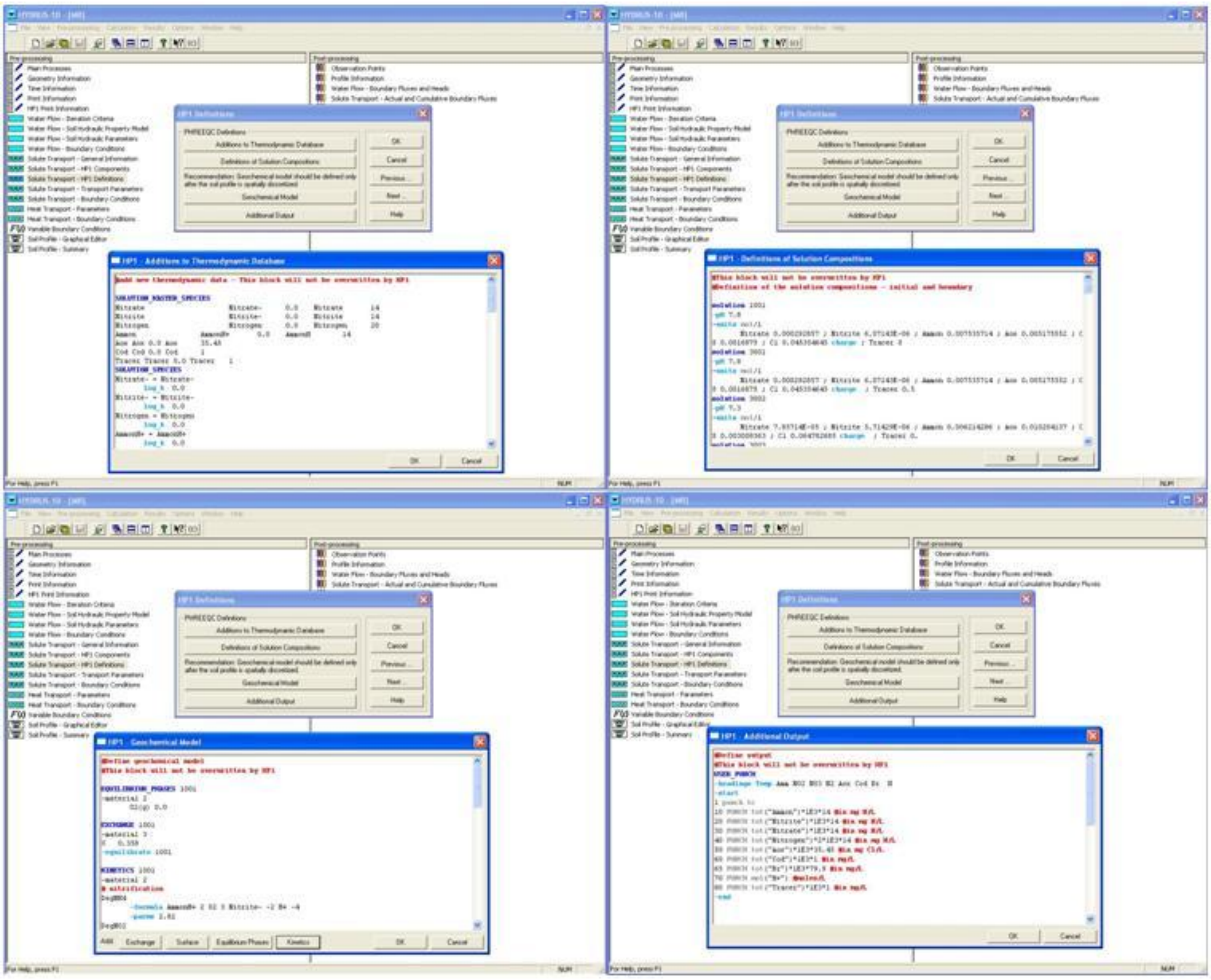
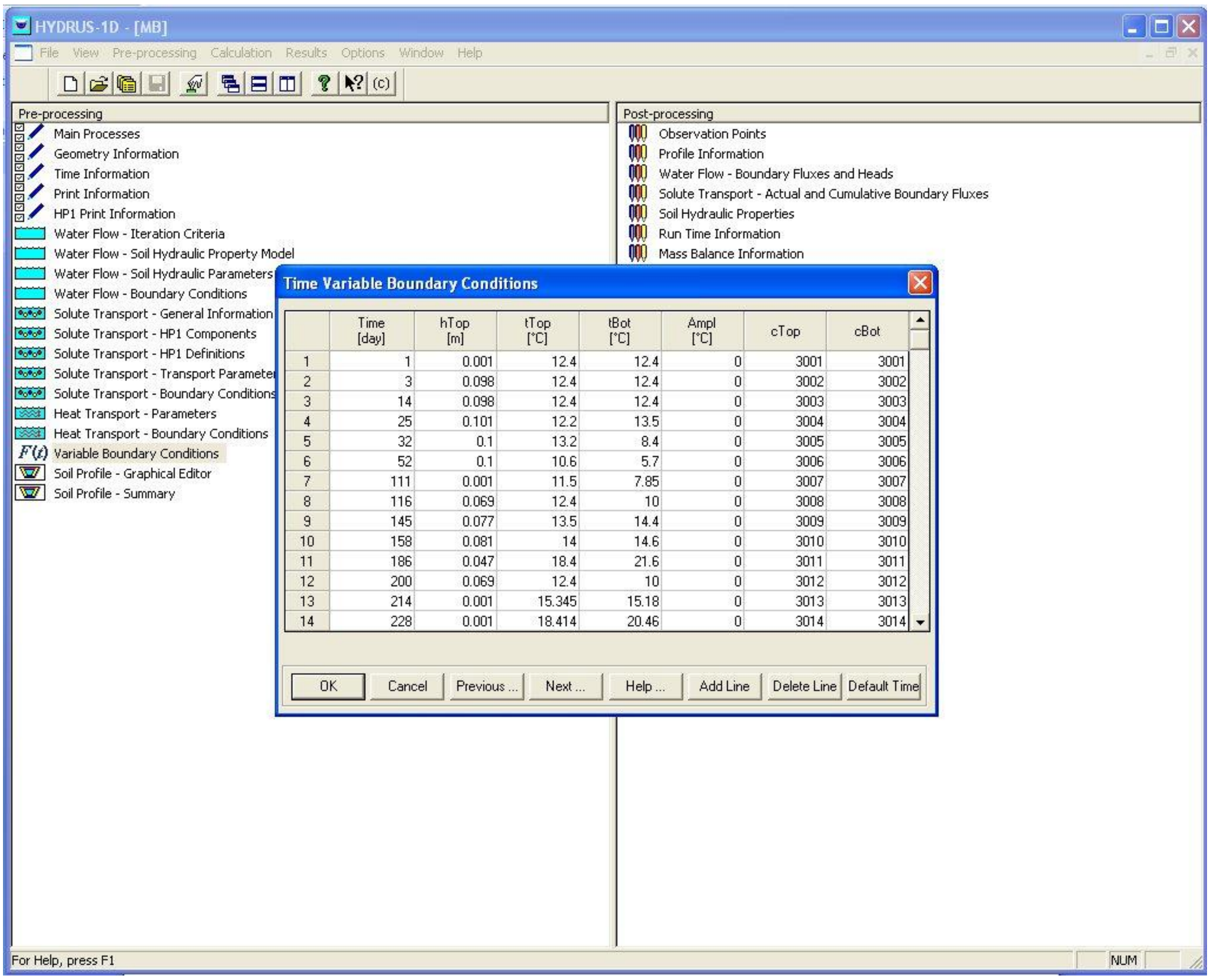


**Figure 14: the HP1 definitions with from left to right: the additions to the thermodynamic database, the definitions of solution compositions, the geochemical model and the additional output.**

The initial and boundary conditions for the mass transport were set to ‘In Solution Composition’. In this case each new influent solution is characterized by a number in the ‘Definition of Solution Compositions’ option. And for each number the concentration of all components is defined. The parameters for the equations that were previously defined are given in the ‘Geochemical Model’. One can appoint different rate constants to the different materials by simply referring to the materials number as defined in the GUI (see further). The required output is defined in the ‘Additional Output’ if the PHREEQC output was previously selected.

The time variable boundary conditions of flow and heat transport are defined by the end of the pre-processing steps (Figure 15). Water flow boundary conditions (BCs) were defined by the variable pressure heads, solute transport by a concentration BC at the inflow and a zero concentration gradient at the outflow, and heat transport by two temperature BCs. The water flow and heat transport boundary conditions are given in this step. The boundary conditions for the mass transport were already defined above and a simple reference to the respective solution numbers is all that is required at this stage. If the initial and boundary concentrations were set to ‘In Concentrations’ the concentrations of all substances should have been given in this step instead of in the HP1 definitions.



Time Variable Boundary Conditions

|  | Time [day] | hTop [m] | tTop [°C] | tBot [°C] | Ampl [°C] | cTop | cBot |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.001 | 12.4 | 12.4 | 0 | 3001 | 3001 |
| 2 | 3 | 0.098 | 12.4 | 12.4 | 0 | 3002 | 3002 |
| 3 | 14 | 0.098 | 12.4 | 12.4 | 0 | 3003 | 3003 |
| 4 | 25 | 0.101 | 12.2 | 13.5 | 0 | 3004 | 3004 |
| 5 | 32 | 0.1 | 13.2 | 8.4 | 0 | 3005 | 3005 |
| 6 | 52 | 0.1 | 10.6 | 5.7 | 0 | 3006 | 3006 |
| 7 | 111 | 0.001 | 11.5 | 7.85 | 0 | 3007 | 3007 |
| 8 | 116 | 0.069 | 12.4 | 10 | 0 | 3008 | 3008 |
| 9 | 145 | 0.077 | 13.5 | 14.4 | 0 | 3009 | 3009 |
| 10 | 158 | 0.081 | 14 | 14.6 | 0 | 3010 | 3010 |
| 11 | 186 | 0.047 | 18.4 | 21.6 | 0 | 3011 | 3011 |
| 12 | 200 | 0.069 | 12.4 | 10 | 0 | 3012 | 3012 |
| 13 | 214 | 0.001 | 15.345 | 15.18 | 0 | 3013 | 3013 |
| 14 | 228 | 0.001 | 18.414 | 20.46 | 0 | 3014 | 3014 |

**Figure 15: the time variable boundary conditions for water flow, heat and mass transport.**

Finally, the profile of the system is defined in the graphical interface by selecting the discretization (mind the earlier selections in PHREEQC!), appointing the correct materials, setting initial conditions and eventual observations points for the Hydrus output (Figure 16). The final step summarizes the inputs that were given in the graphical editor and allow for manual changes.

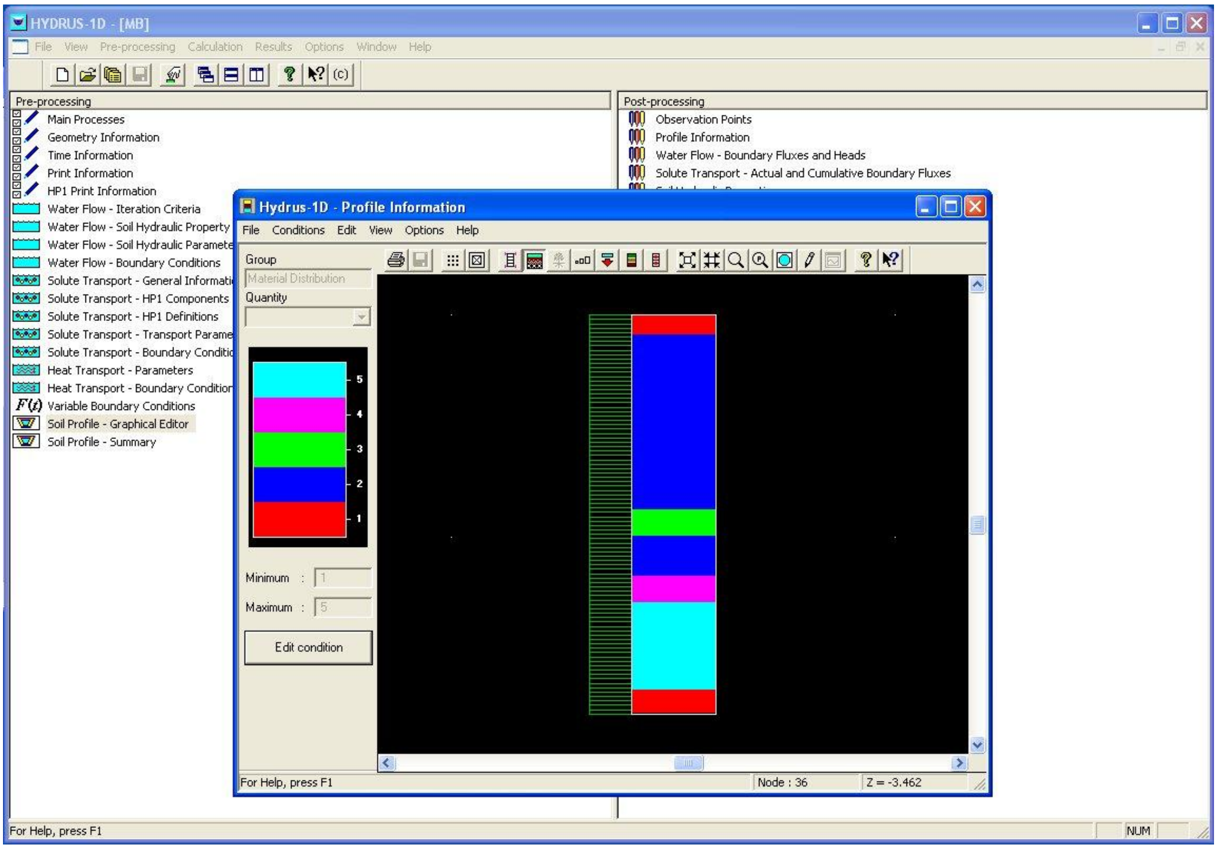
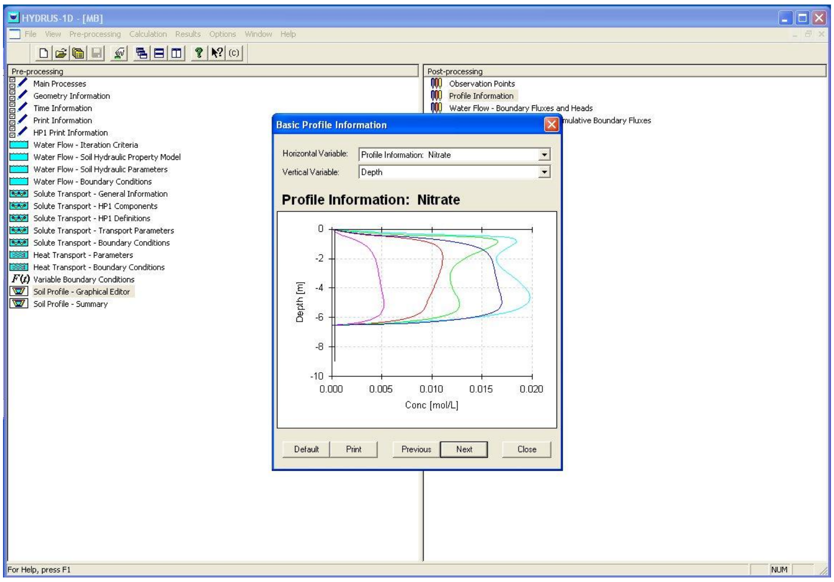


**Figure 16: the graphical editor of the soil profile defining the different materials in the system etc.**

### 7.3.2 Outputs

The program is started by pressing the green button at the top and the output of Hydrus is shown in the post-processing menu in the screen at the right. Information is supplied for the defined observations points, the entire profile, the boundary fluxes and some run time and mass balance information. The standard Hydrus output looks like Figure 17 but you can use the Hydrus or PHREEQC output in other software packages to create output like in Figure 18.



Horizontal Variable: Profile Information: Nitrate

Vertical Variable: Depth

Figure 17: standard Hydrus output for the Nitrate profile in the system in time

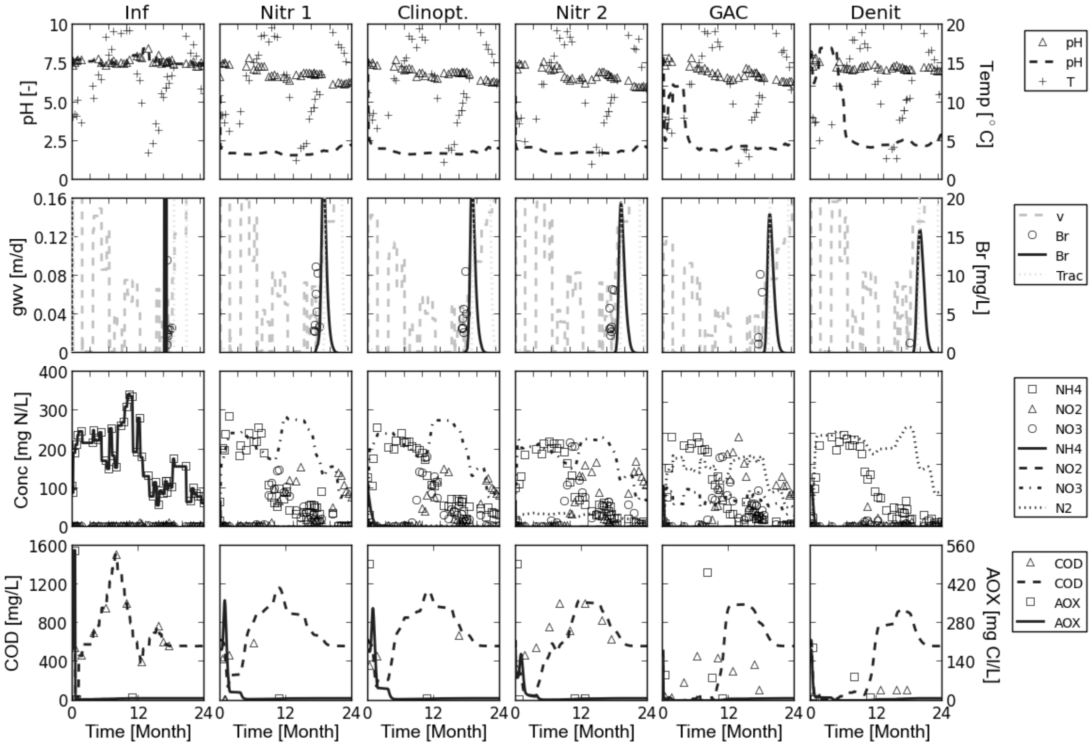


Figure 18: The PHREEQC output was imported in Python and processed using Matplotlib. The simulation of contaminant dynamics in the multifunctional permeable reactive barrier treating landfill leachate (simulated: lines, observed: dots). The barrier consists of five different compartments: nitrification, ion-exchange (clinoptinolite), nitrification, sorption (granular activated carbon) and denitrification to remove ammonium, halogenated aliphatics (AOX) and other organic compounds (COD) from the landfill leachate. The top graphs show the pH and temperature profiles throughout the barrier. The second row of graphs show the pore water velocity (v), and the bromide tracer. The third row of graphs show the different nitrogen components and the bottom row indicates the observed and modelled concentrations of AOX and COD.

# 8 CONTACTS

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