Final report

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1 EXECUTIVE SUMMARY

AQUAREHAB is an EU financed research project (FP7) that started May 1st 2009 with 19 project partners. The overall quality status of fresh water resources is determined by (1) the kind and quantity of contaminants that are released in the water system and (2) the migration of the pollutants (via groundwater and run-off) towards different rivers, lakes, and seas. The migration of pollutants towards vulnerable receptors (drinking-water reserves in the subsurface, surface waters, water wells) is of particular concern. Within the AQUAREHAB project, different innovative rehabilitation technologies for soil, groundwater and surface water were studied to cope with a number of priority contaminants (nitrates, pesticides, chlorinated compounds, aromatic compounds, mixed pollutions…) within heavily degraded water systems. Methods were elaborated to determine the (long-term) impact of the innovative rehabilitation technologies on the reduction of the influx of these priority pollutants towards the receptor. Efforts were made to connect the innovative technologies and river basin management. A diverse set of results was obtained, which may be relevant for national and local water managers, planners and other stakeholders (drinking water companies, industry, agriculture, recreation and nature conservation), to revive highly polluted areas. The main outcomes of the AQUAREHAB project are summarised in Figure 1 and described below.

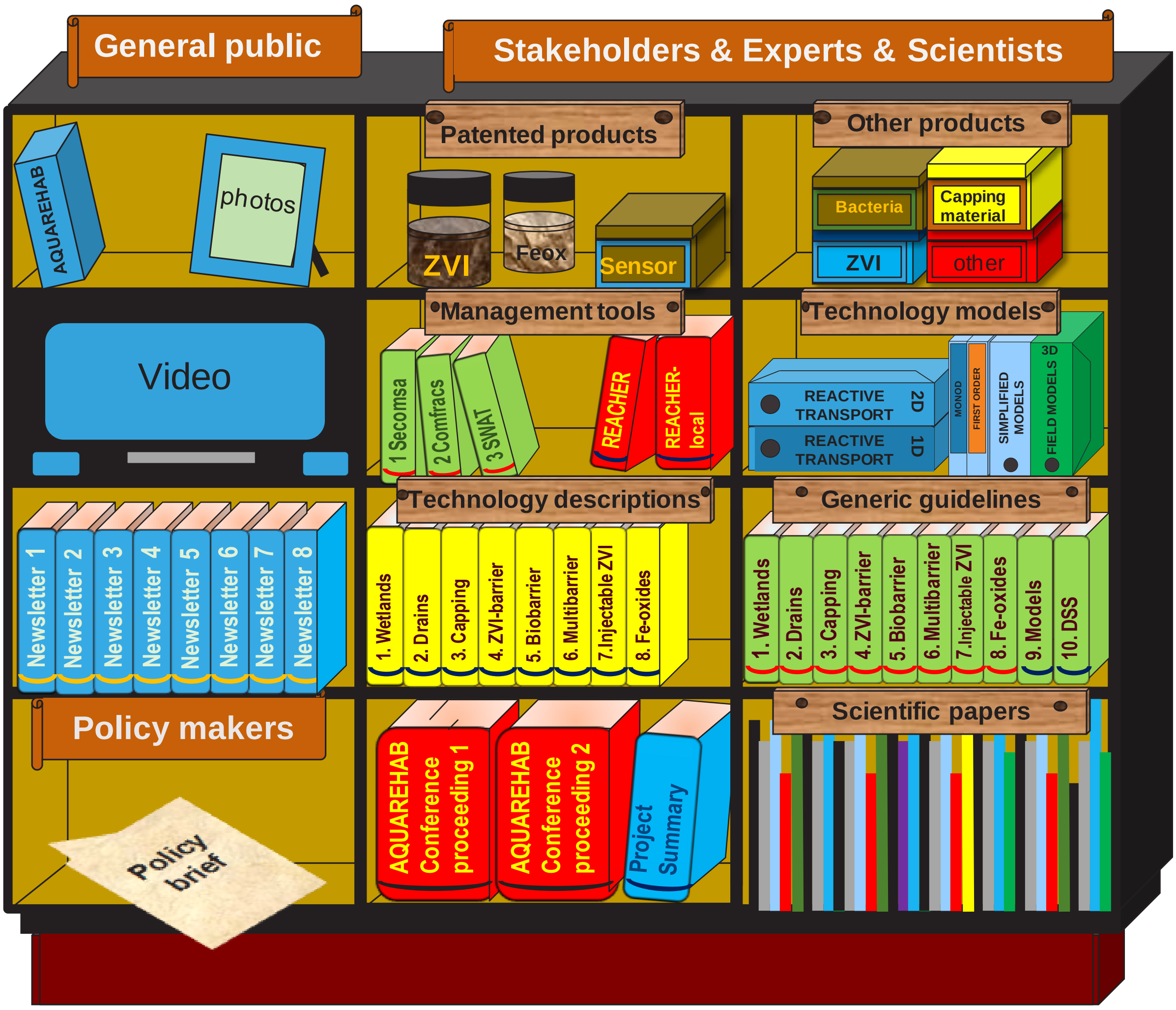


Figure 1. Overview of AQUAREHAB output –more details are available at aquarehab.vito.be.

2 A SUMMARY DESCRIPTION OF PROJECT CONTEXT AND OBJECTIVES

Fresh water resources consist of surface water and groundwater. Water utilisation is influenced by water quality, whether it be for drinking, industrial, recreational or irrigation purposes. The overall quality status of fresh water resources is determined by (1) the kind and quantity of contaminants that are released in the water system by a variety of inputs, being either diffuse or point sources and (2) the migration of the pollutants (via groundwater and run-off) towards different rivers, lakes, and seas. The migration of pollutants towards vulnerable receptors (drinking-water reserves in the subsurface, surface waters, water wells) is of particular concern.
Currently, rehabilitation technologies that intend (1) to remove source zones or (2) to prevent further migration of the pollutants into ground- and surface waters, are mostly not addressing the impact of the remedial action on the whole water system. This makes the integration of remedial actions and needs into river basin management difficult.

AQUAREHAB is an EU financed large scale research project (FP7) that started May 1st 2009 with 19 project partners. The AQUAREHAB consortium worked together on the project for 56 months (2013). Within this project, different innovative rehabilitation technologies for soil, groundwater and surface water were developed to cope with a number of priority contaminants (nitrates, pesticides, chlorinated compounds, aromatic compounds, mixed pollutions…) within heavily degraded water systems. Methods were developed to determine the (long-term) impact of the innovative rehabilitation technologies on the reduction of the influx of these pollutants, of which some are on the list of priority substances, towards the receptor. Possible connections and barriers between the innovative technologies and river basin management were evaluated. Some target outcomes of the project were (1) generic guidelines for the use & design of the technologies and (2) a generic river basin management tool that integrates multiple measures with ecological and economic impact assessments of the whole water system.

In a first stage of the project (year 1-3), the technologies and approaches for integration of their impact in river basin management were developed linked to contaminated areas in three different river basins (Denmark, Israel, Belgium), representing different large-scale complex problems.

The Odense river basin (Denmark). The Odense river basin is situated at the island of Funen, Denmark (Figure 2). The catchment is draining a land area of approximately 1.100 km^2 and includes 1.100 km streams and 2600 lakes and larger ponds. Agriculture is dominating the land use (1/3 of the catchment), but also grasslands and forests are represented (1/4 of the catchment). Other 6% are covered by mires, freshwater and costal meadows. The Odense River is the final receptor in the basin. The Odense River is heavily impacted by agriculture and receives nitrate and pesticides from adjacent groundwater bodies and atmosphere. The Odense river basin has several re-established wetlands and a comprehensive amount of data is available related to wetland restoration (Funen County 2003).

Secher-Besor Basin (Israel). The groundwater within the chalk aquitard in the Bessor-Secher Basin at the northern Negev is heavily contaminated with industrial pollutants, including halogenated contaminants, pesticides and hydrocarbon residues, which are relatively stable (or with relatively long halve-life times) in the sub-surface environment. This groundwater section is located in the most upper part of the Bessor basin endangering the down-stream streams as well as local and regional groundwater resources of the southern coastal aquifer of Israel and of Palestine Authority (WP2, Figure 2). Of particular concern is the potential of contaminants seeping from the shallow elevated groundwater through the riparian zone to the Secher wash that accumulate hazardous dissolvable salts along the stream beds to be later rapidly transported downstream in the event of floods.

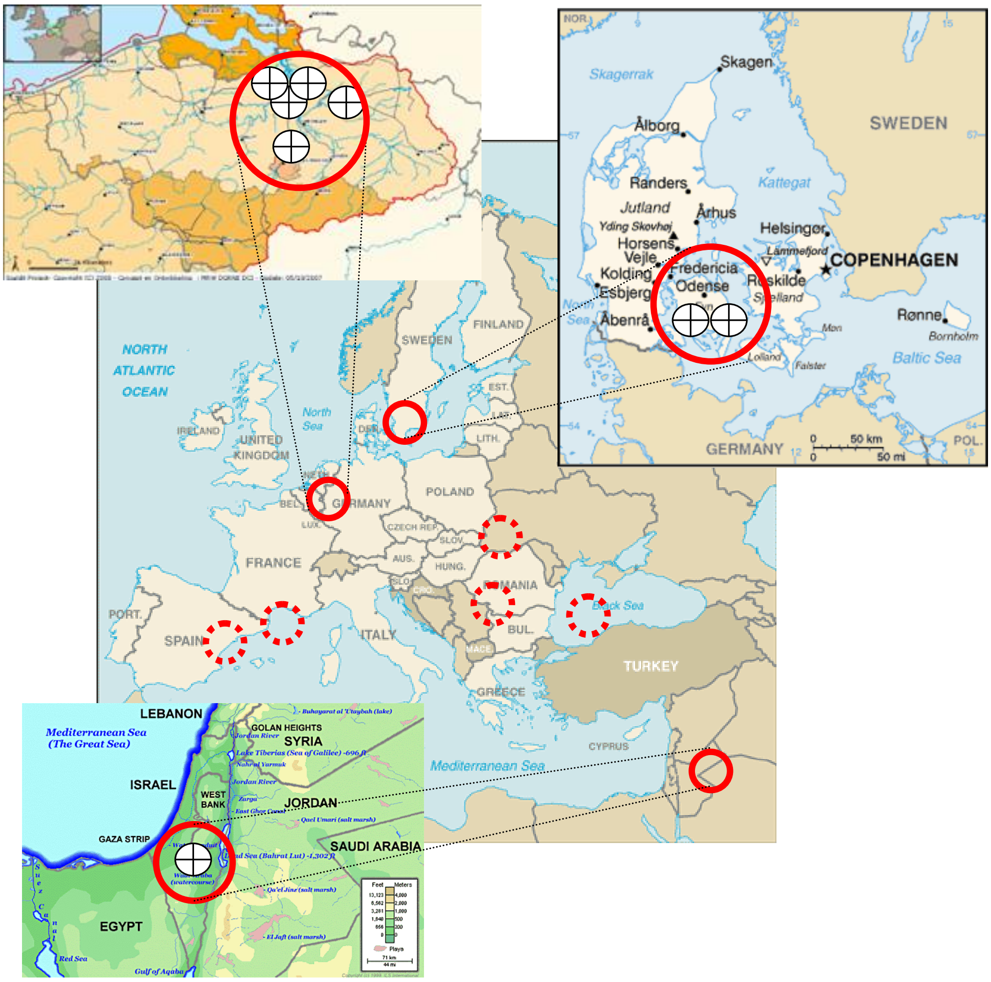


Figure 2: Overview of case studies and river basins studied in the AQUAREHAB project. (full circle: river basins selected for first phase of the AQUAREHAB; dashed circles: potential river basins for second phase of AQUAREHAB)

<u>Scheldt river basin</u> (Belgium). The transboundary Scheldt extends from northern France, across Belgium to the southern Netherlands (Figure 2). It is one of the most polluted water systems in Europe, due to pressures from a high population density, and intensive industrial and agricultural activities. Crucial final receptors that are threatened include surface waters (high COD, low oxygen, little fish) and the ground water drinking reserves. Within the Scheldt river basin, the downstream estuary of the Dender into the Scheldt river is considered. Especially (1) the Zenne river, which up until 3 years served as the open sewage system for the domestic wastewater of Brussels, and which is in addition under pressure from industrial point sources and groundwater pollution (WP3); and (2) the Antwerp region where the groundwater is degraded due to industrial and urban activities, hereby threatening surface water and drinking water reserves in the subsurface (groundwater) (WP4&5).

In a second stage (Year 3-5), the generic approaches and tools developed were extrapolated to other locations to evaluate the generic character.

The project concept is visualized in Figure 3. The basic idea is that multiple pollution sources (diffuse and point source) exist which result each in a flux (M) of pollutants towards receptors. As such the receptors receive degraded water, being the sum of different fluxes (M1+M2+M3+M4+…). The aim of rehabilitation technologies is to reduce the fluxes to an acceptable level, which is a function of the vulnerability of the area, ecotoxicological characteristics of the pollution and socio-economical aspects. The aim was to evaluate whether the whole water system, including surface water as well as groundwater, can be managed by a generic river basin management tool that integrates the investigated rehabilitation technologies with ecological and economic impact assessments of the whole water system.

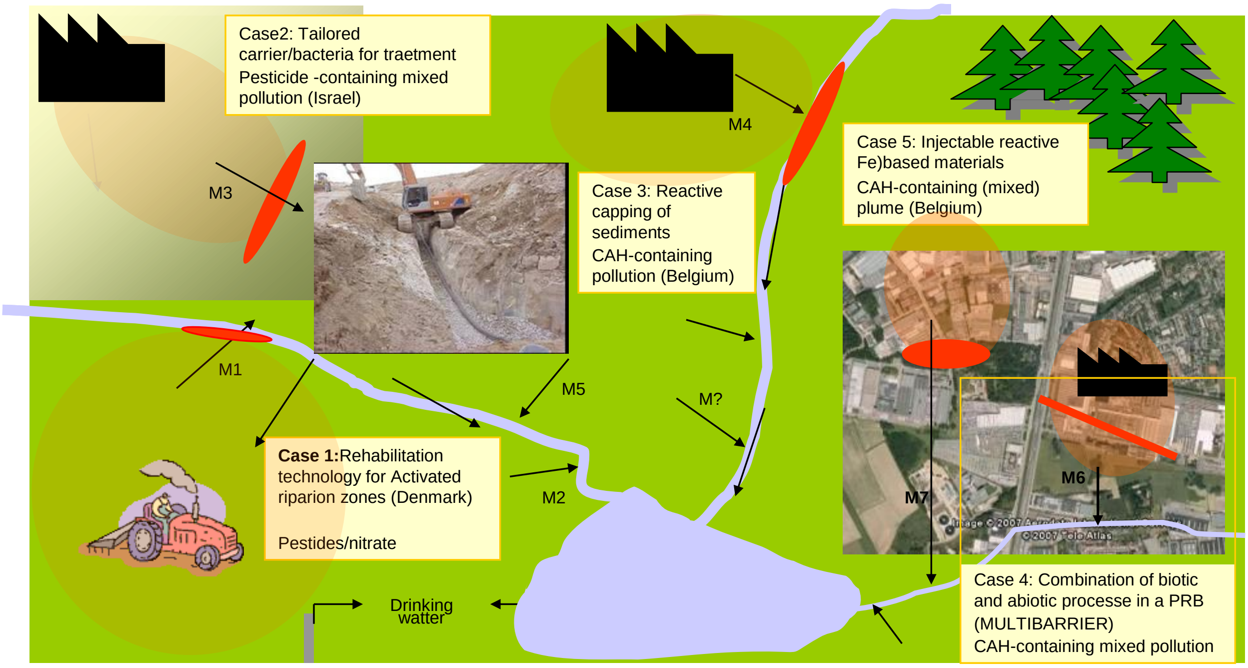


Figure 3: Schematic overview of different pollutant fluxes (M1, M2, M3, …) influencing the quality status of a river basin part. The different innovative rehabilitation technologies that are considered in the project are indicated.

The project aimed to be an aid in underpinning river basin management plans being developed in EU Member States, and to demonstrate cost-effective technologies that can provide technical options for national and local water managers, planners and other stakeholders (drinking water companies, industry, agriculture, recreation and nature conservation) to revive highly polluted areas.

The objectives of AQUAREHAB were:

1. To develop within the first 3 years of the project a variety of innovative rehabilitation technologies for representative types of pollution (source zones, contamination plumes, diffuse pollution) and compounds that are of concern in degraded water bodies (e.g. pesticides, nitrate, Chlorinated Aliphatic Hydrocarbons, BTEX). The innovative rehabilitation technologies that were studied in the project are:
    - ❖ Activated riparian zones/wetlands (diffuse pollution –nitrate & pesticides) (WP1);
    - ❖ Bioremediation of pesticide-containing degraded water in open trenches with smart biomass containing materials (WP2);

- ❖ Bioreactive zones in aquifer and sediments (capping) to rehabilitate surface water degraded by influx of pollutants from the groundwater (chlorinated ethenes)(WP3);
- ❖ Multifunctional permeable barriers (multibarriers) for mixed groundwater contamination plumes (WP4); and,
- ❖ In-situ reduction or oxidation of hazardous pollutants in groundwater/aquifer with injectable Fe-based particles (chlorinated compounds & BTEX)(WP5).

2. To develop methods (feasibility tests), tools (numerical models) and guidelines to design the mentioned rehabilitation technologies and to determine their (long-term) impact on local fluxes of pollutants (WP1-5, 7).
3. To develop a collaborative management tool 'REACH-ER' that can be used by stakeholders, decision makers and water managers to evaluate the ecological and economical effects of different remedial actions on river basins (WP6).
4. Development of an approach to link the effects of the rehabilitation technologies with a river basin management tool REACH-ER (WP7).
5. To evaluate and disseminate in the second part of the project the generic rehabilitation guidelines, approaches and tools by applying them to other river basins with other pollutant conditions, climates, etc. in collaboration with end-users (WP8).

The relation between the different work packages (WP) are schematically represented in Figure 4.

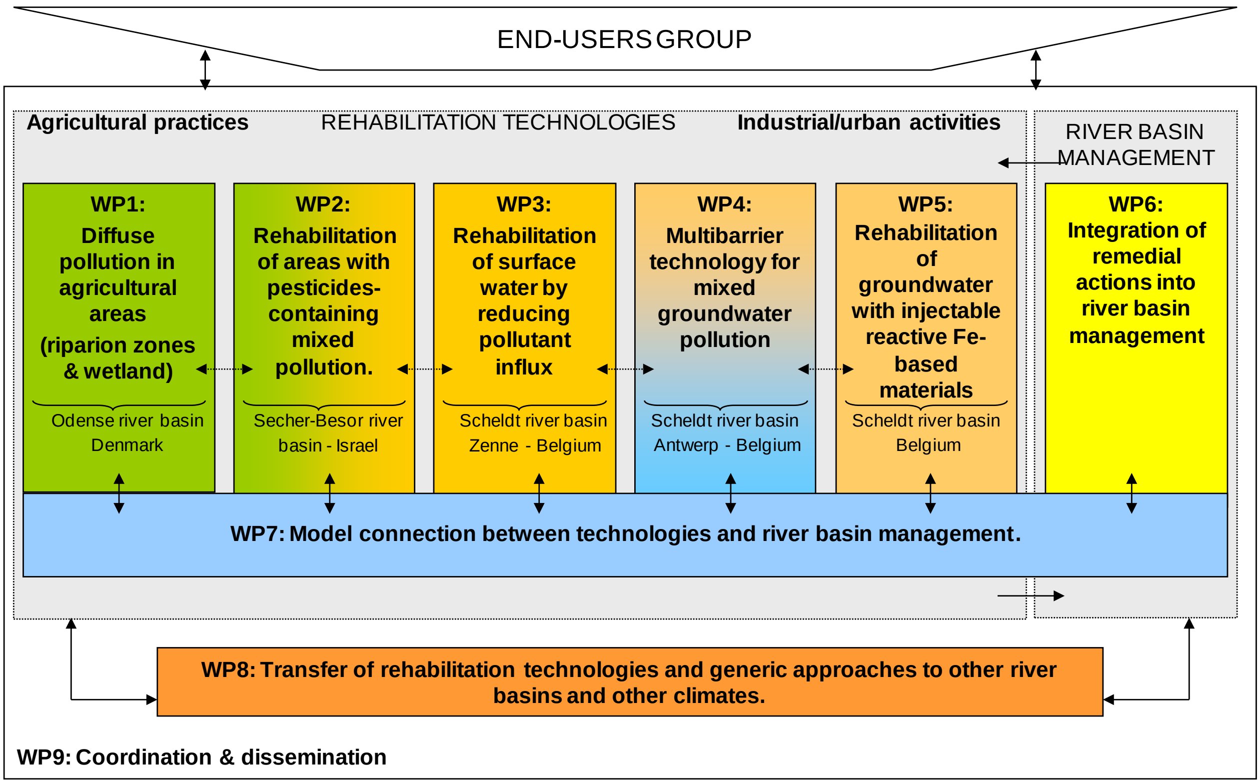


Figure 4: Schematic overview of the links between the different work packages defined within AQUAREHAB.

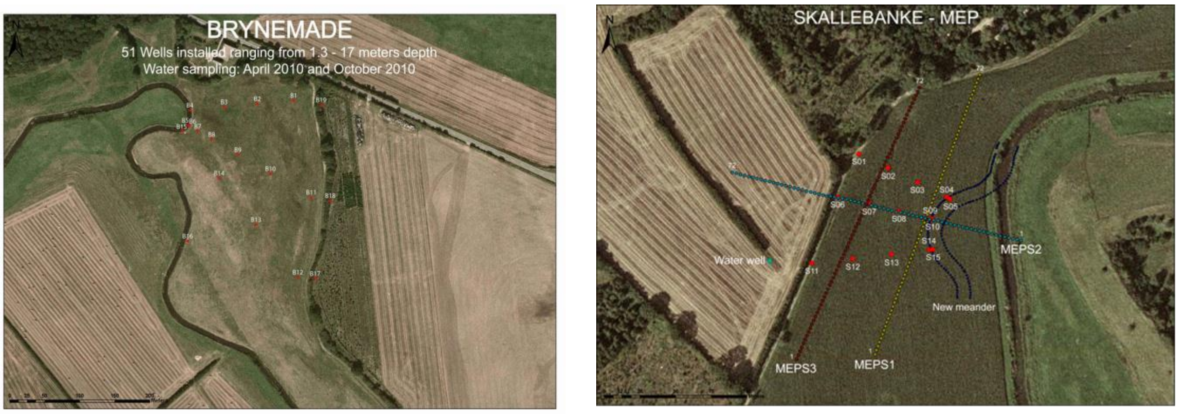
3 A DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUNDS

3.1 ACTIVATED RIPARIAN ZONES/WETLANDS (DIFFUSE POLLUTION – NITRATES & PESTICIDES) (WP1)

The installation of wetlands in riparian zones is considered as a very promising approach for mitigating the diffuse pollution of agricultural pollutants. In this part of the AQUAREHAB project, we studied and quantified how wetland zones mitigate pesticides and nitrates diffuse pollution into surface water and how this could be activated and optimized. The processes contributing to nitrates and pesticides removal in wetlands were studied at the field and at laboratory scale, and the collected data were subsequently used for modelling the fate of nitrates and pesticides in wetland riparian zones. In total, four wetland field sites were studied. Two wetland field sites within the Odense River Basin District (Denmark) were equipped for field monitoring: (1) the “Brynemade” site, as a model of a well-established wetland, and (2) the “Skallebanke” site, a freshly restored wetland. A controlled flooding basin (Bernissem, Belgium) was studied in terms of aerobic pesticide mineralization capacity at the sediment-surface water interface. Finally, denitrification activity was studied with soil from a fourth site, a Phragmites wetland in the Sebes Natural Reservation of Flix, (Tarragona, NE Spain).

3.1.1 nitrate- and pesticide-removal in field wetland systems

Characterisation of the wetland sites. Two wetland field sites have been selected. The “Brynemade” site, as a model of a well-established wetland, has been largely characterized regarding geology, geochemistry and geophysics. The “Skallebanke” site is a freshly restored wetland. Both wetlands were equipped for field monitoring (Figure 5). Instrumentation consisted of a piezometer network along several transects in the wetland in order to monitor groundwater hydrological and chemistry parameters. Moreover, the sites were characterized in terms of geology by means of hand drilling, surface geophysics (Multi-Electrode Profiling (MEP)) and borehole logging. Several monitoring campaigns were performed at the two wetland field sites in order to develop their respective hydrogeological models and to acquire information about the groundwater chemistry. Based on these measurements, a hydrogeological model of the Brynemade wetland site was proposed. The groundwater chemistry showed (1) the existence of a stable nitrates plume at upstream locations near the agricultural field and of an aerobic-denitrification-iron oxidation zonation as the ground water flows to the river, and (2) the absence of detectable pesticide concentrations. In contrast, the redox zonation at Skallebanke was very heterogenous with patches of oxygenated water with high nitrates concentrations along the transects. Also at Skallebanke, no pesticides were detected in the groundwater. Information was obtained on pesticide biodegradation capacity and denitrification capacity via laboratory scale degradation tests. Regarding pesticide mineralization, MCPA was mineralized aerobically by all top soil samples (0-1m), and to a variable degree in deeper samples and peat samples. Anaerobically, MCPA was only mineralized in samples from the agricultural field (2-5 m) with nitrates as the electron acceptor. No MCPA mineralization occurred with iron as the electron acceptor. Bromoxynil was aerobically mineralized by all top soil samples (0-1m) and, more slowly, in peat samples. Bromoxynil was not mineralized at all in deeper samples. Anaerobically, bromoxynil was only mineralized by samples from a depth of 1.2 m at the edge of the wetland, and only with iron. Isoproturon showed only aerobic mineralization by surface samples (depth 0-10 cm) taken from the agricultural field. Batch denitrification tests with peat soil suggested that the available carbon and microbial activity in the study area are sufficient for nitrates removal.



"Brynemade" site "Skallebanke" site

Figure 5: Wetland field selected as study area within AQUAREHAB.

Site conceptual model. Based on all measurements, a hydrogeological model of the Brynemade wetland site could be proposed (Figure 6). The wetland hydrogeology can be characterized by a three-layer system, i.e. an upper 1-2 m thick peat layer followed by an approximately 8-18 m thick heterogeneous sand aquifer, and a lower more silty/clayey layer with an unknown thickness. The thickness of the peat layer was identified by the hand-drillings when meeting more sandy/gravelly sediments. In the south-eastern section the MEP image suggests such a transition to a more sandy-gravelly layer but does not show the presence of the low-resistive peat layer. However, in the north-western part (near the stream) the existence of an upper thin layer with low resistivity is visible in the MEP image, but not the presence of a more sandy/gravelly layer below.

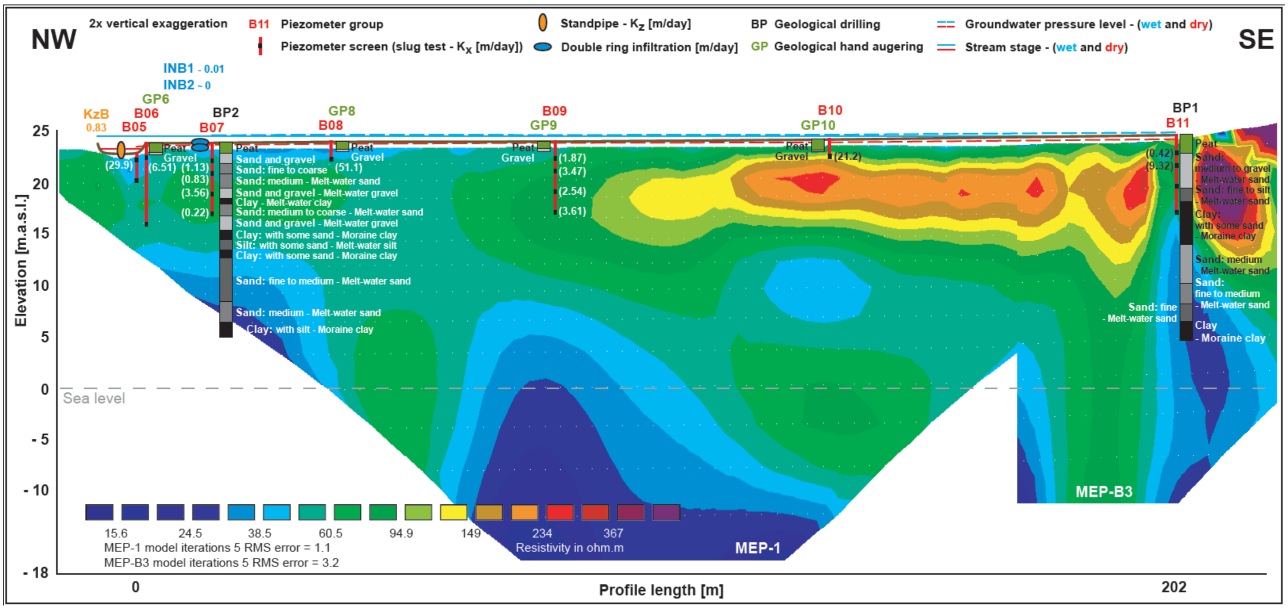


Figure 6. Hydrogeological model of the Brynemade wetland site. The main profile (B05-B11) 2x vertical exaggeration is shown. The profile shows inversion results on two performed MEP profiles with electrode spacing of 3 m, resistivity values are in ohm meters. Two deep geological wells with geology based on sample description for every meter (BP). Colour scheme indicate apparent colour and assumed hydraulic conductivity (Higher K-value with lighter color). Installed piezometers in groups of 1-4 with slug test results shown in brackets. Results of top soil mapping (peat) with Eijkelkamp hand auger equipment (GP). Double ring infiltrometer tests (INB) and standpipe measurement (KzB). Groundwater pressure levels (dashed line) and stream stages (solid line) are shown for the wet period 17 January 2011 (blue) and for the dry period 10 May 2011 (red).

The FeFlow pesticide transport model was implemented for predicting the fate of pesticides at the Brynemade site and using data from literature to feed the model. The model clearly demonstrates the effects of different fluxes (ground water discharge, infiltrating rainwater, floods from the river, and vertical leakage) on the transport of pesticides at the site. Feflow was also used to describe the nitrates reactive transport at the “Brynemade” site based on literature data regarding denitrification rates. The model was calibrated to the groundwater nitrates concentrations observed in the field. The model shows that the nitrates plume moves through the aerobic zone and that high denitrification rates in the anaerobic zone, ensure rapid nitrates removal. The model can help to understand the fate of pesticides that end up in a wetland due to erosion, drainage or run-off.

Ecological status. Four ecological surveys of the study area have taken place and all confirmed the good ecological status.

3.1.2 Pesticides removal in laboratory wetland microcosms

Soil samples from the upper 10 cm of wetland sites in Brynemade (Odense, Denmark) and Bernissem (Sint-Truiden, Belgium) were used to investigate the mineralization of MCPA and IPU under flooded conditions. Laboratory microcosm experiments showed the capacity to degrade/mineralize the pesticides isoproturon (IPU) and MCPA in the above surface compartment of a wetland (Figure 7). Based on the observed mineralization kinetics, the development of a conceptual model that describes the reactive transport of pesticides in the stagnant areas above the surface layers of a wetland was initiated. The model can help us to understand the fate of pesticides that end up in a wetland due to erosion, drainage or run-off. Furthermore, indications for the effects of seasonal disturbances on pesticides degradation were obtained but the experimental design needs to be improved to discriminate between the mineralization of the actual pesticide and of biomass which has assimilated the pesticide. On the other hand, a survey of the IPU and MCPA mineralization capacity of a wetland (Bernissem, Belgium) at different time points over a period of two-years (2011 – 2013) did not give indications for seasonal changes.

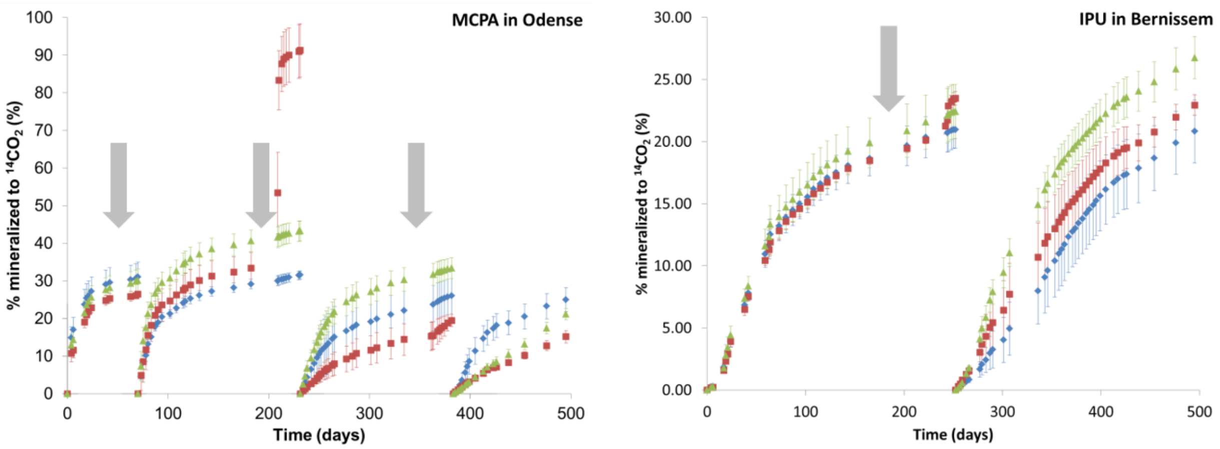


Figure 7. Cumulative mineralization of MCPA (left) and IPU (right) as a response to laboratory controlled disturbances. Disturbances (freezing and drying) are indicated by the vertical arrows. At the moments of spiking the microcosms with ^{14}C-herbicides, the cumulative mineralization curves were set to zero. The data shown are average from triplicate microcosms. Setups: drying (◆), freezing (■) and control (▲), with the error bars indicating the standard deviation.

3.1.3 Nitrates removal in laboratory wetland microcosms

This task focused on the study of the role of soluble organic matter present in several wetland soils for denitrification activity. Superficial soils were sampled from Brynemade (October 2009) and from a *Phragmites* wetland in the Sebes Natural Reservation of Flix, (Tarragona, NE Spain) (April 2010 and 2011). Batch denitrification tests were performed using leaching solutions of the soils (Figure 8). Results showed similar trends with the elimination of more than 90% after 3 days of spiking.

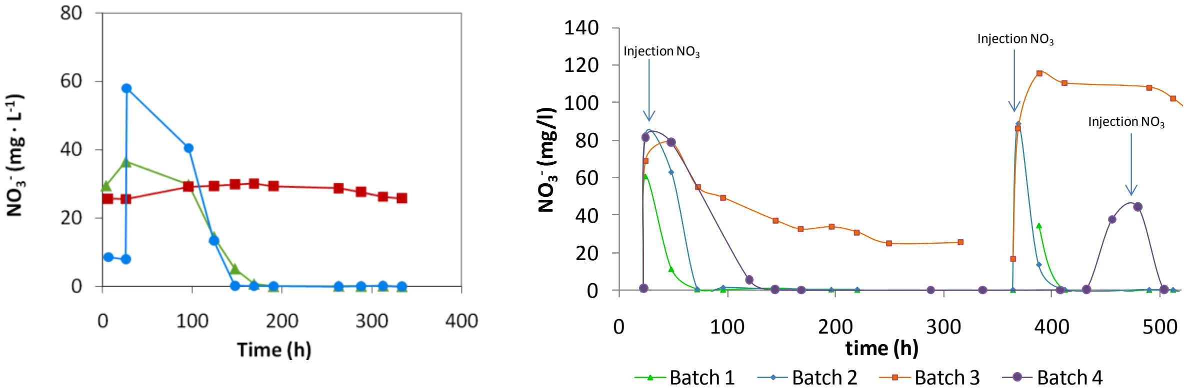


Figure 8. Denitrification batch tests with superficial soil from Brynemade (left) and Flix (right) showing the evolution of nitrate spiked in a stirred mixture of soil and water. Dead control are indicated by using squares (■)

Next, a continuous wetland microcosm experiment with a nitrates solution was run continuously in a sand bed that has the Flix peat soil in the upper part irrigated with water. Results revealed a correlation between the removal of nitrates and the Dissolved Organic Carbon (DOC) at the exit of the setup, showing a correlation of DOC from the soil and denitrification. From the experience accumulated within the AQUAREHAB project, in order to allow denitrification processes, the activation of Riparian Zones needs the combination of soil layers with the following properties:

- High content and high quality of Dissolved Organic Carbon (DOC) as shown in soil leaching tests. The quality of DOC is linked to the season and influences the fraction of the DOC that is used as electron donor in the denitrification processes.
- Soils rich in organic matter and microorganisms, as often the case in wetlands soils, are a good starting point as they can supply sufficient DOC for denitrification and allow aerobic microorganisms to consume available oxygen and create anoxic zones.
- A capacity of denitrification as shown in batch denitrification experiments that is related to the presence of DOC of sufficient quality and denitrifying microorganisms.
- A low vertical hydraulic conductivity in the vadose soil zone in order to increase the contact time between the infiltration water and the zone rich in proper (leachable & bioavailable) DOC in order to obtain high levels of DOC in the water entering the aquifer.
- Avoid local mechanisms of soil aeration. If dissolved oxygen is sufficient (ca >0.5 mg/l) denitrification is inhibited.
- Low content of ammonium in soil leaching. Denitrification approach will not eliminate its concentration and could increase water toxicity.

If these properties are met (as in the Brynemade site and partially in the Flix soils) or are activated in riparian zones, denitrification kinetics will be a very fast reaction considering the hydrogeological residence times, and nitrates and nitrites will be eliminated from the groundwater.

3.2 Bioremediation of pesticide-containing degraded water in open trenches with smart biomass containing materials (WP2)

The overall objective of this part of AQUAREHAB was to develop a semi-passive rehabilitation technology to cope with aqueous pesticide pollution. The basic idea of the rehabilitation technology is to treat the pollutants in open-air trenches that drain contaminated groundwater from the riparian zone and that contain tailored materials as support for microbial biofilms that degrade the pesticides in the contaminated drainage water (Figure 9).

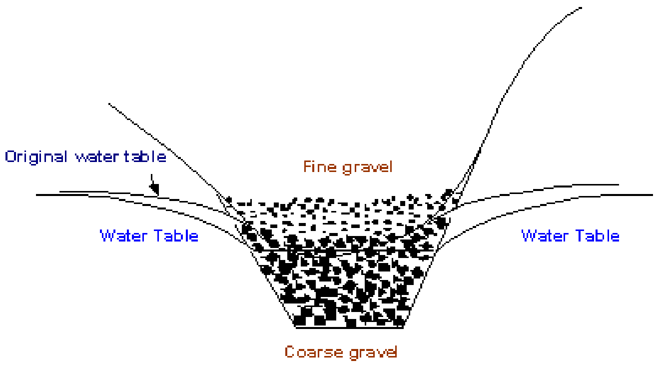


Figure 9: Cross-section of a drain with coarse carrier material, on which pollutant-degrading bacteria can form a biofilm that will degrade pollutants (pesticides) in the passing groundwater.

3.2.1 Selection of bacteria-carrier combinations

Different bacterial strains were tested for their interactions with both artificial and natural carrier materials. Among the strains tested were the *Pseudomonas* sp. strain ADP that degrades atrazine, *Variovorax* sp. SRS16 that degrades linuron, Chelatobacter heintzii SR38 that degrades atrazine, Aminobacter sp. MSH1 that degrades BAM, Sphingomonas sp. KN65.2 that degrades carbofuran and Rhodococcus sp. KS1 that degrades metamitron. An atrazine-enrichment culture and carbofuran-degrading consortia were also isolated from the field test site in Israel and evaluated. Carrier materials tested were: white chalk (WC), grey chalk (GR), gravel (GR), sand (SA), activated carbon (AC), biosep beads (synthetic), XAD-7HP (synthetic), XAD-2 (synthetic), IRC-50 (synthetic), and synthetic material based on calcite and activated carbon. All of the tested material enabled the formation of a microbial biofilm, regardless of the specific surface area or hydrophobicity of the carriers. White chalk (WC), grey chalk (GR), gravel (GR), sand (SA), and activated carbon (AC), immersed in the contaminated groundwater, each attracted different native microorganisms forming significant biofilms. The composition of the attached populations on these materials appeared to be related to the carrier properties.
Although the attached biomass was active in mineralizing simple compounds, such as benzoic acid, the activity of these bacteria towards the different pesticides was very slow, with the exception of bacteria grown on sand and atrazine (Figure 10). The biodegradation of the different pesticides by carrier bacteria combinations was extremely dependent on the strength at which the organic pollutants were sorbed onto the carrier. For example, the mineralization of ^{14}C-BAM by *Aminobacter* sp. MSH1, in the presence of different carriers, showed that it was able to mineralize 50% of the added compound in the presence of the XAD 7HP carrier and was not able to mineralize the compound when activated carbon was used as a carrier. These observations suggest that the dynamic of sorption/desorption from the carrier is the most important factor allowing degradation. Promising bacteria-carrier combinations that were identified comprise gravel and the resin XAD-7HP.

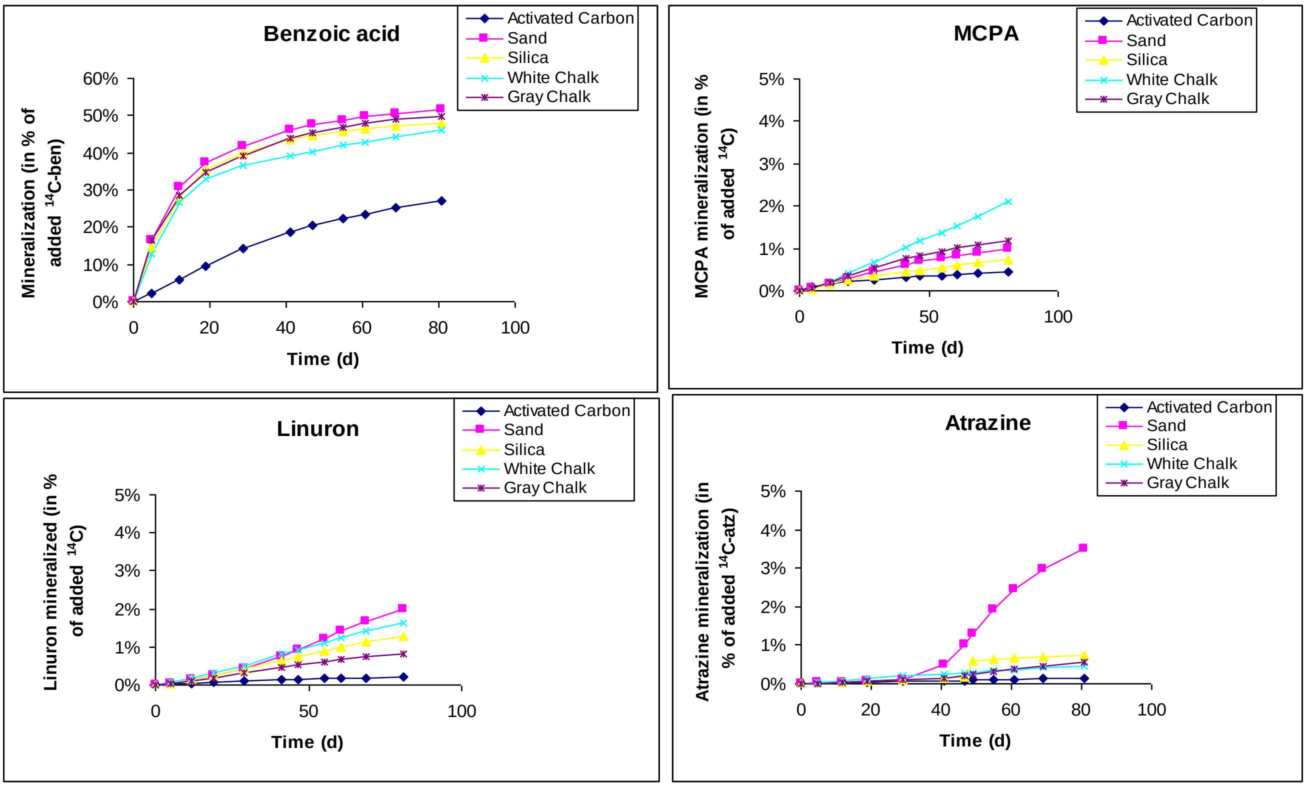


Figure 10: Mineralization of benzoic acid and selected pesticides by carrier incubated within the drained in situ water.

Sand column experiments were set-up with different carrier materials. The results suggested that if organisms are very robust, concerning carbon source concentration changes, all columns perform well and XAD-7HP is not necessarily needed (e.g., in the case of linuron degradation by *Variovorax* SRS16). However, the presence of the resin has a positive effect in cases where the strains are less robust. In these cases, the resin either acts as a buffer to absorb pesticides, when the organisms are not yet reactivated, or provides a continuous flow of pesticides during the period of pesticides absence in the inflow medium, thus maintaining the degradation activity. The latter effect was observed with the strains *Aminobacter* MSH1 and *Sphingomonas* KN65.2 after the medium had been left without the respective pesticides for a longer period of time. Switching back to the medium with the pesticides revealed that the columns with a XAD-7HP / sand ratio of 1:500 showed the most stable pesticide-degrading performance. The column experiment with a gravel carrier and natural bacteria from the test site with artificial groundwater, amended with a mixture of pesticides and background compounds, suggested that the site's natural microbial population is not able to degrade the target pesticides but is able to degrade background contaminants. This led to the enrichment of atrazine and carbofuran-degrading consortia from the site water. Additionally, the ability of pure cultures to degrade pesticides at the site water high salinities and in the filtered site water was evaluated; carbofuran degradation by indigenous bacteria was efficient in the presence of the gravel as a carrier. Atrazine mineralization, however, was dependent on the availability of sand as a carrier and an additional carbon source. From the tested pure cultures, *Sphingomonas* sp. KN65.2 that degraded carbofuran was active at high salinities, as well as in the actual groundwater (Figure 11). Importantly, we noted that abiotic reactions also took place. The *Pseudomonas* sp. strain ADP that degraded atrazine was adapted only for high salinities in a defined medium.

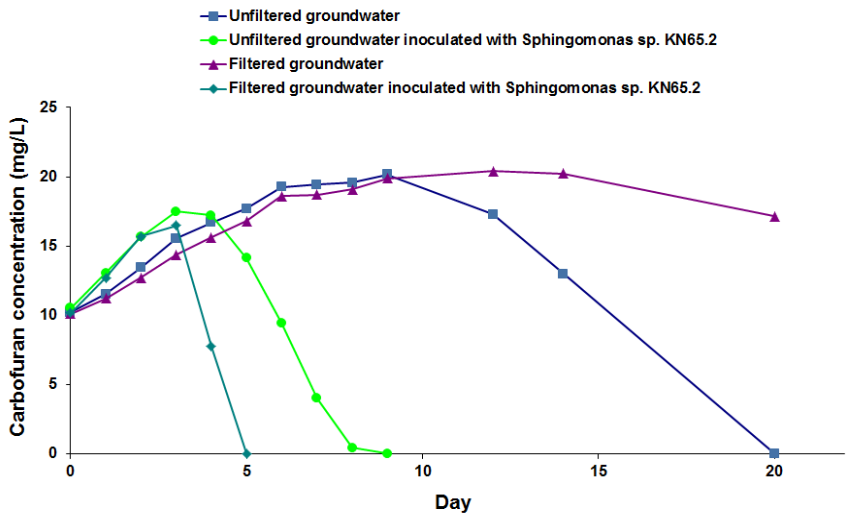


Figure 11: Biodegradation of carbofuran by Sphingomonas sp. KN65.2 with gravel as a carrier and with water from the site. The initial increase in concentrations is due to our inability to separate between carbofuran and degradation products.

3.2.2 Pilot test in the field

A pilot field system that simulates flow conditions within the drainage channels was built in order to evaluate the introduction of bacteria/carrier combinations. The pilot system contains three columns filled with clean gravel, as well as with contaminated gravel from different sections of the site's drainage system (Figure 12).

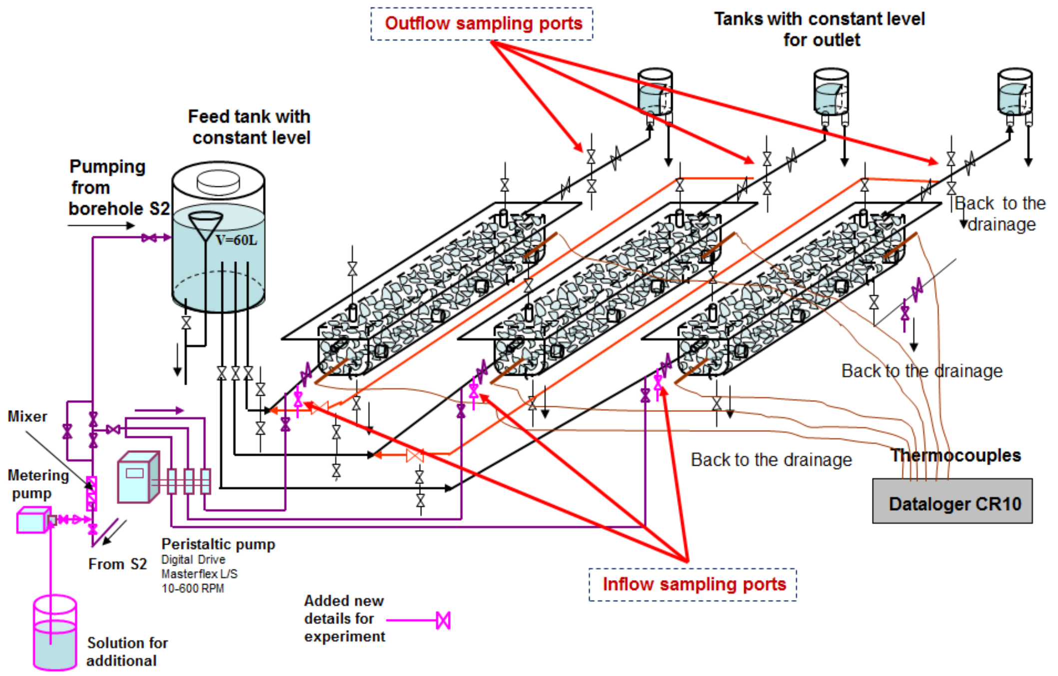


Figure 12: Scheme of the pilot system with the addition of the peristaltic pump and carbofuran container.

In the field experiments, with gravel-packed columns, the carbofuran degradation by the native bacteria was affected by environmental factors, such as temperature and dissolved oxygen. In the pilot system, the influent DO was initially relatively low (~0.8 mg/L) and decreased in the effluents to less than 0. 5 mg/L. Temperature was as high as 37 C° in the summer and decreased to below 10 C° in the winter. Initially, some degradation of carbofuran was observed in the system (40-50%), but the levels diminished with time till below 10%. Introducing *Sphingomonas* sp. KN65.2 to the column resulted in a transient improvement in degradation (until max 25%). Attempts to oxygenate the water passing through the column failed because of clogging due to iron minerals within the contaminated water.

3.2.3 Conclusion

In conclusion, the carrier / bacteria technology requires that the carrier will not strongly adsorb the target pollutant, that the introduced bacteria will be active in the site water and that it will be possible to control the environmental conditions at the site to accommodate the physiological characteristics of the introduced bacteria.

3.3 Bioreactive zones in aquifer and sediments (capping) to rehabilitate surface water degraded by influx of pollutants from the groundwater (chlorinated ethenes) (WP3)

For WP3 the main aim was to develop techniques to prevent the influx of Chlorinated aliphatic hydrocarbons (CAHs) from a groundwater plume into a river. As a test case, the Zenne site in Vilvoorde Machelen (Belgium) was selected. The Vilvoorde site is characterized by typical contamination problems of an urban and industrial nature which are discharging into the river, *i.e.* (1) municipal sewage from the city of Brussels and (2) contaminated groundwater plumes from the industrial sites located on the bank of the river. The main industrial contaminants reaching the river are *cis*-dichloroethene (cDCE) and vinylchloride (VC) but other chlorinated ethanes are also present. The techniques considered were (1) stimulation of the biodegradation just upstream of the sediment zone in the aquifer by the injection of carbon sources, and (2) capping of the sediment with a permeable biodegradation stimulating material. In addition, the effects of oxygen infiltration by surface water into the sediments (natural attenuation) were investigated. Further, the dynamics of the microbial and overall ecology of the river sediment was monitored over a period of 2 years (September 2009 to September 2011).

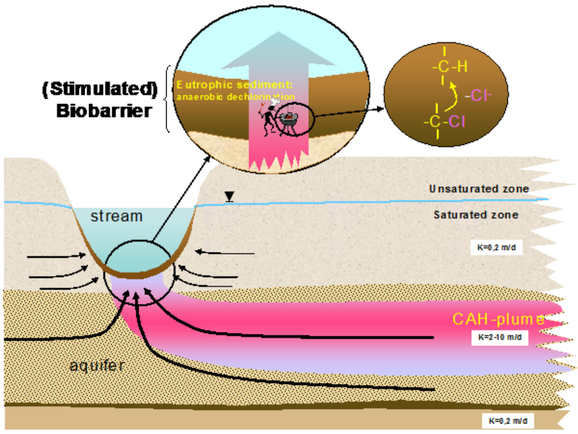


Figure 13: Stimulated sediment/aquifer biobarrier technology to inhibit the influx of pollutants from the groundwater into the surface water.

3.3.1 Stimulation of CAH degradation by carbon sources in aquifer compartment

CAH degradation by the indigenous bacterial population in the aquifer (comprising *Dehalococcoides mccartyi* population) discharging into the Zenne River was evaluated using different carbon sources in batch cultures. Reductive dechlorination of trichloroethene (TCE) took place only when external carbon sources were added, and occurred concomitant with a pronounced increase in the *D. mccartyi* cell count as determined by 16S rRNA gene-targeted qPCR. This indicated that native dechlorinating bacteria are present in the aquifer of the Zenne site and that the oligotrophic nature of the aquifer could prevent a complete degradation to ethene. The type of carbon source, the cell number of *D. mccartyi* or the reductive dehalogenase genes, however, did not unequivocally explain the observed differences in degradation rates or the extent of dechlorination. Neither first-order, Michaelis-Menten nor Monod kinetics could perfectly simulate the dechlorination reactions in TCE spiked microcosms (Figure 14). A sensitivity analysis indicated that the inclusion of donor limitations would not significantly enhance the simulations without a clear process understanding. Results point to the role of the supporting microbial community but it remains to be verified how the complexity of the microbial (inter)actions should be represented in a model framework.

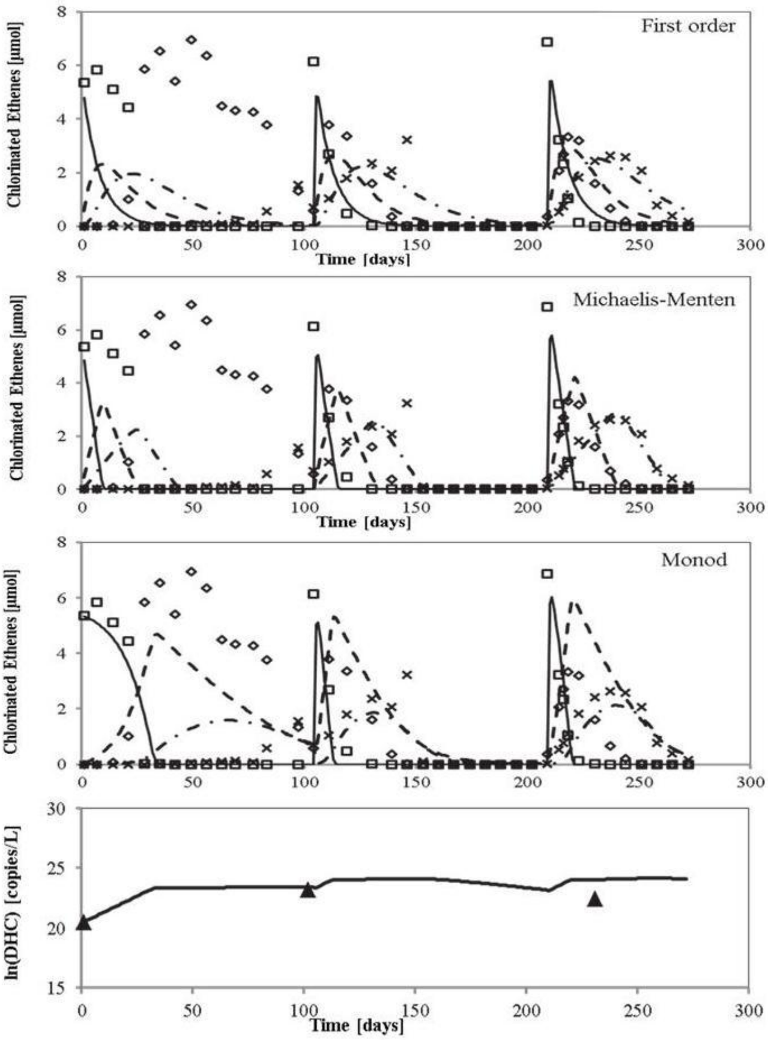


Figure 14: Model results using First-order (top), Michaelis-Menten (middle) and Monod (bottom) kinetics for the aquifer of one location to which sediment extract was added. Observed data: □ TCE, ◊ cDCE, × VC and ▲ 16S rRNA gene copy numbers of Dehalococcoides mccartyi. (DHC). Modeled data: — TCE, ---- cDCE, -·-· VC and — cell numbers of DHC. The 16S rRNA copy numbers were calculated from triplicate qPCR measurements and are presumed to represent DHC cell numbers in a 1 to 1 relationship.

3.3.2 Sediment capping of the sediment compartment

In case of limited CAH attenuation in the aquifer and riverbed sediment, discharges of CAH contaminated groundwater into surface water systems, presents an additional environmental concern. *In situ* capping is a promising technology for reducing the exposure of biota present in the surface water column to contaminants present in or leaking from the sediments. *In situ* capping involves placing a layer of clean fill material (typically sand) at the sediment-water interface to physically isolate contaminated sediments but also to stimulate the CAH biodegradation. To test the application of solid polymeric organic materials (SPOMs) as capping material, different SPOMs such as tree bark, crustacean waste, hay, straw, and wood chips were amended to sediment microcosms. Compared to the natural attenuation (no amendments), it was clear that all tested capping materials had a positive effect on the degradation of VC and cDCE. Tree bark was selected as the most promising capping material since it stimulated cDCE degradation for more than a year but also resulted in the enhanced stimulation of *D. mccartyi* in competition with methanogens.

3.3.3 Oxygen infiltration from surface water into the sediment compartment

Oxygen in surface water that infiltrates into the river-beds plays an important role in determining redox zones and microbial processes. Often, especially in sediments with high organic matter content, a sharp redox boundary exists between the aerobic benthic sediment and underlying anoxic sediment. The existence of such oxygen/redox gradients in hyporheic zones is of major interest for biological degradation of contaminants present in discharging groundwater and in particular for the biodegradation of CAHs. Anaerobic sediments in deeper layers provide ideal conditions for reductive CAH dechlorination by organohalide respiring organisms while more oxic sediment layers at the surface water-sediment interface, can be conducive to aerobic degradation of less-chlorinated daughter products. As such, a scenario of sequential anaerobic-aerobic degradation can be anticipated that results in the conversion of CAH to harmless products, before the groundwater reaches the surface water.

The fate of VC and the dynamics of bacterial guilds involved in aerobic and anaerobic degradation of VC was studied in microcosms containing surficial sediments of the hyporheic zone of two locations - P26 (containing fine grained sand) and P25 (containing coarse sand) - at the test site under both anoxic and oxygen-exposed static conditions. Results suggested the co-existence and co-activity of anaerobic and aerobic VC degraders in the same small volume of surficial sediment of the Zenne River (Figure 15), and that oxygen distribution, as determined by sediment grain size and organic matter content, affects the local VC degrading bacterial community and VC biodegradation pathways.

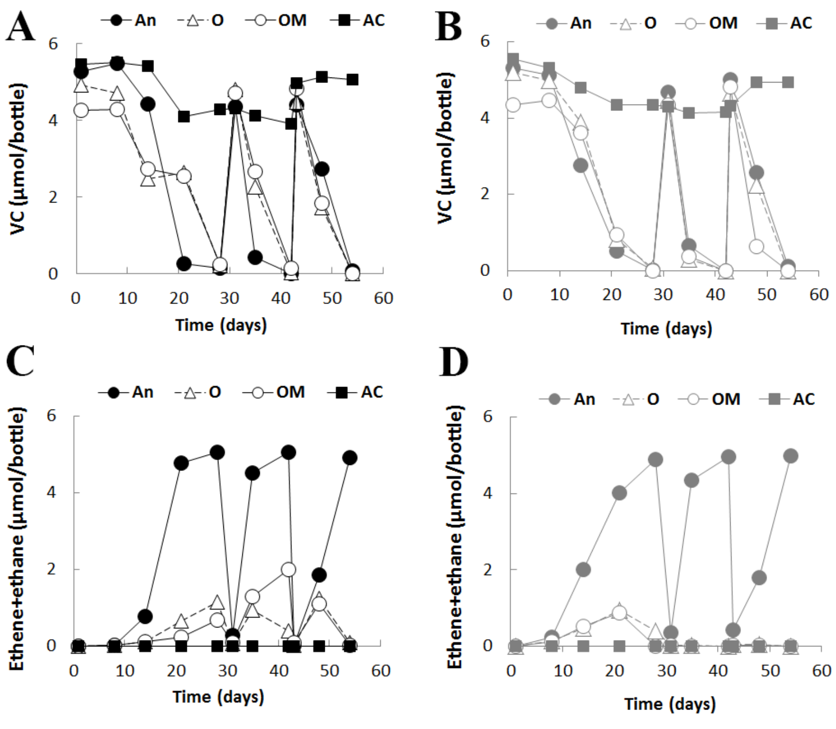
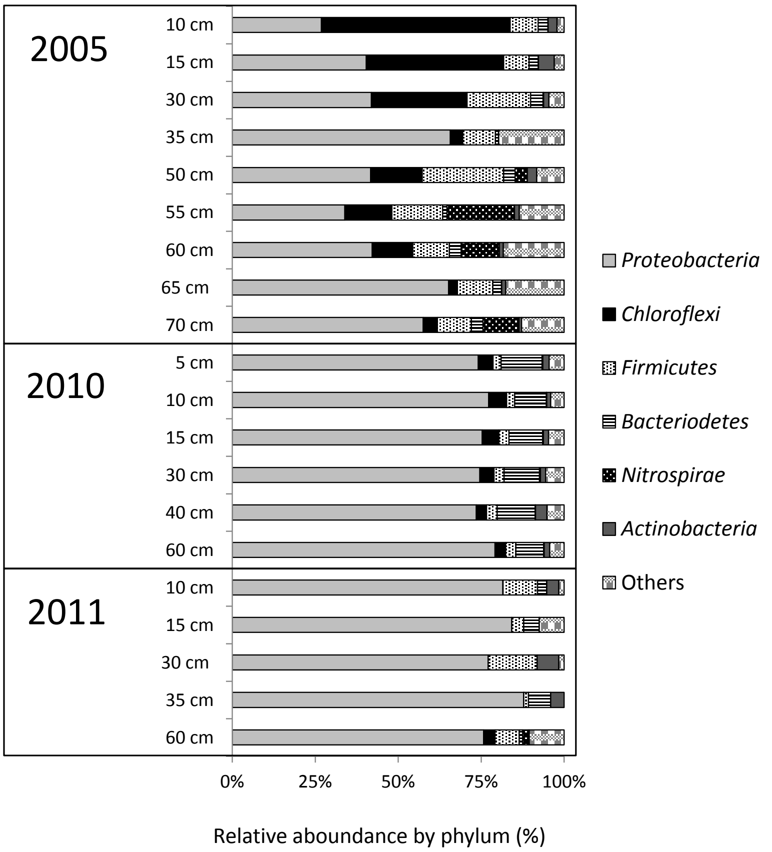


Figure 15: VC degradation (A and B), accumulation of ethene and ethane (C and D) in oxygen-exposed and anoxic microcosms containing sediment from location P26 (panels A and C) and P25 (panels B and D), respectively. An: anoxic, O: oxygen exposed microcosms, OM: oxygen exposed microcosms amended with methane, AC: abiotic control. Note that for the Y axes of panel E and F different concentration scales are used. Data shown are average values obtained from duplicate microcosms.

In addition, we investigated the response of hyporheic sediment-associated microbial communities involved in biodegradation of VC/cDCE to periodic redox fluctuations in sediment microcosms under static/dynamic conditions. In contrast to the resistance and resilience of aerobic degraders toward strict anoxic conditions, a high sensitivity of *D. mccartyi* was observed to oxygen exposure, which is consistent with previous reports using pure and enrichment sediment free cultures. However, the site physico-chemical properties might shield *D. mccartyi* against local redox fluctuations. Therefore, at locations with high organic carbon load, infiltration of oxygenated surface water into hyporheic sediments is probably not detrimental to *D. mccartyi*.

3.3.4 Study of the effect of a municipal waste water treatment plant (MWWTP) on the restoration of the (microbial)ecology in the aquifer and sediment compartment at the Zenne site

The implementation of a wastewater treatment plant (WWTP) upstream of the test site resulted in important physico-chemical changes in surface water, such as a decreased organic carbon content and increased dissolved oxygen. Analysis by pyrosequencing of PCR amplified partial 16S rRNA genes and by targeted Real-time quantitative PCR (qPCR) in vertical sediment profiles taken in 2005 (2 years before construction of the WWTP in 2007), 2010 and 2011, indicated shifts in bacterial community composition and in particular in the organohalide respiring bacteria that are dependent on organic carbon-derived electron donors and reducing conditions (Figure 16).

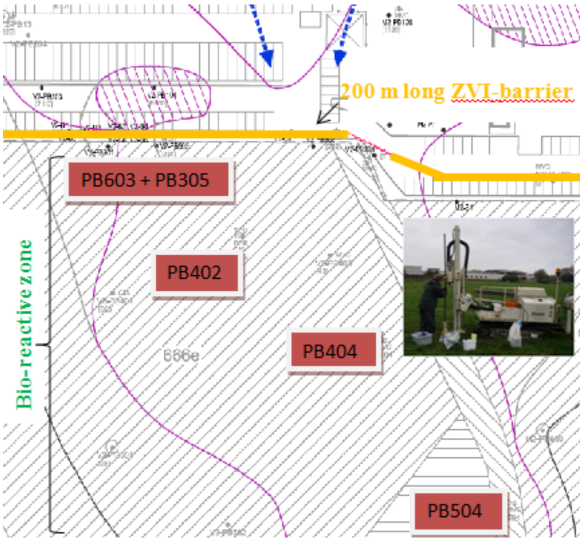


The physico-chemical assessment showed a “less than good” status since insufficient oxygen levels to support a healthy ecosystem was noticed during all sampling campaigns from 2009 to 2012. Generally, the overall ecological status of the Zenne River at the studied site is classified as bad (Class 5), as a result of the low scores for the general degradation module of benthic invertebrates. The overall surface water status did unfortunately not improve during this period. Both the chemical and ecological status indicate that the Zenne River is still one of the most polluted streams in Europe.

Figure 16: Relative abundance of the dominant bacterial phyla at different depths in the sediment core samples taken in 2005, 2010 and 2011.

3.4 MULTIFUNCTIONAL PERMEABLE BARRIERS (MULTIBARRIERS) FOR MIXED GROUNDWATER CONTAMINATION PLUMES (WP4)

The multibarrier technology is an innovative in-situ remediation technology for groundwater, consisting of a combination of permeable reactive barriers and reactive zones, in which different pollutant removal processes are combined. They are especially useful for the treatment of mixed pollutions and to be integrated in a rehabilitation approach for specific sites/regions. Multibarriers are tailor made technologies as the multibarrier-design, i.e. the combination of different removal processes, is a function of the pollutants and site specific aspects. Within AQUAREHAB, WP4 was dedicated to multibarriers with the focus on the identification and determination of crucial parameters to predict the short and long term impacts of multibarriers on the environment at the local scale. The main multibarrier considered within AQUAREHAB consists of 2 compartments to eliminate chlorinated aliphatic compounds (CAHs), being (1) a zerovalent iron barrier and (2) a biological reactive zone stimulated with the injection of an electron donor (Figure 17). Earlier, based on laboratory scale tests, this multibarrier concept was found to be a suitable solution for an industrial site (site A) in Belgium (Scheldt river basin). A full scale continuous ZVI-barrier (200 m long, depth up to 6 m, 30 cm thickness) was implemented in 2005. Different aspects of the multibarrier concept of Site A were studied, being: (1) identification of crucial parameters required to predict short and long-term impact of ZVI-barriers; (2) development of an updated feasibility test in the laboratory to derive these parameters; (3) determination of biodegradation rates via classical laboratory scale degradation tests, as well as via new approaches that were explored within the project; and (4) interaction between ZVI and biological processes. In parallel, field data from site A were collected with the focus on parameters that influence the functioning and longevity of the multibarrier.



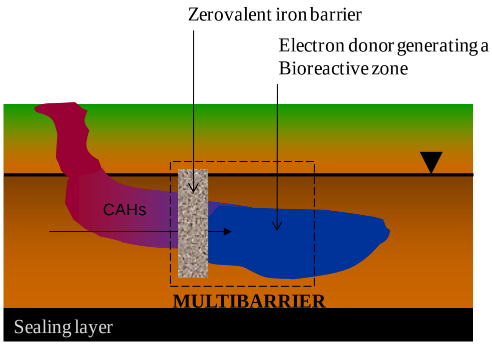


Figure 17: (Left) Multibarrier at site A comprising (1) a 200 long ZVI barrier and (2) a bioreactive zone with monitoring wells; (top) schematic representation of the multibarrier at site A.

3.4.1 ZVI-part of the multibarrier (at site A)

Crucial parameters influencing the performance of ZVI-barriers comprise pollutant concentrations, pollutant degradation rates, groundwater flow velocity, oxygen concentration and other geochemical characteristics of the groundwater and barrier design parameters. In addition, the iron corrosion rate was identified as a crucial parameter for which rates were not yet available for site A. A laboratory scale experiment was performed during which hydrogen production by the ZVI was followed in time as an indicator for corrosion. A fast corrosion phase (0-6 weeks: Fe corrosion rates = 6-8 mmol/kg/days) was found to be followed by a less intensive corrosion phase (Fe corrosion rates = 1-3 mmol/kg/days). The change in corrosion rate over time does complicate the prediction of the ZVI life-time. For modelling purposes, the initial corrosion rate can be used for worst case scenarios, while the second phase corrosion rate is expected to lead to scenarios closer to reality, when taking into account a time span of years to decades. The impact of the groundwater flow velocity on the type of mineral precipitates formed was identified as a point of attention, but could not be verified with laboratory scale experiments.

An improved feasibility test procedure was elaborated to derive all required parameters for ZVI-barrier design, including corrosion rates and mineral precipitation, that influence the life time of ZVI-barriers.

A multicomponent geochemical model was developed to assess PRB durability and efficiency (Carniato et al., 2012a, b). The model is implemented with the general PHAST simulator (Parkhurst et al., 2004) and comprises of a saturated groundwater module, an advective-dispersive solute transport module, and a comprehensive reaction network module. Key reactions include iron corrosion, VOCL degradation by iron, inorganic equilibrium chemistry of dissolved components (ion complexation, acid-base reactions …), and mineral precipitation reactions. The latter are the key to simulate decreased performance of iron reactive media, as minerals form nonreactive coatings on reactive iron particles. Data from a laboratory column experiment were used to calibrate the reactive transport model and assess the identifiability of the model parameters (see WP7).

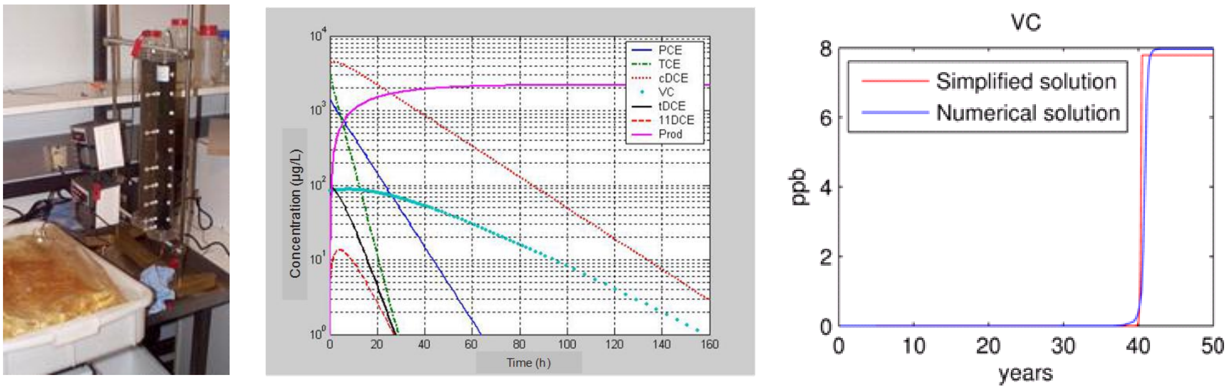


Figure 18: Column test setup (left), simulated evolution of CAH-concentration within a ZVI-barrier (middle), and expected CAH-concentration at the barrier effluent site predicting the longevity of a ZVI-barrier (right).

3.4.2 Bioreactive part of the multibarrier (at site A)

Degradation rates were determined **via laboratory scale fed-batch tests** using aquifer samples from site A taken at 4 different distances from the barrier (PB603/PB305, PB402, PB404, PB504, see Figure 17). At all locations, a clear biodegradation potential for the complete degradation of PCE and TCE to ethane was found present, but the degradation rates differed considerably from location to location, and lag-phases between 0 to 10 months were observed. Only at the front of the contamination plume (PB504), where the TOC-values were the highest (5.4 % DW, versus 0.4 % DW for the other locations), was CAH-degradation observed. For the other spots, lactate addition was required to stimulate the CAH biodegradation.

The **possibility to determine degradation rates from DNA/RNA-copy numbers** present in the groundwater was investigated. It was decided to focus on *Dehalococcoides* and on catabolic genes encoding for enzymes involved in the degradation of CAHs (tceA, vrcA, bvcA). As analyses on RNA can be directly linked with activity, q-PCR analyses were performed on RNA (transcript numbers) as well as DNA-extracts (copy numbers) slurry samples during the biodegradation test (see above). The different tested genes were found to be homogeneously distributed over the test site. However, correlations of the biomarkers and the degradation rates appeared to be batch dependent and influenced by the aquifer material used to setup the microcosm. Different genes dominate the different batches. Univariate analyses revealed a correlation between the degradation rates of PCE and gene copy number (DNA-level) of pceA, tceA, vcrA and bvcA. TCE degradation rates were positively correlated with tceA and vcrA. No correlations were found between the degradation rates of cDCE and VC. A multivariate analysis showed a large variability in the correlation between dechlorination rates and microbial markers between the sampled locations. Additionally, differences in the correlation of genes and the corresponding transcripts to degradation rates were identified. The large variation in the observed degradation rates and its correlation to microbial markers indicate that natural attenuation rates are difficult to determine *in situ,* even when using biostatistical analyses. The new approach needs further investigation before it can be reliably applied. Degradation rates are preferably derived from column experiments but the variation at the field scale should be acknowledged when these rates are used in the experimental design.

3.4.3 Interactions between the ZVI-barrier and the biologically reactive zone.

Hydrogen formed by ZVI can serve as an electron donor for CAH-biodegradation, this was experimentally proven within AQUAREHAB and suggests ZVI may be a good habitat for dechlorinating bacteria. Further it is known that the ORP-reducing characteristic of ZVI is beneficial for the dechlorinating bacteria, but the associated pH-increase may be less favourable. Nevertheless, CAH-biodegradation within the ZVI-barrier could be proven in the field.

Compound specific Isotope analyses (CSIA). To differentiate between biotic and abiotic CAH-removal in ZVI-barriers, fractionation factors of isotopic shifts during CAH-degradation by ZVI were determined via laboratory scale batch degradation experiments using artificial groundwater with PCE, TCE, cDCE and VC separately. Further, additional site specific stable isotope fractionation factors for these CAHs during biological degradation were derived via laboratory experiments. As both degradation processes induced an enrichment of the heavier C-isotopes in the non-reacted remaining part of the pollution, carbon based CSIA is not able to distinguish both degradation processes. An innovative approach was elaborated to use fractionation factors to quantify the complete dechlorination of CAH at contaminated sites (Eisenmann et al., 2012).

3.4.4 Field work at site A

Site information available from several years before the start of AQUAREHAB was completed with new measurements during more than three years and used as input for the numerical model. Two to four times per year, the following parameters were monitored in up to 20 monitoring wells: field parameters (pH, EC, DO, ORP), CAHs, methane, ethene, ethane, Ca, Mg, Cl, sulphate, (bi)carbonates, total iron, TIC, TOC, Hydrogen, CSIA, gene based molecular analyses. The new data set revealed seasonal changes. After installation of the ZVI-barrier, the CAH-concentrations decreased rapidly in the downstream wells close the ZVI-barrier. Due to the slow groundwater flow (2 m/year), the effect of the ZVI-barrier was not yet observed in the second row of the downstream monitoring wells. In the bioreactive zone a gradual decrease in CAH-concentrations can be observed. CSIA results contributed to clarifying the local groundwater flow paths and provided clear evidence for natural attenuation processes at the site. Across the ZVI-barrier, a more drastic isotopic shift was measured, referring to the abiotic degradation of CAHs induced by the ZVI. Data from continuously monitoring groundwater levels, temperature, and EC gave insights into hydraulic gradients across the iron barrier at site A, and the dynamics of solute concentrations (EC) before (paved surface) and after (unpaved surface) the barrier. Also resistivity transects were completed to collect information on the spatial distribution of subsurface sediments (like the low-permeable clay layer), which is useful for model development.

Angled core samples. Angled core samples were taken across the 6-year old ZVI-barrier to evaluate its performance over time. The samples comprised, besides ZVI-barrier material, of also aquifer samples just before and just after the ZVI-barrier (Figure 19; Bastiaens et al., 2012). The porosity and reactivity were determined, as well as the presence of inorganics. The ZVI-barrier was found to be still as reactive as the original ZVI and the porosity remained sufficiently high. No higher concentrations of mineral precipitates was observed near the upstream part within the ZVI-barrier as compared to the effluent part. The angled core samples were also used to examine in detail the microbial population present across the ZVI-barrier, using q-PCR and 16S tagpyrosequencing. A diverse microbial population was found present in the ZVI-barrier, comprising of dechlorinating bacteria (Chloroflexi).

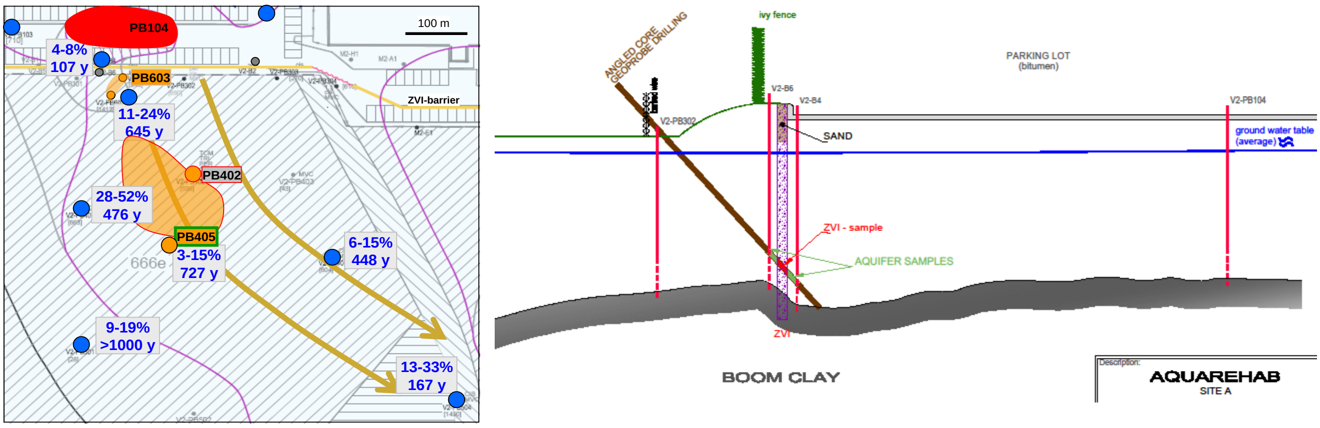


Figure 19 Conceptual site model derived from CSIA data (left), and scheme of angled core sampling (right).

Field numerical model. A theoretical approach was used based on numerical modelling (collaboration with WP7), with the aim of predicting the functioning of the ZVI-barrier and the bioreactive zone over time. The data collected via laboratory scale tests (like degradation rates, corrosion rates) and the collected field data were used as input for the field numerical model, elaborated within WP7. The model was used to simulate the impact of a number of remediation scenarios (no intervention, ZVI-barrier (PRB) and biostimulation) on the groundwater contamination at site A, as depicted in Figure 20.

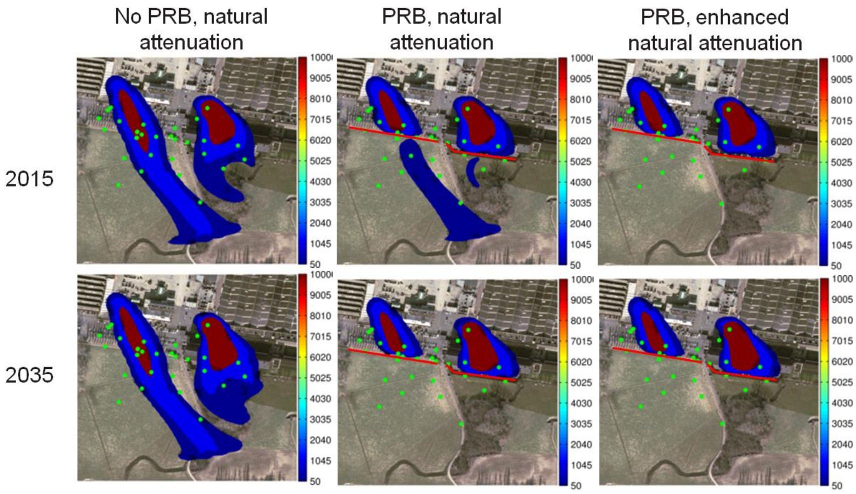


Figure 20: Simulation of groundwater plume evaluations over time and under different scenarios.

Extrapolation to other multibarriers. The approach to design and to implement multibarriers comprises the following steps: (1) site characterisation, (2) selection of suitable pollutant removal mechanism, (3) laboratory scale tests 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. The approaches and procedures studied within AQUAREHAB WP4 were mainly focused on the multibarrier at site A. As multibarriers are tailor made, a key-question was whether the findings are sufficiently generic to be applicable to other multibarrier designs. Therefore, in a second phase of WP4, two additional multibarrier concepts were considered. The result for site H, focussing on a multibarrier concept (ZVi barrier followed by inoculated aerobic biobarrier) for a mixed contamination plume containing BTEX, CAHs and MTBE was considered (see Figure 5). It was concluded that (1) ZVI-dedicated tests and model tools can be used for ZVI-parts of other multibarriers; (2) For new types of barrier parts, the specific feasibility tests will be different, but the same logic can be followed.

ZVI Biobarrier

(3) A 1-D model approach using HP1 (HYDRUS1D-PHREEQC) was found suitable and flexible to integrate generic knowledge to come to a tailor made experimental design of multibarriers and to predict the impact of multibarriers on the pollution (Haest et al., 2013).

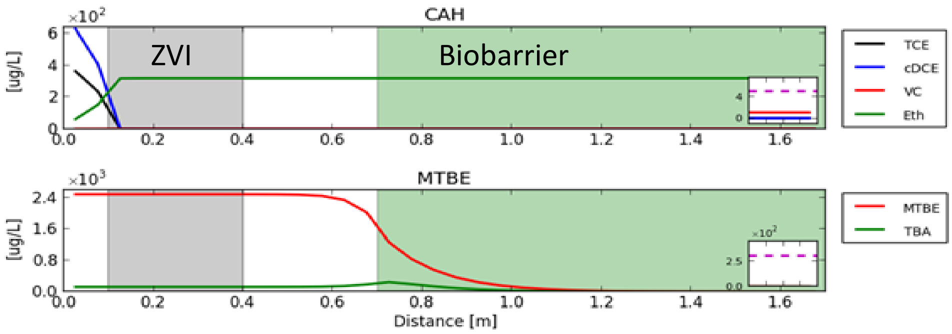


Figure 21: Simulation of the CAH and MTBE-concentration at site H as determined via the HP1 approach.

3.4.5 CONCLUSIONS

A combination of a good site characterisation, laboratory scale feasibility tests and technology modelling is advised to design (multi)barriers and predict their performance. Progress has been made in respect to predicting the longevity of barriers, especially ZVI-barriers, but showed to remain a challenging task. Multibarriers were shown to be suitable to cut-off property boundary exceeding plumes, preventing new inflow of contamination in the downstream properties.

3.5 IN-SITU REDUCTION OR OXIDATION OF HAZARDOUS POLLUTANTS (CHLORINATED ETHENES & BTEX) IN GROUNDWATER/AQUIFER WITH INJECTABLE FE-BASED PARTICLES (WP5)

Within the AQUAREHAB project WP5 focused on the development of groundwater rehabilitation technologies with injectable Fe-based micro- (100 nm < d < 100 µm) and nanoscale particles (< 100 nm). The idea was to inject small sized particles into the subsurface where they spread over a certain distance before sedimenting or attachment to the aquifer matrix. They then either directly react with the present contaminants or build a permeable reactive zone where the dissolved contaminants (plume) are being degraded. The advantage of this technology is that installing these zones or barriers via injection is fairly inexpensive and not intrusive (in other words, the beneficial usage of the site is not disturbed by the remediation efforts). Two strategies were pursued: (1) The use of <u>reducing</u> Fe-based particles for reductive dehalogenation of chlorinated solvents. This technology is based upon the state of the art technology of reactive permeable barriers. Hence, the research could be based upon a strong foundation and, as planned, resulted in the successful demonstration on two field sites; (2) Application of iron oxide particles as electron acceptors for <u>oxidative</u> biodegradation of BTEX contaminants. This technology was totally novel, hence it did not yield a field application within the frame of AQUAREHAB. Nevertheless, the outcomes of AQUAREHAB facilitated the development of this approach to a point where field applications were ready for application. Both approaches were accompanied by the development of monitoring technologies and ecotoxicology studies.

3.5.1 Screening of Different Injectable Fe-based Materials

Reducing Fe-based particles. A high diversity of pollutant removal capacities was observed between the > 20 different particles tested (Velimirovic et al., 2013a). Differences were also observed towards the set of pollutants (tetrachloroethene - PCE, trichloroethene -TCE, cis-dichloroethene - cDCE, 1,1,1-trichloroethane - 1,1,1 TCA) that could be degraded by the different Fe-based particles. Based on various aspects 11 particles, with a potential for the here envisaged application (from the reactivity point of view) were identified. A new ZVI-type was developed within AQUAREHAB, for which a patent was applied. The comparison of reactivity data with particle characteristics led to the following conclusions that a higher carbon content in the particles is increasing the probability for sorption of the contaminants on the particles, while reducing the degradation rate (Velimirovic et al., 2013b). The presence of sulphur in the iron powder appears to increase degradation activities, especially for TCE and 1,1,1-TCA. An increased amount of surface oxides is decreasing the degradation activity for the iron powders. With respect to stability and mobility, it was concluded that sufficient sedimentation stability is negatively correlated to particle size. For microscale zerovalent (mZVI) particles it is only provided using guar gum to stabilize the suspension. From a mobility point of view, particle size is the most critical factor. Based on the data obtained herein, transport through the pores of any appreciable distance is only possible for particles smaller than d_{50} of the porous media. Larger particles will either be strained out of suspension or will sediment very close to the injection point. For upscaling two particles produced within AQUAREHAB were used. Commercially available particles NanoFer 25s (nanoiron) and BASF MS 200 were also tested as a reference.

Oxidizing Fe-based particles. Ferrihydrite nanoparticles were selected for examination in the AQUAREHAB project. These nanoparticles showed the highest reactivity in microbial reduction experiments (Braunschweig et al., 2012), a high sustained microbial availability under simulated environmental conditions and a potential to accelerate toluene oxidation (Bosh et al., 2010a, 2010b, 2012). Additionally, these particles showed a high degree of colloidal stability.

3.5.2 Small Laboratory-Scale Reactivity, Longevity and Mobility Test

Colloidal stability of Fe-based particles and guar gum rheology. Oxidizing Fe-based particles have a typical size, in the order of a few nanometers, and are sufficiently stable when dispersed in pure water. Conversely, reducing Fe-based particles, in a size range of a few to tens of microns, are prone to very fast sedimentation, and consequently the use of viscous, shear thinning polymeric solutions have been studied (Gastone et al., in prep.). In particular, guar gum solutions proved effective in improving the colloidal stability of the iron suspensions, even at very high particle concentrations (Gastone et al., in prep.). Mixtures of guar gum and xanthan gum were also studied (Xue and Sethi, 2012). The guar gum solutions were fully characterized from the rheological point of view. It was also evidenced in column filtration tests with guar gum that impurities in the solution might cause pore clogging and a preparation procedure for slurry preparation was defined. Constitutive relationships have been derived for the design of iron slurries linking polymer concentration, particle size and density, and desired stability time (Gastone et al., in prep.).

Reactivity of reducing Fe-based particles. The most reactive irons have the highest corrosion rate and the shortest longevity (Velimirovic et al., under review). Addition of guar gum stabilizes mZVI in suspensions, but leads to a temporal deactivation of ZVI. This observed negative influence of guar gum can be explained by hydrogen bonding between iron and polysaccharides. After guar gum breakdown by enzymes and intensive rinsing off guar gum breakdown products, the iron efficiency towards CAHs is restored (Velimirovic et al., 2012a). Based on data of the dose tests, it appears that microscale particles could be efficient in pollutants removal at a concentration comparable to that of nanoscale particles. This is an encouraging observation for further examination and exploitation of mZVIs, which are significantly cheaper than nZVI.

Transport of reducing Fe-based particles. The laboratory tests showed that for permeation in sandy porous media only small particles (diameter in the order of few µm) can be used, because larger ones are mechanically filtered. The preparation of micro-iron slurries had to be performed carefully, to avoid the formation of aggregates which could clog the porous medium. Sedimentation tests performed for the two iron samples selected for fracturing injection (HQ from BASF and H4 from Höganäs) provided evidence of a fast increase of stability against sedimentation with increasing guar gum concentration (and consequently the suspension viscosity). The dependence of sedimentation half time on guar gum concentration can be modelled by an exponential law.

Reactivity of Iron-Oxides. The rates of BTEX degradation vary depending on the BTEX species. At the maximum it amounts approximately to a five-fold enhancement of microbial BTEX degradation by iron oxide nanoparticles in comparison to conventional bulk iron oxides. Iron-oxide colloid mediated microbial iron reduction now can be suggested as a viable mechanism in the environment of contaminant remediation (Fritzsche et al., 2012; Lee et al., 2012). Nanoparticulate ferrihydrite colloids also sustained their high intrinsic reactivity and bioavailability under flow conditions and attached to a porous matrix. The results from the soil column experiments indicate the high stability of iron oxide nanoparticles under realistic in-situ conditions. No limitation of particle lifetime can be observed. As iron oxide particles are reduced very fast, a full reduction will take place before any particle degradation (e.g. by remineralisation) can take place. The high rates observed in the large-scale column studies open new perspectives for the turnover of the microbial iron in the environment, and on the potential for the application of iron oxide nanoparticles for groundwater remediation.

Transport Iron-Oxides. Data suggest that ferrihydrite mobility can be controlled by adjusting the ionic strength of the suspension and the injection rate. If the nanoparticles are not supposed to travel far from the reactive zone, the colloidal suspension can be prepared adjusting the ionic strength to the value that provides the desired travel distance (Tosco et al., 2012).

3.5.3 MODELLING the transport of Fe-based particles in porous media

A software was developed for simulating transport in porous media of highly concentrated suspensions of iron particles dispersed in non-Newtonian fluids using a dual-site approach accounting for straining and physico-chemical deposition/release phenomena (Tosco and Sethi, 2010). The progressive clogging of the porous medium, due to deposition and filtration of a relevant mass of particles and aggregates, was modelled. Changes in pore velocity, viscosity, density and porosity, due to the progressive deposition of iron particles, as well as flow rate and fluid viscosity are included. The transport model was first implemented for 1D domains (E-MNM1D, for the analysis of column transport tests) and then extended to a radial geometry for the simulation of large-scale injection of iron micro particles via permeation (Tosco et al., in prep.). The radial model, called E-MNM, is intended as a tool supporting the design of field-scale applications of mZVI and nZVI–based remediation, for the estimate of the radius of influence of the slurry injection, when the injection is performed via permeation (i.e. in unconsolidated, medium-to-highly permeable porous media). The flow of non-Newtonian fluids, without suspended iron particles, through a porous medium was also studied at the micro scale via computational fluid dynamics (CFD) simulations (Tosco et al., 2013).

3.5.4 Large scale laboratory experiments, Constitutive Relations and Monitoring

Large scale laboratory experiments. Flow experiments on a radial flow domain performed with nano-sized iron colloids showed that transport over a distance of nearly two meters was possible. It was also shown that continuous flux is preferable to pulsating flux for injection. The influence of the injection rate is less pronounced in the large scale experiments than in the column experiments due to the hyperbolically decreasing seepage velocity in a radial flow field. Nevertheless the injection at the higher injection rate performed slightly better. Especially the concentrations close to the well were lower, avoiding the risk of clogging. From the experiments performed with micro iron particles it became clear that the reservoir had to be improved to make sure that all the iron particles stay in suspension and that the injection had to be performed with a constant injection concentration. It was shown that a funnel shaped reservoir combined with an inline circulating dispersing unit are effective measures to solve the sedimentation problem of the micro iron. Furthermore, it was shown, based on these results, that the transport of micro iron particles (2 µm) by permeation is not feasible for the given porous media. The micro scale iron particles used in these experiments are about the smallest particles commercially available (de Boer et al., 2010). They proved to be very difficult to inject and were not far enough transported. To get micro iron colloids emplaced inside a porous medium other means will have to be applied. The concentration of guar gum could be increased much more to further reduce sedimentation (Comba and Braun, 2012). However, the pressures necessary to inject such highly viscous fluids would be very high, these kind of pressures could not be applied in the lab experiment for controlled testing. In the field this would result in fracturing of the porous medium. The iron colloids would then be placed inside these fractures.

Constitutive Relations. The wide range of tested velocities and injected volumes, as well as the different iron concentrations, led to the following conclusions concerning the propagation of micro iron in a sandy porous medium: (1) no clogging occurs during the injection, since it was proved that particle deposition rate is constant with time; (2) micro iron in guar gum suspension is much more mobile than micro iron in water over a wide range of seepage velocities; (3) particle mobility decreases as it travels farther from the well; (4) the radial flow field can be reproduced using an empirical model, that transfers to the radial field what was observed for thin sections of porous medium in 1D column tests; (5) according to the model prediction, micro iron in water cannot be economically used in a field remediation, as the distance from the well reached by particles is limited (0.5 m); (6) micro particles in a weak suspension of guar gum can be distributed to a distance of 2m from the well using sufficiently high flow rates (e.g. 0.004 m^3/sec); (7) to design a field application, the relationship between injection rate and seepage velocity in the porous medium should be established.

Monitoring. A monitoring strategy, including the necessary tools, has been successfully developed. The tools include a master and slave system connected to a number of sensor arrays (Buchau et al., 2010). Each array consists of (1) race-track coils to directly measure ZVI content, (2) temperature sensors to monitor temperature changes brought about either due to the injection of slurry or due to chemical reactions, and (3) a number of depth oriented micro-pumps to ensure adequate sampling (no negative pressure for volatile compounds) of the site. The monitoring strategy also gives an indication of the optimum number of slaves (and thus sampling arrays) and their placement. For research purposes it is of course desirable to install as many arrays as possible.For practical applications, three to five arrays should suffice, depending on the extent of the remediation field and the local conditions, especially the anisotropy and/or heterogeneity of the subsurface. It needs to be emphasized that these arrays were solely developed for Darcian flow and transport. Application of high pressures and/or high injection rates might yield a development of preferential flow paths. These might or might not encounter the sensors; therefore identification and quantification of ZVI for non-Darcian flow is not reliable with these new sensors.

3.5.5 Pilot Scale Test, Including the Environmental Impact of the Technology on the Environment

Pilot test. In total 70 potential pilot sites were screened and after a four step screening process a site in Aarschot was selected for the demonstration of the new technology (Figure 22). The pilot test demonstrated that mZVI slurries stabilized with guar gum can be prepared at the pilot scale and delivered in the subsurface (Velimirovic et al., under review). Direct push injection has been selected as the injection strategy, taking into account: (1) iron mass required for dechlorination, (2) the ratio between average ZVI particles dimension and average porous media size; (3) distribution; and, (4) the sedimentation time of the slurry determined by screening laboratory experiments.

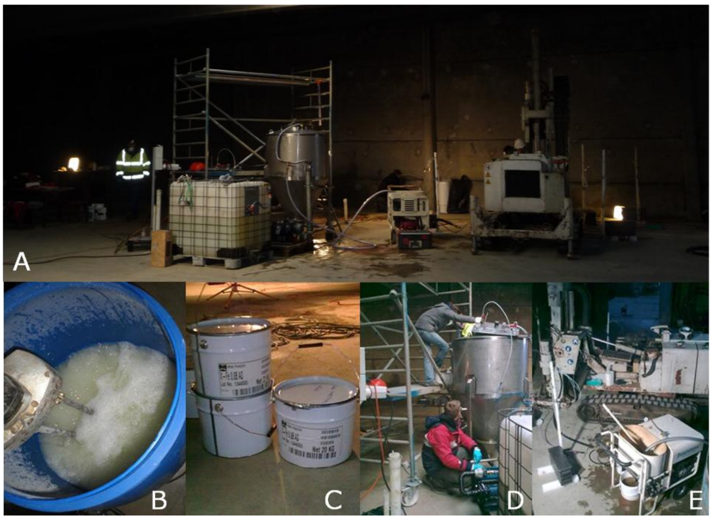


Figure 22. Iron injection set up. (A) injection area, (B) guar gum preparation, (C) mZVI, (D) mixing of guar gum and mZVI, (E) Geoprobe injection.

Monitoring data show a heterogeneous distribution of iron, due to the injection technology where preferential flow paths were created. Visual observations, H_2 measurements and guar gum analyses on the soil samples, proved that mZVI reached a maximum radial distance from the injection well of about 2.5 m. Once emplaced, indications were found for 1,1,1-TCA degradation in the field. Batch reactivity tests proved that the iron is reactive 2 months after the injection, despite the presence of guar gum in the injection fluid. Points that were identified for improvement are: (1) the guar gum preparation method is applicable for small amounts of guar gum. For larger quantities a different approach needs to be worked out; (2) The delivery of the mZVI at the envisioned depth remains challenging. Another injection approach envisioning a smaller radius of influence may lead to better results ; (3) Observations made at the field indicate that further improvements of the iron sensor are needed to make it a reliable and functional system.

Impact on the environment. The impact of different injectable Fe-based materials on the environment was evaluated with the main aim to examine whether the materials do not pose a threat when used in large scale field applications. Potential ecotoxic impacts of Fe-based particles (and acidic Fe materials) on both aquatic (bioluminescent bacteria, algae) and soil (plants - two species, annelid worms) biota were assessed (Jesenská et al., 2011). The overall benefit-to-risk ratio was concluded to be positive considering the minor and local scale of ecotoxicological impacts (few square meters for the worst case situations, in case day lightening of the injection fluid occurs). An adenosine tri phosphate (ATP) bioluminescence assay was prepared to examine worst case scenario for CAH-degrading enrichment cultures. The stimulating effect on the bacterial activity was observed as well as reduced activities when high doses were applied. It was found that nZVI particles have more negative influence on CAH-degrading enrichment cultures than mZVI particles. The observed inhibiting effects could be related to pH increases above pH 7.5, which are induced by ZVI. Whether the bacteria are killed or only temporarily reduced in activity cannot be concluded from the test. The presence of an aquifer matrix is nevertheless expected to act as a buffer protecting the bacteria. As such the impact in the real environment is expected to be minimal. The impact of different ZVIs on the microbial soil community was also presented. These tests did not reveal elements that are conflicting with the use of mZVI particles for in situ remediation.

3.6 Development of groundwater remediation technology models for use in water management strategies at the river basin scale (WP7)

To predict the performance and longevity of groundwater remediation technologies under field conditions reactive transport models were considered. Reactive transport models simulate water flow and solute transport in the subsurface. Generally, reactive transport models contain a reaction network, specific for each type of contamination and the transformation reactions of the chemicals, induced under natural conditions and by the respective technology. Subsequently, the reaction network is coupled to a hydrological model specific for the field site. The objective of the work in WP7 of Aquarehab is to use reactive transport models to design laboratory and field experiments for evaluation of the technologies, to model field application of the technologies and to reduce the complexity of reactive transport models for inclusion in water management tools at the catchment scale.

3.6.1 Optimal experimental design

Figure 23 shows the optimal experimental design strategy for groundwater technology assessment.

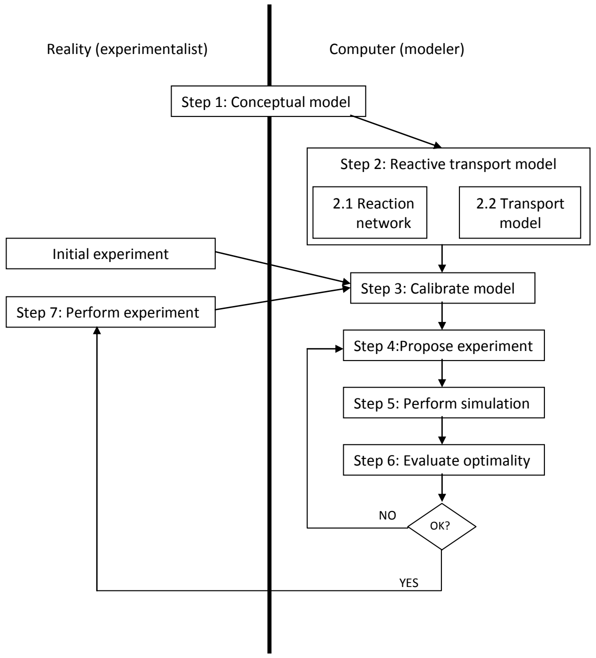


Figure 23: Optimal experimental design procedure for groundwater remediation technology performance assessment

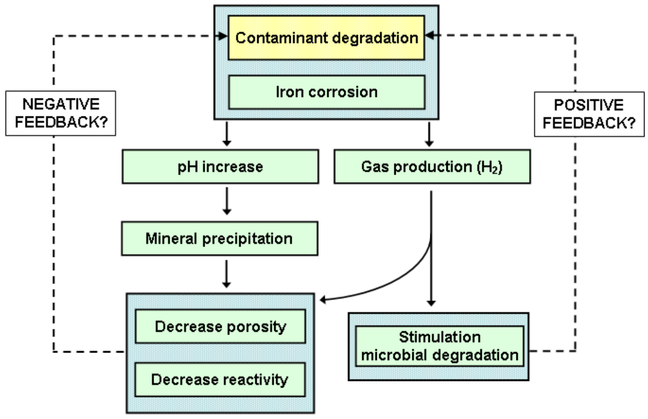


Figure 24: Conceptual model for the reaction network of an Fe^0 reactive barrier

Steps 1 and 2 comprise the construction of a reactive transport model for a specific groundwater remediation technology or a field scale model for a monitoring programme. Step 1 consists of defining a conceptual model framework containing all relevant physical, chemical and biological processes for the technology at hand. Step 1 requires interaction between experimentalists (the technology/engineering experts setting up a feasibility or field test for a certain technology) and the modellers (the mathematical/IT experts that implement the processes in a computer code). An example of a conceptual model is shown in Figure 24 for a reactive barrier. Step 2 involves the setup of a reaction network containing all relevant chemical reactions (e.g. sorption, mineral precipitation, aqueous speciation) and biological transformations (e.g. degradation kinetics) in the system. Secondly, the reaction network is coupled to a hydrological model, simulating the transport of an aqueous component in the groundwater. The reactive transport model may have been calibrated on the basis of data from an initial experiment or default or literature parameter values can be assumed (Step 3). Once a preliminary (calibrated) model is available, the experimental degrees of freedom and constraints or boundary conditions for the experimental design procedure can be defined (Step 4). Before any search for an optimal experiment can be initiated, an optimality objective has to be defined (Step 5). In optimal experimental designs, this usually refers to maximization of the information content and minimization of costs.

3.6.2 Reactive transport models

An overview of the AQUAREHAB reactive transport models is given in the table below.

Technology	Code	Processes included/characteristics of the model
Wetlands (WP1) (Figure 25)	FeFlow (Diersch, 2005) Feflow 6.0 was used to simulate 2D flow and reactive transport. http://www.feflow.info/	• 2D variable-saturated steady-state flow and multi-species transport • redox-zone dependent sequential first-order degradation of agrochemical compounds and metabolites. It is assumed that denitrification occurs sequentially from NO3->NO2->½N2, with each step governed by a first-order reaction.
Smart carriers in field drains (WP2)	Hydrus-1D (Simunek et al., 2013) User manual and notes on how to use HP1: http://www.pc-progress.com/en/Default.aspx?hydrus-1d	• Solute advection and dispersion (in one dimension): flow in the trench is conceptualised as 1D flow • Sorption: depending on the carrier material used, the sorption properties will differ • Degradation: degradation is incorporated in the model as a first-order reaction process with temperature dependency • Heat transport: important for the technology is to know how the performance alters with temperature; therefore a heat flow equation was used to estimate the temperature in the trench.
Groundwater river interaction zones (WP3)	PHREEQC VS2DH (Healy and Ronan, 1996 The HP1 code is fully incorporated into the Hydrus-1D (Simunek et al., 2013)	• A first-order model in containing advective-dispersive solute transport with first order degradation was developed to represent the degradation of VC in the river sediment. • 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 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.
(multi)Barriers (WP4) (Figure 21)	MIN3P (geochemical model) MODFLOW and PHAST PHREEQC	Reaction model used to predict barrier longevity simulates groundwater flow and multi-component reactive transport. Fifty three complex aqueous reactions and 3 mineral phases were included. Sixteen dissolved species were also included in the model to

Technology	Code	Processes included/characteristics of the model
		reproduce the concentrations profiles: perchloroethylene (PCE), trichloroethylene (TCE), trans-dichloroethylene (t-DCE), cis-dichloroethylene (cis-DCE), vinyl chloride (VC), ethene, Ca2+, Cl-, Na+ , Fe2+, Fe3+, S6-, S2-, TIC (total inorganic carbon), H+ and H2.
Injectable iron (WP5)	PHREEQC model MNM1D (Tosco T. et al., 2010)	To simulate observed geochemical changes from a batch experiment performed with one iron type. Simulation of the iron concentration in the soil matrix

As an example, the wetland model in FeFlow was evaluated/calibrated based on the following field data: (1) Hydraulic head data during dry and wet periods; (2) Presence/absence of nitrates; and (3) Lab-derived denitrification rates. Figure 25 shows two possible scenarios: (1) using only laboratory-derived parameters based on a zonation with four rates (with high rates in the peat layer and very low rates in the sand) and (2) calibrating the denitrification rates in the sand. Scenario 2 matches best the observations with a disappearance of nitrates between two sets of wells. In the simulations, the denitrification rates only needed to be so high as to remove nitrates quickly. It is believed that this rate is still due to some DOC leaching/diffusing into the sand from the peat. The simulation results further indicated that some denitrification must occur in the deeper sand as well, and it is speculated that another denitrification process with pyrite maybe on-going.

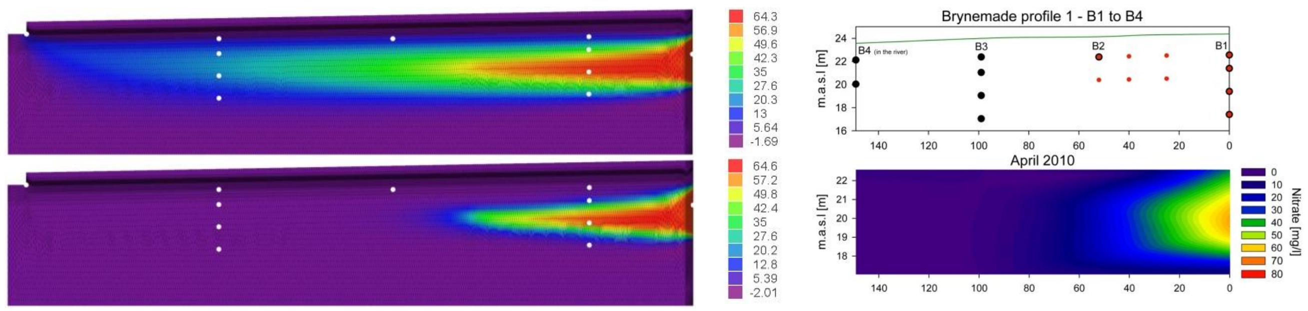
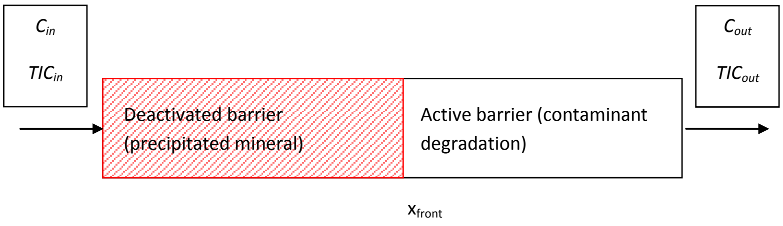


Figure 25: Feflow modelled scenario 1 (left top) and 2 (left bottom). The figure is with 3x vertical exaggeration. White circles are well screens. Measured nitrate profiles at Brynemade. Profile 1 – B1 to B4 (right top), measured nitrate April 2010 in existing piezometers (black dots) (right bottom). Nitrate is in mg/L.

3.6.3 Reduced models for water management

The implementation of reactive transport models in catchment scale water management and rehabilitation models, 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 are then plugged into decision support tools. The following reduced models were worked out: (1) the wetland plug flow reactor; (2) reactive barrier lifespan calculator (Figure 26); and (3) tanks in series model for groundwater-surface water interaction.



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

Figure 26: Simplified model conceptualization. C = contaminant concentration (mol L^{-1}), TIC = total inorganic carbon concentration (mol L^{-1}), q = darcy velocity (m_{bulk} s^{-1}), ϕ = porosity (-), mv = average mineral volume of carbonate minerals ($m^3_{mineral}$ mol^{-1}), S_0 = reactive surface ($m^2_{reactive\ surface}$ m^{-3}_{bulk}) and Tc = thickness parameter ($m^3_{mineral}$ $m^{-2}_{reactive\ surface}$).

The latter was used for a CAH polluted groundwater plume discharging in the Zenne river. Three remedial options were discerned: no action (= natural attenuation, NA), biostimulation in the aquifer, and the application of a capping material (e.g. straw) on top of the sediment. The input data used comprised of (1) degradation constants that were derived in lab-scale experiments, and (2) starting concentrations of *cis*-DCE and VC (600 and 1560 µg/L, resp). Estimated removal rates based on concentrations entering and concentrations leaving the groundwater – river interaction (GRI) zone according to the aforementioned scenarios, are compared for both model approaches in HP1 and the mixed tanks in series. The results with high flow rates show that the removal of DCE in the GRI is somewhat underestimated by the tanks-in-series model (Figure 27). Removal rates for VC were overestimated by the tanks-in-series model as compared to HP1. For low flow rates, both models predict nearly similar removal rates (close to 100%) for all scenarios. Overall, the agreement between predicted removal rates by both model approaches is adequate for management purposes. The tanks-in-series model can be used as a reduced approach for the processes in the GRI.

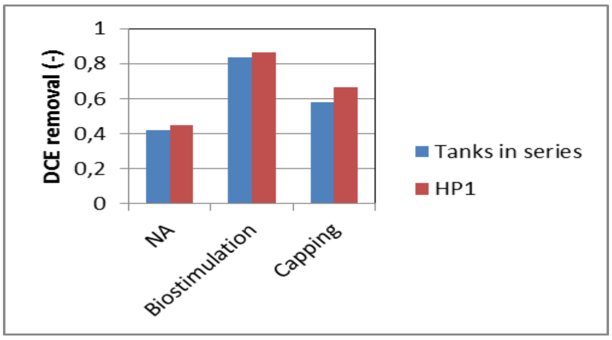


Figure 27: Calculated removal rates (fraction leaving GRI versus influent) using HP1 and the tanks-in-series model for three different scenarios of removal (NA = natural attenuation, aquifer biostimulation, and sediment capping) in the GRI for high flow rates (50 cm/d).

3.6.4 CONCLUSIONS

The modeling work in the Aquarehab provided methods to design laboratory and field experiments for determining the performance of in situ groundwater remediation technologies. The following general conclusions can be drawn: (1) a thorough schematisation of the subsurface is needed for site modelling, since the subsurface is heterogeneous in nature, which can affect the performance of the technology and the model; (2) the determination of source zones and their history is crucial, since the source term is an important driver for observed concentrations in groundwater and the design of the technology; (3) the parameterisation of field models is an issue for the practical application of the models by consultants since a great deal of parameters need to be estimated for technology performance assessments; (4) reasonable approximations are obtained with reduced models for performing first screening calculations of the performance for some in situ technologies, but data availability may still be an issue; (5) for uptake in decision support tools (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 the amount of parameters needed. Therefore simplified versions of the models need to be provided.

3.7 THE INTEGRATION OF WATERSHED FATE MODELS, ECOLOGICAL ASSESSMENT AND ECONOMIC ANALYSIS OF WATER REHABILITATION MEASURES IN THE REACHER DECISION SUPPORT SYSTEM (WP6)

Water managers have to make decisions on the implementation of measures to improve the status of the aquatic ecosystem. A decision support system (SSD) named REACHER was developed as a prototype. The REACHER DSS architecture basically consists of three main components:

1. **Models** consist of fate models, economic models and ecotoxicological models. Fate models are used to calculate the fate of chemicals in the soil-groundwater-surface water continuum for assessing the effects of measures on water quality. Economic models allow to establish a relationship between load reduction needed to obtain good water status and costs associated. Ecotoxicological models are used to calculate effects from doses.
2. **Databases** contain data from literature (e.g. measures and costs), inventories (e.g. pollutant emission data), expert knowledge, data from laboratory tests (performance of technologies) and output data from models.
3. **The user interface** allows for (1) User entries: choice of management options for a certain geographical unit, choice of evaluation criteria, … and (2) User output: visualization of effects (indicator showing status) on maps, cost information, tables, graphs, probabilities…

For every component, choices in software were made. Free and Open Source Software (FOSS) was used for the implementation. Table 1 shows examples of FOSS for these three components.

Table 1: Modules and example tools for implementation of a DSS

DSS Module	Example tools
Model	Bayesian Belief Network (e.g. GeNIe)
Database	PostgreSQL, PostGIS
Web-based Visualization	Apache, Mapserver, Openlayers, Extjs, WebKit

For REACHER we use a light-weight Bayesian Belief Network to perform the modelling as the complicated process-based fate models need too much calculation time for a web application. A Bayesian Belief Network (BBN) can represent the model results in a comprehensive and probabilistic way without having the high computing demand for many process-based models. It is a suitable management tool in constructing the decision support model. An example of a BNN is the GeNIe modelling environment in combination with the SMILE graphic user interface (developed by the Decision Systems Laboratory of the University of Pittsburgh). The WebDSS user interface is designed to communicate with the database following data transform standards.

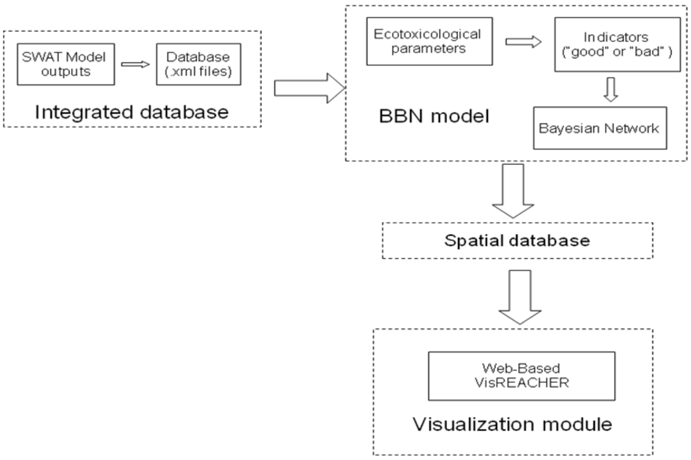


Figure 28: General layout of the DSS for evaluation of rehabilitation technologies in a geographical framework

3.7.1 Reacher DSS components

Hydrological models. The catchment model SWAT was used and adapted to accommodate for artificial drainage and wetlands. SWAT was applied to the Odense river catchment (Figure 29). Besides SWAT, a new conceptual modelling platform programmed in PCRASTER – Python, called SECOMSA, was developed to account for multiple sources (point sources, diffuse sources) and multiple mitigation measures in the catchment (wetlands, riparian zones, connection households to waste water treatment, cattle reduction) and to model the impact of the measures on water quality at the outlet of the sub-basin. The model was calibrated and evaluated for the Scheldt river basin.

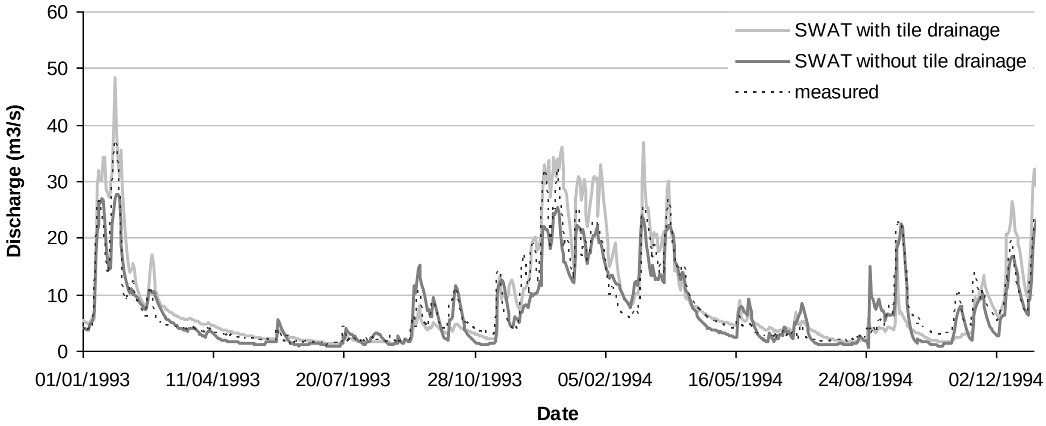


Figure 29: Evaluation of the performance of the adapted SWAT model for artificial drainage in the Odense catchment

Economic models and scenario analysis. The aim of the economic assessment is to identify the most cost effective course of action. This can be performed by simulating the impact of different management scenarios on selected substances (emissions or concentrations) in a river basin and to put them into balance with the total cost of these scenarios. The basic equation in cost-effectiveness analysis can be formulated as an optimization problem:

$$Minimize \sum c_i \alpha_i \qquad \sum \alpha_i \geq RT$$

where c_i are costs for reducing pressures coming from source *i*, which are a function of α_i, reduction of pressure by that source. The total of reductions must not be less than the total required reduction target *RT*. This formulation implies the ranking of measures by average cost per unit effectiveness. The calculation is also often represented as the calculation of cost-effectiveness ratios R, which are defined as:

R = AEC/Effectiveness

where *AEC* is the Annual Equivalent Cost (euros/year). '*Effectiveness*' can be defined as the quantitative change in the pressure on the resource or the improvement of the state of the environment. The cost-effectiveness ratio R is implemented in REACHER. In the REACHER DSS, the user selects a scenario for visualisation and a combination of measures. The model calculates concentrations and compares this with the base value. Additional columns will be added to display results of the economic analysis. For each measure in each sub-basin, a database with total annual costs, total annual load reduction (kg/year) 2015-2021-2027 is established. Depending on the selection of measures and the selected year, the sum of all costs and load reductions for all selected measures per sub-basin is made. Results are shown in additional columns in a tabular view. One column displays all costs per sub-basin, one column displays all load reductions per sub-basin. It should be remarked that in the scenario runs all measures were applied homogenously over the entire catchment. A column displaying cost-effect ratios (costs divided by load reductions) is also added.

Status visualisation. The classification schemes in the REACHER DSS follow the WFD methodology for assessment of the overall status of a surface water body. Specific descriptions of the ecological status assessment can be summarized as follows. Ecological status is a result of "the worst case scenario" bringing together the below scores of the three evaluated biological quality elements (BQEs) – benthic diatoms, macrophytes, benthic invertebrates (three sub-parameters – general degradation/saprobity/stream morphology) for each site and year. Ecotoxicological criteria are derived for specific chemicals based on the Species Sensitivity Distribution (SSD) approach resulting in PAF, ms-PAF or weighted mean PAFs. If single chemical concentrations are measured for a certain river basin (site, locality), concentrations can be translated into the PAF value. The PAF value predicts the hazard that specific fraction of a community (0-1) is likely to be affected by the chemical concentration (e.g. PAF of 0.05 indicates that it is likely that 5% of the community is affected; higher PAF value indicates higher hazard). If multiple chemical concentrations are measured for a certain location, concentrations can be translated into msPAF value. The ms-PAF value predicts the hazard that specific fraction of a community (0-1) is likely to be affected by the mixture of chemical concentrations (e.g. ms-PAF of 0.05 indicates that it is likely that 5% of the community is affected; higher PAF value indicates higher hazard). If the dynamics of chemical concentrations are known through either high-frequent monitoring or modelling, the concentrations can be translated into weighted mean PAF values. Details of the methods used can be found in Jesenská et al. (2013).

Nitrogen is one of the substances for which water quality targets (at the scale of a river basin) are difficult to reach. The substance is also emitted by a multitude of sources and for international river basins, in different Member States. Conventional measures, included in the river basin management plans, typically include wastewater treatment for households (collective or individual) and reducing agricultural emissions by reducing livestock, fertilizer use or performing manure processing. Wetlands and buffer strips are also included in the different management plans and are considered effective in reducing run off losses. Information on point source emissions, costs and effectiveness of the measures is included in REACHER, and implemented for the Scheldt river basin in France and Belgium.

3.7.2 Application of REACHER DSS for Scheldt & Odense river basin

The prototype REACHER DSS is accessible through a weblink with login and user password. A catchment can be selected and its groundwater status and surface water status (both summer and winter averages) can be visualised (Figure 30). The user can select a scenario by applying one or multiple measures (cattle reduction, fertilizer reduction, buffer strips, waste water treatment, or wetlands).

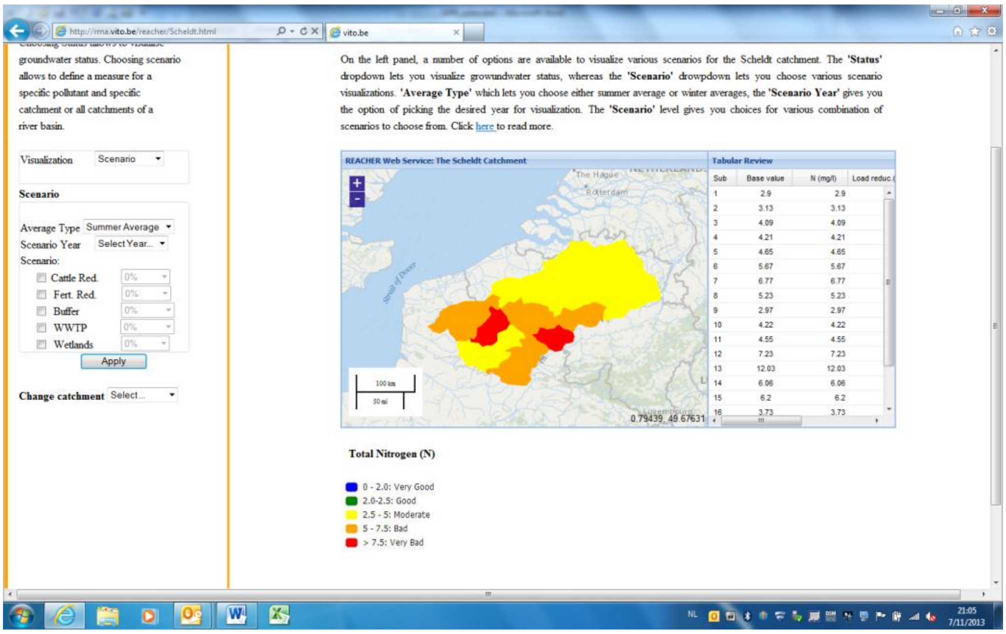


Figure 30: Surface water status visualisation in the REACHER DSS. The status window consists of a geographical delineation of sub-basins and colour coded classification of the N status at the outlet of the sub-basin. The N concentration values are given in tabular view for each sub-basin.

The effect of implementing one or multiple measures is displayed geographically and in tabular view. The table shows the load reduction in each sub-basin achieved with implementation of a measure, the associated cost and the cost-effectiveness. The effects can be visualized and assessed for three time steps, i.e., 2015, 2021 and 2027. The REACHER also allows to visualize chemical status (good or bad as compared to environmental quality standards), ecological status (according to the WFD classification) and ecotoxicological hazard (for individual substances, for mixtures of substances, or dynamic substances) for point locations in a river basin. The prototype REACHER DSS for the Scheldt is fed with data from pre-calculated runs with the SECOMSA model for the different scenarios (Haest et al., 2013). The SECOMSA predictions were evaluated using discharge measurements and nitrates concentrations for various sub-basins in the Scheldt catchment.

3.8 Extrapolations (WP8)

Four extrapolation cases were determined 3 years after the start of the project with the aim to evaluate the generic character of technology guidelines and developed modelling and management tools.

Table 1: New case studies presented for extrapolation

Study proposal	Aim/ Final chosen site	Partners / References
WP1+: Wetlands	To validate and improve subsurface models directed to nitrate and to compare/acquire more information on subsurface denitrification rates across wetlands determine the role of type of soil (peat/sand) and DOC in denitrification / Hygild site, Denmark To validate the “above surface compartment” model that aims at describing reactive transport of pesticides entering the wetland through erosion, run-off and drainage and validate pesticide degrading wetland activity in this compartment / Bernissem, Belgium, Moldova site	KUL, GEUS, UCPH, CTM, EI (Engesgaard et al., 2013) (Johnsen et al., 2013) (Vandermeeren et al., 2013)

Study proposal	Aim/ Final chosen site	Partners / References
WP4+: ZVI-barrier	To extrapolate the optimized feasibility test procedure for ZVI-barriers and the associated numerical models to another test site. The aim was to derive parameters needed for the design of the ZVI-barrier and to estimate its longevity. In addition the use of numerical tools (estimation longevity) by non-modelers was evaluated. A new iron type developed within WP5 was used,. **/**Ghent, Belgium	VITO, TUDelft, SAPION, HB and MU (Bastiaens et al., 2013)
WP5+: injectable ZVI	To verify and compare permeation and preferential flow path injections with 2 different microscale ZVI materials and techniques with the iron distribution and iron reactivity. To verify the numerical model for distribution of ZVI in the subsurface (focus distribution) – permeation and to test the developed detection system under permeation condition (focus distribution). To test the newly developed reactive particles in the field (distribution and reactivity) under preferential flow injection conditions – / Industrial site in Belgium	VITO, POLITO, USTUTT, HB, Sapion (Velimirovic et al., 2013) (Klaas et al., 2013) (Luna et al.;, 2013)
WP6+: REACHER local	A display of the current groundwater quality status for a selected set of contaminants. Modeling the evolution of the pollutant concentration in the groundwater, with and without measures – impact on state. To develop a technology selection module to propose technologies suitable to accomplish the required flux reduction or mass removal (conventional + innovative technologies) – measures and effectiveness. Estimate the loss of economic value due to groundwater pollution (now and for future use) and remediation costs in order to propose a cost-benefit analysis – disproportionate costs **/** Flanders region, Belgium	INERIS, VITO, USFD (Haest et al., 2013) (Broekx et al., 2013) (Jesenská et al., 2013)

4 POTENTIAL IMPACT

4.1 AQUAREHAB OUTPUT TARGETED TO DIFFERENT AUDIENCES

A diversity of outputs from the AQUAREHAB project was delivered for different target audiences. A visual overview is given in Figure 1 (page 4). In the sections below a short general overview of the output types and their impact is given.

4.1.1 Output for the general audience

Importance of water: Water is one of the most important substances on earth. All plants and animals must have water to survive. If there was no water there would be no life on earth. In contrast to salt water, it is mostly only the fresh water that can be used. A large amount of water is present on earth (1.4 billion km^3), which comprises mostly salt water. Only 2.5% of the total available water is fresh water. The major part of this fresh water is stored as ice (~ 70%) and groundwater (~ 30%), while surface water and soil moisture together represent less than 0.01%. This emphasises the importance of groundwater as a ‘reserve’ source of fresh water now and in the future. For this reason, the quality of the groundwater cannot be ignored and all possible efforts need to be made to (1) prevent the pollution of groundwater and (2) prevent the spreading of contaminants that are already present in the groundwater and subsurface.

Generally, it can be stated that the general public is becoming increasingly more aware of the importance of clean water. However, the step towards the acceptance of a higher cost-price for clean water is not made everywhere. Further, it was experienced that people have more affinity with the water types that they can see, smell and/or taste (drinking water, surface water), than with more 'invisible' water such as groundwater. AQUAREHAB focussed on water in general, but the groundwater compartment received special attention. In this way AQUAREHAB has tried to contribute to making the general public more aware of the existence and importance of groundwater.

AQUAREHAB newsletters, a general description of the project, a video and other visual material were developed and disseminated to inform the general public about AQUAREHAB activities and the importance of water.

Newsletter: In the course of the project, 8 newsletters have been prepared describing the progress made during the project.

An **AQUAREHAB video** was prepared in 2011 in collaboration with the WATERDISS project and gives a short visual overview of the aim and diversity of activities performed within AQUAREHAB.

A **general article on AQUAREHAB** 'going with the flow' was published by International innovation, Environment-October 2011, with the message 'water without borders'.

4.1.2 Outputs for stakeholders, experts & scientists

Patented products: Three patents have been filed for products developed within AQUAREHAB. One patent was filed by Höganäs and VITO related to a new type of zerovalent iron (ZVI) that was tested in numerous laboratory scale tests and two field applications for the degradation of chlorinated compounds. In addition, a patent was filed by Helmholz Zentrum Munich for another type of injectable reactive particle, being nano-scale ironoxides . The ironoxide particles were tested at the laboratory scale for the stimulation of biodegradation of BTEX-compounds. Finally, the University of Stuttgart submitted a patent describing sensors for the in-situ detection of magnetic particles, such as ZVI. Their functioning was evaluated in large laboratory facilities and the sensors were also implemented into the subsurface of two AQUAREHAB field experiments where mZVI was injected.

Other products: In multiple WPs within AQUAREHAB, bacteria were isolated from environmental samples (soi/groundwater/sediment) and were studied for their capacity to degrade certain pollutants. Enrichment cultures for aerobic and anaerobic degradation of chlorinated compounds were isolated, as well as pesticides-degrading bacteria, comprising an aerobic atrazine degrading strain. Further, materials for capping riverbeds to prevent influx of pollutants from the groundwater into the river water, were identified via laboratory scale tests. The materials are good carrier materials for bacteria and release C-source needed for bacteria to degrade for instance chlorinated compounds. Also a large set of micro-scale ZVIs was screened from which the most reactive were selected.

Technology descriptions: The AQUAREHAB project focussed on a number of rehabilitation technologies as examples. These comprised: activated wetlands (WP1), activated drains (WP2), stimulation of the hyporheic zone (interface between groundwater & surface water) by for instance capping (WP3), the (multi)barrier technology (WP4) and the injectable reactive iron particles technology (WP5). For each of these technologies, a 5-7 page document was prepared describing general background information and the application area and boundary conditions of the technology. The aim is to inform authorities, consultants and site owners briefly about the technology.

Technology models: To evaluate the impact of remediation technologies on the water quality in time and space, technology models were composed by modellers with input from technology developers (Seuntjens et al., 2013a). The technology models worked out within AQUAREHAB are related to a specific technology and aim (1) to develop reactive transport codes and hydrological models for simulating pollutant removal in riparian zones, river beds and groundwater, (2) to design experimental work related to the technologies, (3) to evaluate models on various cases and to generalize the model results, and (4) to develop a common modelling framework for incorporating model results into catchment scale models. Typical users are water managers, consultants, land owners. Some examples of models developed are: Wetland-FeFlow; PRB – PHAST; GRI- HP1; Wetland reactor; PRB lifetime calculator; GRI- TIS model and a particle distribution model. The software that was used to construct the technology models should be bought by the user on a license basis. On the other hand, input files for the different case studies and case descriptions will be made available via the AQUAREHAB website. Information on where to obtain the software and the contact details of the partner, who developed the model, will be added.

Management tools: Prototypes for two management tools were developed within AQUAREHAB.

- REACHER: The generic collaborative management tool 'REACHER' can be used by stakeholders, citizens or water managers to evaluate the ecological and economical effects of different remedial actions on water bodies. The tool consists of four major parts: (1) fate models to integrate the fluxes of chemicals at the river basin scale; (2) an assessment of the ecological effects of chemicals in river basins; (3) an economic analysis of the rehabilitation technologies (costs and benefits); and (4) the integration of fate, effects assessment and economic analysis tools into a collaborative management tool or DSS REACH-ER with a users' interface (Seuntjens et al., 2013b). The tool covers a river basin scale with the Scheldt river basin and the Odense river basin as examples, and focussing mainly on surface water.
- REACHER-local: The second prototype tool focuses on groundwater at a regional scale (Marti et al., 2013). Users are able to explore the status on polluted sites across a region, how this status evolves in time with/without remediation, which potential impacts can be expected for different sites, which societal cost we bear due to the environmental damage or the benefits that can be achieved by reducing pollution levels, and which technologies can be implemented for different sites and score best on costs, effectiveness (speed).

The REACHER and REACHER–local software is open and will be made available through the AQUAREHAB website. Georeferenced data on specific contamination are protected and fall under confidentiality agreements with the data providers. Public data can be obtained by a specific data request to the public authorities. The developed fate models, SWAT, SECOMSA, COMFRACS and MCA are freely available and input files will be put on the AQUAREHAB website.

Generic guideline documents are prepared for most technologies and describe the technology in more detail. Further, they provide generic guidelines to evaluate the feasibility of the technology, and to design, implement and/or monitor the technology. This information is especially useful for scientists and consultants who are considering the application of the technology for a site, and may also support authorities charged with the follow up of the impact of the technology. Generic guideline documents have also been composed for technology models and decision support systems. The aim of the guidelines is to group knowledge and experiences from the AQUAREHAB project and make them available for the outside world.

Scientific publications: To date, more than 30 scientific peer reviewed papers on AQUAREHAB work have been published. In addition, other reviewed papers have been accepted recently, or were submitted or are being prepared. In addition, more than five PhD dissertations were linked to AQUAREHAB work.

Other publications: AQUAREHAB organised 2 external conferences where different aspects were presented. A significant number of proceedings papers on AQUAREHAB work were prepared and are available to the public via the AQUAREHAB websites.

- Proceedings of the 1st European Symposium on Remediation technologies and their integration in Water Management (comprising the first AQAUREAB conference). September 26-26, 2012, Barcelona, Spain. ISBN 978905870093
- Proceedings of the 2nd European Symposium on Water technology & Management (comprising the second AQUAREHAB conference). November 20-21, 2013, Leuven, Belgium. ISBN 9789058570109.

4.1.3 Outputs for authorities

Water managers have to make decisions on the monitoring of water quality and the implementation of measures to improve the status of the aquatic ecosystem. Considering the different water types (river water, lake water, groundwater, ...), the multiple aspects related to water quality, the variety of (innovative) rehabilitation measures and limited available budgets, water managers do have a challenging task.

The policy context for water management in Europe is largely defined by the European Water Framework Directive (WFD). This Directive, adopted in 2000, sets ambitious objectives to meet the good status of all waters by 2015. To ensure that this goal will be met, Member States must publish river basin management plans for each river basin district detailing the status we are in now, the status we will be in in the future if we do nothing (BAU), and how this status will evolve towards 2015, 2021 and 2027 if we implement specific combinations of measures. This means that technologies to rehabilitate degraded waters need to be able to restore good ecological and chemical status by 2015 and be integrated into water management activities at the river basin level.

In general the quality of river water, lakes and ground water across Europe has improved thanks to a range of EU environmental directives since the 1970s, but there still remain significant "hot spots" of degraded waters from both point and diffuse sources. There are in addition approximately 250000 soil contamination sites across EEA member countries. Potentially polluting activities are estimated to have occurred at nearly 3 million sites (including the 250000 sites already mentioned) and investigation is needed to establish whether remediation is required. If current investigation trends continue, the number of sites needing remediation will increase by 50% by 2025" (EEA, 2007). For groundwater, 80 % of groundwater bodies achieved good chemical status, while 87 % achieved good quantitative status in 2009 (EEA, 2013). By 2015, some 89 % and 96 % of groundwater bodies are predicted to be in good chemical and quantitative status, respectively.

Within the AQUAREHAB project, the quality of water and possible measures to improve the general water quality were considered, but the groundwater compartment (= water reserve of fresh water for the future) received special attention. A set of remediation technologies were studied from a groundwater remediation point of view, with special attention to estimate the impact of the technologies on the water quality in time and space. In parallel, a decision support tool was elaborated by other partners for water management at river basin scale conforming to the WFD. Discussions within the AQUAREHAB consortium between partners working in these different parts revealed that groundwater aspects are only partially considered in the current WFD-based approach. A clear gap was identified between groundwater management (driven by local legislation) and water management at river basin scale (driven by the WFD).

As AQUAREHAB aims were set to focus on 'integrated water management', special efforts were made to bridge this gap:

1. A first important aspect was to make people working in the water management area and people focusing on groundwater management aware of this gap, and bring them in contact with each other for discussions. This proved to be very challenging, as it was like bringing together two nearly completely different worlds. In September 2012, AQUAREHAB and the WaterDiss2.0 project organised a Policy (implementation) session in Barcelona aiming to match the needs of policy makers and practitioners to the new solutions provided by research projects in order to meet the objectives set out in the Water Framework Directive and related directives. One central issue for the groundwater management discussion was that currently the integration of groundwater management and remediation in 'water management' does not seem to be fully accomplished by EU policy. It was observed that Water Framework Directive (WFD) is mainly focussed on the long term and large scale management of surface water within water bodies – so that activities related to groundwater, as part of the remediation of contaminated sites, are probably at a too local scale for the WFD and are mainly addressed by regional environmental authorities. This might be so but there could be more effort to harmonise standards and legislation concerning risk assessment and management of contaminated sites and pollution incidents. Since local groundwater contamination can often affect large groundwater bodies, it is still important to consider the effects of the parcel scale on the larger scale. Furthermore, groundwater is an important reserve for clean water in the future, and should be considered as a receptor and not just a path of pollutants to reach surface waters. Besides scale, the pollutant types listed in the WFD are mainly based on the needs of maintaining good surface water status, while other compounds are of more concern to groundwater quality status. In addition, the limited dynamics of groundwater complicates the use of tools and legislation developed for highly dynamic surface waters. At the moment it seems that more public information is needed concerning the status of the groundwater to increase the awareness and understanding of its impacts and the best remediation approach. In addition, it is important to establish relations between the use of the groundwater and the quality in order to assess whether all groundwater reserves are adequate for all uses or whether there should be more restrictions on use depending on the quality. So a clear gap was identified between groundwater management (driven by local legislation) and water management at river basin scale (driven by the WFD).

2. Further, it was decided to elaborate not only a prototype for a general water management tool, but also a tool for groundwater management.
    - **<u>REACHER:</u>** Within AQUAREHAB, REACHER was developed as a prototype for a decision support tool for general water management at river basin scale. The initial aim was to integrate the impact of measures, including groundwater remediation, in the tool and link it to ecological and economical evaluations. This tool focuses on large scale areas and includes rather highly dynamic processes which have an effect on goals set in the

Water Framework Directive. Groundwater is considered within the REACHER, but in an abstract (inexplicit) way. Diffuse pollution resulting from agriculture can be considered within REACHER, and efforts are made to include the impact of wetlands on the water quality. However, it turned out to be impossible to link groundwater management to the existing REACHER, especially local groundwater pollution is difficult to integrate and consequently most innovative technologies (besides wetlands) have no links with the REACHER to date. As such, a more locally oriented tool is required that is specifically aimed to prioritize measures.

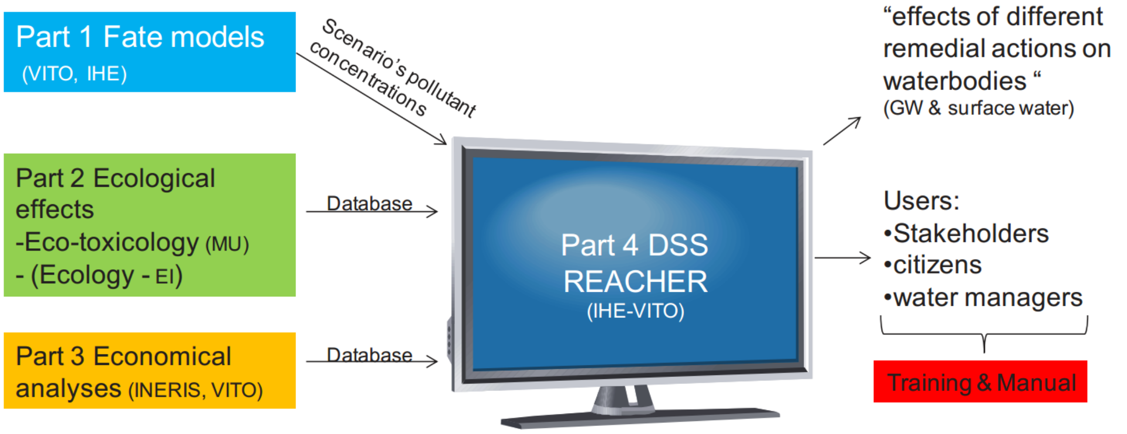


Figure 31 Schematic representation of REACHER, a prototype for a decision support tool for general water management at river basin scale.

- **REACHER-LOCAL:** To elaborate the prototype tool REACHER-local for groundwater management at a regional scale, the Flanders region was selected. The Public Waste Agency of Flanders (OVAM) was contacted as a stakeholder and available datasets were obtained from this agency. The REACHER-local tool aims at regional-scale management of groundwater pollution of the phreatic layer. The following aspects were elaborated for the prototype tool: (1) Mapping the groundwater quality, taking into account selected pollutants (BTEXs, CAHs); (2) Modelling the evolution of the pollutant concentration in the groundwater, with and without measures and visualisation; (3) A technology selection module is included that connects to the general guidelines that are developed by the AQUAREHAB project partners; (4) Economic considerations to relate remediation costs to loss of economic value due to groundwater pollution; and, (5) Visualization with user interface. The REACHER-local decision Support System as such has 4 parts: a status module, an impact module, a technology selection module, and a cost-benefit assessment. Considered pollutants for the prototype version are PCE/TCE/DCE/VC and BTEX. The tool is being developed in cooperation with the technology specialists. The REACHER local is a tool that addresses the gap between river basin management and groundwater remediation technologies.

3. Finally, it was decided to dedicate a policy brief on 'integration of groundwater management in water management' with recommendations for policy makers. Recommendations from AQUAREHAB to policy makers & authorities comprise:
   - Groundwater may require a different approach to river basin management in comparison with surface water;

- However, both approaches need to interact and it is preferred to combine them in an integrated water management approach;
- Groundwater quality management may be preferred at a scale smaller than the groundwater-body scale, considering 'local' groundwater fluxes;
- Groundwater that is not discharged immediately into surface water and that is not included in currently defined drinking water catchment areas, is also to be considered as a receptor (reserve of fresh water) and not only as a path between source and surface water as receptor;
- The quality assessment parameters for groundwater are currently limited to quantification of a limited set of listed pollutants, while no approaches are described to evaluate the ecology. Therefore, the currently available data (which may be limited to concentration data for a few wells in an area of up to 5,827 km^2) may not be a reliable indicator for the groundwater quality in this area. Recommendations related to this issue include:
    - The pollutants that are considered in the integrated water management approach should be extended with compounds relevant for the groundwater – even if they may not be that relevant for surface waters (such as volatile compounds);
    - In respect to groundwater pollution monitoring, it is recommended to use a denser net of monitoring wells, but to sample less frequently. This recommendation is based on the less dynamic character of groundwater in comparison to surface water.
    - It may be considered to identify additional parameters (besides chemical analyses) to evaluate the groundwater quality. A possibility may be to identify and define micro-organisms relevant for the (anaerobic) subsurface, to complement the quality evaluation with an ecological parameter. These micro-organisms could also be useful to evaluate the impact of remediation agents in the subsurface.
- The groundwater monitoring network in river basin management is currently installed mainly to evaluate diffuse pollution originating from agriculture. It may be worth to consider the use of the extensive 'Site management' data bases on groundwater pollutants to evaluate the global groundwater quality.
- Although data are available for many areas, there is no global inventory of the groundwater related 'local problems in Europe'. A reason may be that this information can be sensitive (depreciation of land, etc.) and is not always publicly available. It is recommended to identify more precisely the existing barriers for composing such inventories, and to invest efforts to lower these barriers.
- Harmonisation of standards (like groundwater intervention values) and legislation concerning risk assessment and management of contaminated sites on European level would be a step forward. It avoids that each country/region has to develop (re-invent) its own system and will give a less confusing message to polluters and site owners. Nowadays regional differences in standards do have economic implications.

4.2 SOCIO-ECONOMIC IMPACT

4.2.1 Impact of groundwater remediation technologies in time and in space

AQUAREHAB did foresee a significant amount of man months to estimate the impact of rehabilitation technologies in time and in space. This was a rather innovative approach as currently groundwater remediation is by law made on a property basis, often with the 'polluter pays' principle. For most technologies listed in Table 2, a technology model was composed to predict the impact.

Table 2 Rehabilitation technologies considered within AQUAREHAB.

Rehabilitation technology	Application area	Pollutants targeted	WP
Activated riparian zones (wetlands)	Interphase groundwater & surface water	Pesticides, nitrate	WP1
Activated drains	Groundwater	Pesticides	WP2
Capping	Interphase groundwater & surface water	Chlorinated ethenes	WP3
Permeable reactive iron barriers	Groundwater	Chlorinated ethenes	WP4
Biobarriers	Groundwater	Chlorinated ethenes BTEX MTBE	WP4, WP3
multibarriers	Groundwater	Chlorinated ethenes BTEX MTBE Ammonium	WP4
Injectable reducing iron-particles	Groundwater	Chlorinated ethenes	WP5
Injectable iron oxides	Groundwater	BTEX	WP5

The following general conclusions can be made:

- The impact of groundwater pollution often crosses property boundaries as pollutants present in the groundwater are transported to downstream areas.
- Although pollutants do migrate, their mobility on a river basin scale or groundwater body scale is mostly negligible due to the low groundwater flow velocities and retardation properties and size of the aquifer.
- Most of the time, the influx of typical groundwater pollutants released from isolated contaminated sites in a surface water body does not lead to detectable higher pollutant concentrations in surface water. This can be explained by the dilution effect (slowly flowing groundwater enters fast flowing river water), volatilisation/sorption and biodegradation under the aerobic conditions in the river system. Chemicals released at the basin scale (diffuse pollution) such as nitrates, phosphorus, pesticides, heavy metals, etc. may well impact the surface water through overland flow and shallow groundwater drainage. Wetlands are a typical example of local rehabilitation measures that may reduce the effect of diffuse pollutants when implemented at multiple locations throughout a catchment.
- The impact of rehabilitation technologies is dependent on several site specific aspects, which make generalisations of 'preferred' technologies difficult. A site-based approach is needed.
- The often unknown quantity of 'bulk' pollutants in a source zone, that can be releases in the groundwater creating groundwater contamination plumes during decades, does complicate the prediction of the impact.
- Due to many unknown parameters in the subsurface and its dynamic character, uncertainties are associated with the predictions of the impact of groundwater remediation technologies. Nevertheless, the modelling work does give useful indications.

- The impact of groundwater remediation technologies is mostly not immediately visible after implementing a rehabilitation technology. It may take several years of monitoring to get a clear picture of the situation.
- Due to the low mobility of the pollutants and the local scale, the presence of groundwater pollutants is mostly not visible via the large grid monitoring approach used at river basins and ground water body scale. As such the impact of the technologies is also mostly invisible. Nevertheless, these multiple ”local pollution” and the associated remediation actions do impact the groundwater quality. As inventories of “local pollutions” for larger regions are mostly not available, it is hard to evaluate whether they have an impact.
- The fact that the impact of groundwater remediation efforts becomes only slowly visible may make the topic less interesting for policy makers to invest money. The effects of decisions and invested money may not be visible within a certain legislation period (cfr WFD 2015-2021-2027 cycles, local governments …).
- Nevertheless, when considering groundwater as a reserve of fresh water for the future, the preservation of the groundwater quality is important and should be integrated in water management.

4.2.2 Integration of groundwater in river basin management

The gap that was identified between groundwater management (driven by local legislation) and water management at river basin scale (driven by the WFD) has been explained in the sections above. Bridging this gap will require a transition process with good communication, changes in current mind-sets and organisations, as well as efforts and investments. It is clear that clean water will have its price.

5 CONCLUSIONS

During more than 56 months the multidisciplinary AQUAREHAB consortium worked on the development of rehabilitation technologies for degraded waters and tried to integrate the impact of the technologies in water management. Good progress has been made for both aspects. The possibilities of the selected remediation technologies were studied more in detail and useful knowledge and new products were developed. Via the technology models the functioning of the technologies was simulated enabling to predict the impact of the technologies in time and space. This required a close collaboration between the modellers and the technology developing people. Also once developed, the use of the models to simulate other situations will probably require multidisciplinary which may be hard to find in one person.

Prototypes of water management systems (Decision Support Systems) were elaborated for river basin scale with the focus on surface water (REACHER) and on a regional scale with focus on groundwater (REACHER-local). Full integration of groundwater into the current river basin management approach was not found possible due to differences in dynamics, scale and pollutant types considered.

6 PROJECT PUBLIC WEBSITE & CONTACT DETAILS

Project website: Aquarehab.vito.be

Table 3: AQUAREHAB partners

Beneficiary Number *	Beneficiary name	Beneficiary short name	Country	Contacts
1Coordinator	Flemish Institute for Technological Research	VITO	Belgium	Technologies (coordinator): Leen.bastiaens@vito.be Modelling & water management: Piet.seuntjens@vito.be
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3	Geological Survey of Denmark and Greenland	GEUS	Denmark	Jens Aamand jeaa@geus.dk
4	Helmholtz Zentrum München – Deutsches Forschungszentrum für Gesundheit und Umwelt GmbH	HMGU	Germany	rainer.meckenstock@gsf.de
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13	UNESCO-IHE Institute for Water Education	IHE	Netherlands	Hans Vanderkwast J.vanderKwast@unesco-ihe.org
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16	Hoganas AB	HB	Sweden	per-olof.larsson@hoganas.com
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18	Institut National de l'Environnement Industriel et des Risques	INERIS	France	jean-marc.brignon@ineris.fr
19	Environmental Institute - SME	EI	Slovak Republic	Jaroslav Slobodnik slobodnik@ei.sk

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TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights[2]:	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
German Patent	NO	02.03.2009	DE102009012834A1	Adjustment of the pH of aqueous suspensions of metallic nano particles	Klaas, Norbert; Steiert, Stefan; Boer, Cjestmir; Ruck, Wolfgang
German Patent	NO	15.09.2009	DE102009047858A1	In-situ ZVI-Detection device	Klaas, Norbert; Buchau, Andre; de Boer, Cjestmir
European	Yes	21/9/2012	EP12185424.4	New powder, powder composition, method for use thereof and use of the powder and powder composition	Per-Olof Larsson - Höganäs bastiaens Leen, Velimirovic Milica - VITO
European	Yes	23/7/2013	EP13177597.5		
EPC	Yes	18/9/2013	PCT/EP2013/069326		
Taiwan	Yes	18/9/2013	TW102134043		
WO	No	27/3/2014	WO 2014044692		
Patent	YES	31.08.2009	EP2334608	Contaminant Remediation	Julian Bosch, Rainer Meckenstock

[2] A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.