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Leen Bastiaens

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Introduction

Water is a key resource for sustainable development. The quality of natural water resources and the availability of clean and/or desalinated water, is a major concern for the coming decades. According to the EU Water Framework Directive, the quality of groundwater and surface water needs to be improved in Europe. This requires actions and measures on different water-related aspects (point sources, groundwater, surface water, wastewater, prevention, ...), and the coordination of these actions/measures. Fresh water is crucial for urban, agricultural and industrial activities. Both the quality and quantity of, for instance, drinking water and water for processing pose challenges, and the interest and necessity of water re-use is on the increase.

The Water Technology & Management Symposium (WT&MS) aims at bringing together scientists, policy makers (local, country and European level), consultants, industrial site owners, water managers and remediation companies who are working on or are involved in water quality. The goal is to improve the interaction between different disciplines as well as between people involved in different aspects of water.

The first edition of the WT&M Symposium was organised September 2012 in Barcelona, and had a special focus on barriers and potential approaches to come to the integration of groundwater and surface water in one water management. Water management in Europe is being developed at river basin scale with the main focus on surface water. The integration of groundwater in the overall water management approach was considered a challenge for the near future.

The current second edition of the WT&M Symposium highlights the importance of water and the diversity of water issues by integrating contributions on groundwater, wastewater, drinking water and surface water. More specifically the symposium is dedicated to (1) innovative groundwater remediation technologies, (2) wastewater treatment technologies for micropollutants, (3) approaches and technologies to prevent (micro)pollutants in drinking water, and (4) water management aspects. To include the impact of remediation technologies in water management programmes it is required to have improved knowledge of the sustainability and durability of the remediation technologies, the associated costs, and the impact on the water quality in the wider environment over time. Efforts in these directions have been made during recent years and will be presented and discussed during the symposium. New developments, as well as lessons learned from the field, are on the programme.

Finally, the Water Technology & Management Symposium also aims at being a platform for different thematic symposia and different projects to disseminate their results. The PRB/RZ-2013 Symposium as well as the Final conferences of the FP7 projects AQUAREHAB and MINOTAURUS have therefore joined forces to host this event. The support of the NANO4WATER and BIOTREAT FP7 projects is appreciated.

Wishing you a pleasant and a fruitful Symposium.

Leen Bastiaens,
Conference chair

Plenary session 1

Oral presentations

Quality & quantity issues related with water in dry regions – Israel

Adar E.

Ben Gurion University (Israel) – Invited speaker

Solutions to water issues in Taiwan

Yu J.

national Sun Yat-Sen University (Taiwan) – invited speaker

‘Source files’ – a joint approach on identifying source related risks for protected areas like drinkingwater winning areas

D’Hont D.

VMM (Belgium) – invited speaker

Microorganism and enzyme immobilisation for upgrading water: goals & major outcomes of the FP7 MINOTAURUS project

Wintgens T.

FHNW – Coordinator MINOTAURUS (Switzerland)

Water science reaching policy and industry, and future opportunities within horizon 2020

Quevauvillier Ph.

European Commission, DG Enterprise (country)

Remediation technologies and integration of their impact in water management: goals & major outcomes of the FP7 AQUAREHAB project

Bastiaens L.[1] & all AQUAREHAB partners[2]

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ABSTRACT: AQUAREHAB is an EU financed research project (FP7) that started May 1st 2009 with 19 project partners (VITO-Belgium, KULeuven-Belgium, GEUS-Denmark, HMGU-Germany, CTM-Spain, TUDelft-Netherlands, Sapion-Belgium, ISODETECT-Germany, USTUTT-Germany, Wageningen univ.-Netherlands, Ben Gurion Univ-Israel; Masarykova univ. -Czech Republic, UNESCO-IHE-Netherlands, Univ. Sheffield-UK, POLITO-Italy, Hoganas-Sweden, Univ. Copenhagen-Denmark, INERIS-France, Environmental Institute – Slovak Republic).
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 (drinkingwater 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 aims and main outcomes of the AQUAREHAB project are summarized in the current paper.

GENERAL OBJECTIVES OF THE AQUAREHAB PROJECT

The general objectives of the large scale FP7 AQUAREHAB are:

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 5 innovative rehabilitation technologies that are considered are specified in the results section.
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, .. in collaboration with end-users (WP8).

The relation between the different work-packages (WP) are schematically represented in Figure 1.

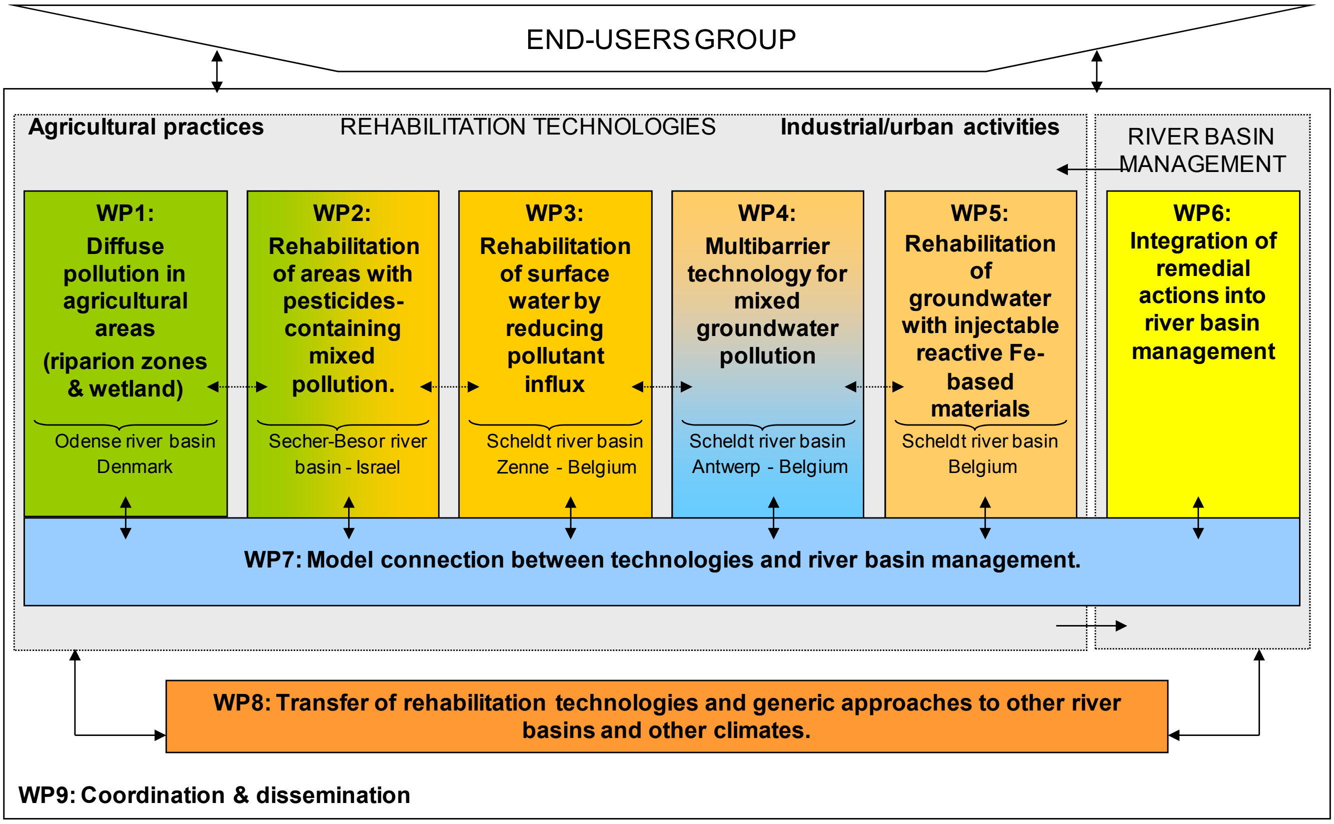

Figure 1: Schematic overview of the AQUAREHAB project structure

During the first years the following 3 river basins were selected as study areas: The Scheldt River basin (Belgium/France), the Odense river basin (Denmark) and the Secher-Besor river basin (Israel). In the second phase, results and findings collected during the first years were extrapolated to other river basins and/or sites in Denmark, Moldavia, Italy, Spain and Belgium.

MAIN OUTCOMES OF THE AQUAREHAB PROJECT

A diversity of outputs from the AQUAREHAB project has been and is being delivered for different target audiences. A visual overview is given in figure 2. In the sections below a short general overview of the output types is given. All this information will be made accessible via the AQUAREHAB website (aquarehab.vito.be).
More details are described per workpackage (WP) by Springael et al.(2013), Roonen et al. (2013), Atashgahi et al. (2013), Bastiaens et al (2013), Velimirovic et al (2013), Seuntjens et al (2013a, 2013b) and Marti et al (2013).

Output for the general audience

For the general audience, AQUAREHAB newsletters, a general description of the project, a video and other visual material were composed.
Newsletter: In the course of the project, 7 newsletters have been prepared describing the progress made in the different part of the project. An 8th and final edition (December 2013) is in preparation.
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.

Outputs for stakeholders, experts & scientists

Patented products: For three products developed within AQUAREHAB patents have been filed. One patent was filed by Höganäs & VITO related to a new type of zerovalent iron (ZVI) that was tested in numerous lab scale tests and 2 field application for degradation of chlorinated compounds. Also for another type of injectable reactive particles, being a nano-scale ironoxide, a patent was filed by Helmholz Zentrum Munich. The ironoxide particles were tested at lab scale for stimulation of biodegradation of BTEX-compounds. Finally, the University of Stuttgart submitted a patent describing sensors for in-situ detection of magnetic particles like ZVI. Their functioning was evaluated in large lab facilities and the sensors were also implemented in the subsurface in two AQUAREHAB field experiments where mZVI was injected.

Other products: In multiple WPs within AQUAREHAB, bacteria were isolated from environmental samples 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 lab 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.

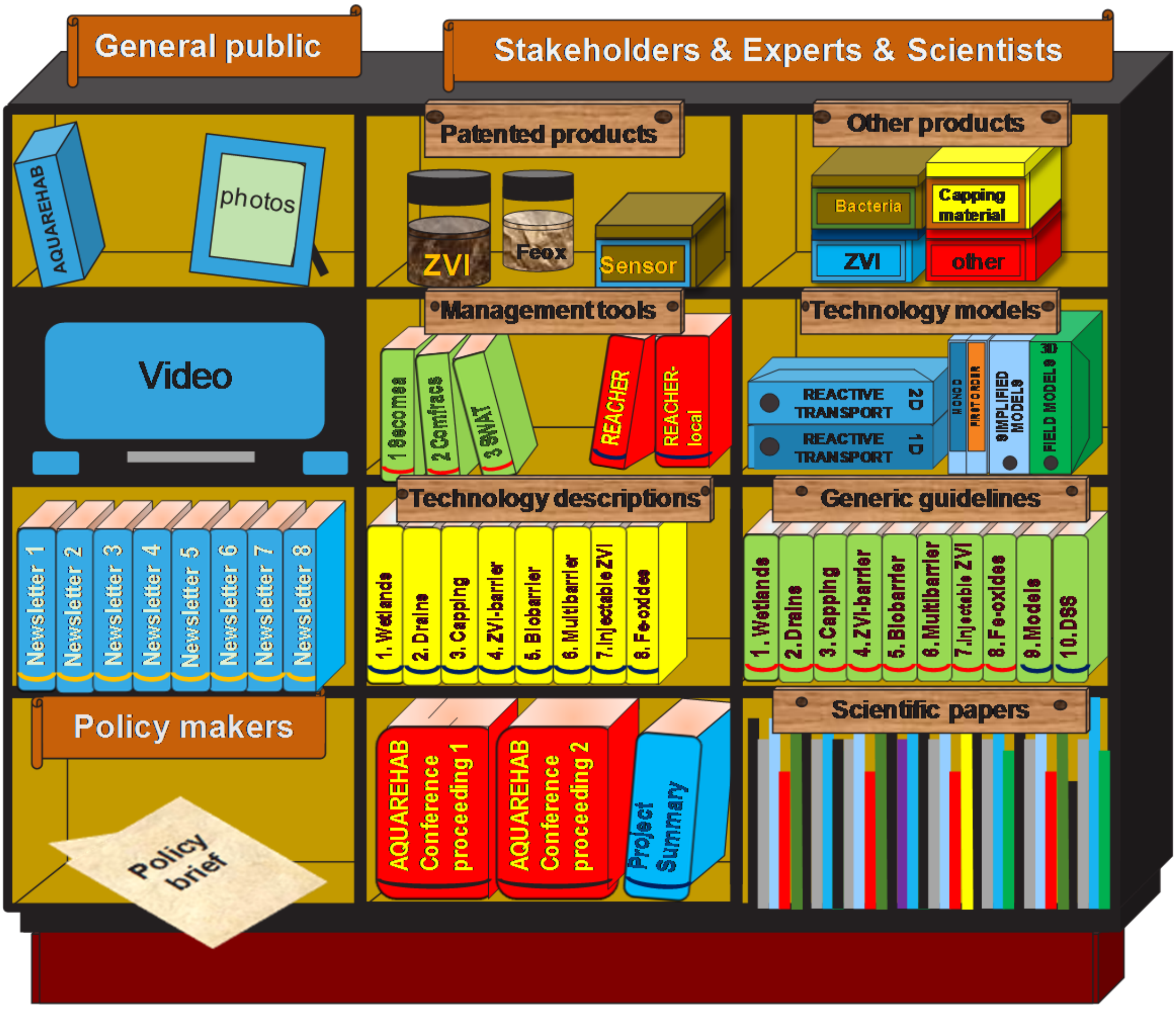

Figure 2: Schematic overview of outputs collected during the AQUAREHAB project.

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 modeling framework for incorporating model results in catchment 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. 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 waterbodies. 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. The second prototype tool is called REACHER-local and 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 are also being 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.

Other publications: AQUAREHAB organised 2 external conferences (Barcelona 2012 & Leuven 2013) where different aspects were presented. A significant number of proceeding papers were prepared and are available to the public via the AQUAREHAB websites.

Authorities

Policy brief: Water and environmental agencies and technology providers share a common interest in applying the best technologies to remediate water degraded areas. In September 2012, AQUAREHAB and the WaterDiss2.0 project organised a Policy (implementation) session 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 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 groundwater quality status. In addition, the limited dynamics of groundwater complicates the use of tools & 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 restrictions on use depending on the quality. AQUAREHAB decided to release by the end of 2013 a policy brief summarising its experiences in relation to the 'integration of groundwater management in water management' and propose recommendations for policy makers.

CONCLUSIONS

During 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 1 person. Prototypes of water management systems (Decision Support Systems) were elaborated for river basin scale with focus on surface water (REACHER) and on a regional scale with focus on groundwater (REACHER-local). Full integration of groundwater in river basin management was not found possible due to differences in dynamics, scale and pollutant types considered.
Currently, major efforts are being made to make knowledge and finding of AQUAREHAB available to the public via the AQUAREHAB website www.aquarehab.vito.be.

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Session 1
Drinking Water

Oral Presentations

A risk based protection of drinking water catchment areas in Flanders (Belgium)

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ABSTRACT: Around 70% of the drinking water produced by the Watergroep (Belgian water company) is extracted at around 80 groundwater pumping sites spread over the region of Flanders. Water safety plans are now being developed in order to control the risks that endanger the drinking water supply. The approach consists of three steps. First, a complete description with respect to the source area of the water wells is compiled as a site specific source file. This file consists of a detailed description of the abstraction infrastructure, of the local hydrogeology and of the existing monitoring network. By means of a hydrogeological model, the extraction zones and groundwater travel times (0-5 yr, 5-25 yr, 25-100 yr and >100 yr) are being determined. As a last part all present hazards, inclusive unknown potential hazards, in the infiltration zones are identified, based on a wide range of databases. Second, risk analysis is performed and the risks are prioritized for each individual extraction site. As a third step a monitoring strategy and action plans are developed in order to control the hazards that form a high risk for drinking water production. The presented approach focuses on the catchment area in order to reduce the costs and risks during purification. The water safety plans include a general as well as a site-specific risk approach. These plans will be updated periodically as the hazards, risks and available information change. The risk based approach deals with water quality as well as water quantity in the catchment area. The hazard identification and the implementation of action plans requires an intensive and constructive cooperation with several governmental institutes to cover hazards that are outside the jurisdiction of water companies.

INTRODUCTION

The Watergroep is the largest drinking water company of Flanders, producing around 120 million m^3 of clear drinking water every year for around 2.8 million inhabitants. Around 70% of the produced drinking water comes from pumped groundwater, for the remaining 30% surface water is used. The groundwater is pumped at 80 sites spread over Flanders from more or less vulnerable aquifers (Figure 1). According to the WHO (WHO, 2011) the most effective means for ensuring safe drinking water is through the use of a comprehensive risk assessment and risk management. In the first place this risk management should focus on the groundwater catchment as this is the first sub-system in the water supply chain (Rosén et al, 2008; Figure 2). Focusing the risk management on the catchment areas also meets article 7 of the European Water Framework Directive that imposes member states to ensure the necessary protection for the bodies of water in order to reduce the level of purification treatment required in the production of drinking water (European Commission, 2000). The Flemish government will also impose the use of a risk based approach for the protection of the drinking water quality by a new decree in 2013.

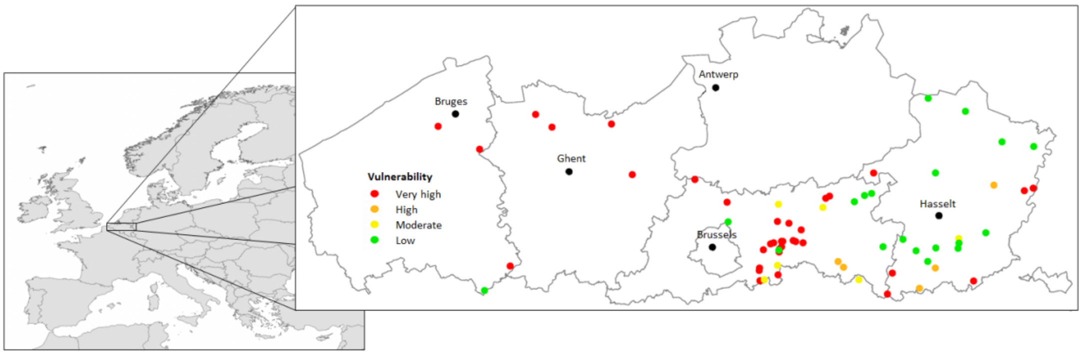


Figure 1: Location of pumping sites of the Watergroep in Flanders, classified by its vulnerability to pollution.

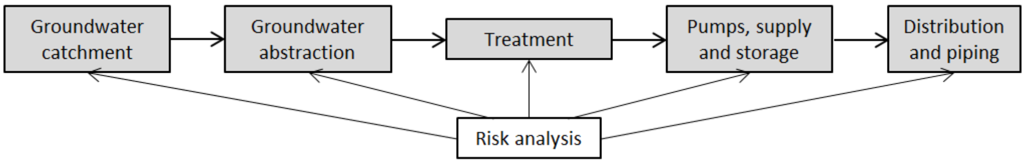


Figure 2: Risk analysis performed on the sub-systems of the water supply chain.

Based on the guidelines of the World Health Organization (Davison et al., 2005; WHO, 2011), on the experience and proposed approach of the European project Techneau (Rosén et al., 2008; Beuken et al., 2008), and on the experience of other drinking water companies (see e.g. Kozisek et al. 2009, Kirch 2011, Schmoll et al. 2011) a workable approach for the risk analysis and risk management was developed in near cooperation with the Flemish Environmental Agency and through internal expert brainstorm sessions (Figure 3).

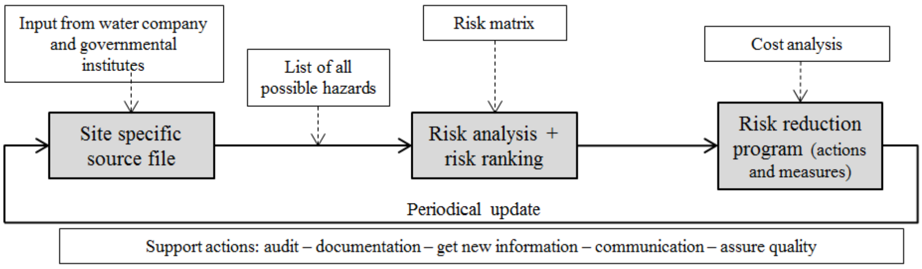


Figure 3: General approach for the risk assessment of the hazards in the groundwater catchment.

GENERAL APPROACH FOR A RISK-BASED PROTECTION OF THE GROUNDWATER CATCHMENTS

Site specific source file

As a first step, an important amount of information and data is collected: a description of the hydrogeological situation, a description of the wells and of the operation of the pumps. Further, a calculation of the zone of influence and of the capture zone, and spatial information on the land-use and other activities that can influence the groundwater quantity and quality is compiled. This information is gathered in near cooperation with the Flemish Environmental Agency (VMM) and stored as a digital site specific source file. The cooperation with governmental institutions is necessary in order to cover the risks that are outside the jurisdiction of water companies. In Table 1 the elements of the source file and the institute responsible for the information is presented. Most of this information is already available in different databases or under different digital formats.

Table 1: Content of the site specific source file, the responsible institute and update-frequency.

Content	File-type	Responsible Institute		Update frequency
		drinking water company	environmental agency	
1) Information on the water extraction site				
Map with the location extraction site	GIS	x		when adjusted on the field
Table with technical information of wells and piezometers	spreadsheet table	x		when adjusted on the field
Map with the monitored piezometers of the drinking water company	GIS	x		when adjusted on the field
Map with the monitored piezometers of the environmental agency	GIS		x	when adjusted on the field
Map with the legal protection zones around the extraction site	GIS	x		when adjusted on the field
Map with the areas of attention	GIS	x	x	every 5 years
Map with the supply areas of the extraction site	GIS	x		every 5 years
Report on the evolution of the groundwater levels	digital report	x		monthly
2) Land-use impact in the areas of attention				
Map of the actual land-use	GIS		x	every 5 years
Map of the areas with soil quality research and remediation projects	GIS		x	yearly
Map of the areas with the risk of flooding	GIS		x	every 5 years
Map of wastewater discharge points	GIS		x	yearly
Map with use of fertilizers	GIS		x	yearly
3) Waterquality in the area of attention				
Results of water quality analysis of the water company	spreadsheet table	x		yearly
Results of water quality analysis of environmental agency	spreadsheet table		x	yearly
Report on the evolution of the pumped groundwater quality	digital report	x		continuous
4) Actions and engagements				
Procedure to be followed in case of calamities	digital report	x	x	every 5 years
Report on the primary groundwater quality and quantity bottlenecks, on the necessary actions and commitments	spreadsheet table	x	x	when necessary in function of water safety plan

The determination of the catchment zones for every groundwater extraction site, is based on a particle tracking analysis in a 3D regional hydrogeological model of Flanders (Lermytte and Thomas, 2008). Inside the catchment area four zones of attention are defined based on the groundwater travel time of the groundwater (Figure 4). Within these zones all hazards will be evaluated.

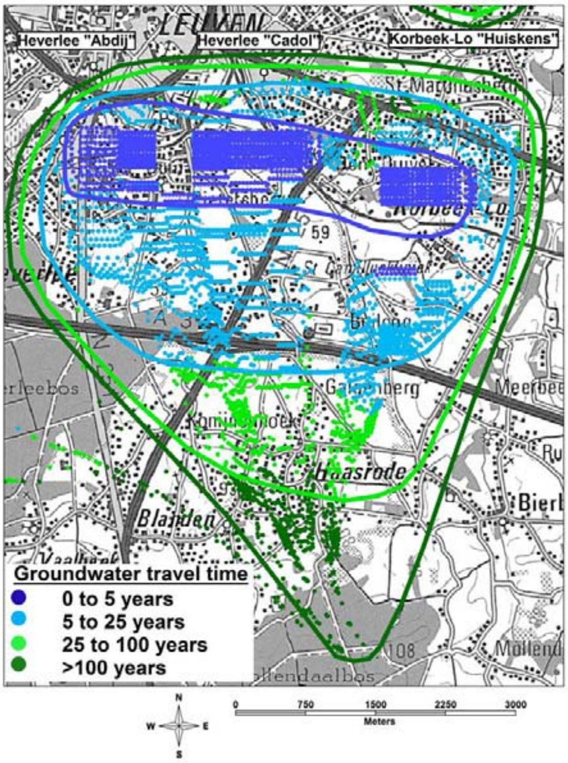


Figure 4: Results of the particle tracking and definition of the areas of attention around the groundwater extraction site of Heverlee and Korbeek-lo (province of Flemish-Brabant, Flanders, Belgium).

The compilation of the site specific source files for every well site has been adopted by the government in the action program of the second generation river basin management plans. In this way the presented approach responds to article 7 of the European Water Framework Directive.

Identification of the hazards

Before performing a risk analysis a general list of possible hazards was made based on available literature (e.g. Beuken et al., 2008) and on brainstorm sessions with colleagues with different expertise. 82 possible hazards were identified and brought together into 13 elementary groups:

1) Open soil energy systems
2) Closed soil energy systems
3) Groundwater wells of third parties
4) Transport and transport infrastructure
5) Sewer systems and wastewater discharge
6) Agricultural practices
7) Household practices
8) Industrial sites/ Activities of public services/ military sites
9) Parking areas
10) Infrastructural works
11) Surface water
12) Rainwater infiltration infrastructures
13) Other activities with a possible impact on groundwater quality of quantity

In Table 2 an example is presented of the description of the hazards related to groundwater wells of ‘third parties’. The hazards were documented with a reference number, with a description of the hazard for the drinking water production, with the type of the event and the type of hazard (Beuken et al., 2008), and with the possible consequence for the drinking water production. This list will be continuously complemented when new hazards become relevant.

Table 2: Example of the hazard description for groundwater wells of third parties (based on Beuken et al., 2008)

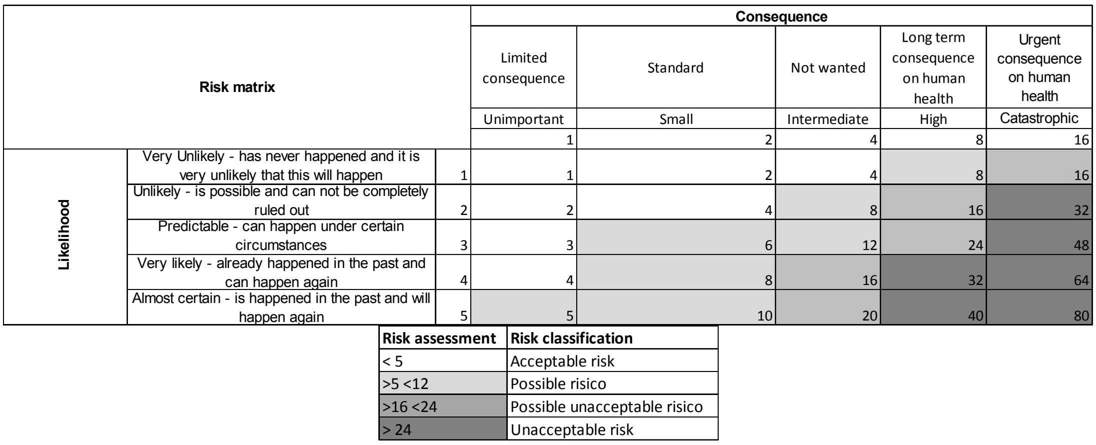
O=operation related, E=external related; ** I=insufficient water availability, Ex=external damage to third parties, B=biologic, C=chemical.

Element	Reference number	Hazardous event	Hazard for drinking water production	Type of event*	Type of hazard**	Possible consequence
1.3 Groundwater wells of third parties	1.3.1	aquifer capacity is exceeded	lowering groundwater levels	O, E	I, Ex	insufficient water
	1.3.2	aeration of the aquifer	pollution of the groundwater	O, E	C, Ph, I, Ex	insufficient water, bad water quality
	1.3.3	water level is too low for the pump	lowering groundwater levels	O, E	I	insufficient water
	1.3.4	infiltration of surface water or polluted water due to the absence of a clay stop	pollution of the groundwater	E	B, C, Ph	bad water quality
	1.3.5	attraction of a polluted groundwater plume as a result of changing groundwater flow	pollution of the groundwater	O, E	C, Ph	bad water quality

Risk analysis

In a next step, the level of the risk is determined as a combination of the likelihood and consequence for each hazardous event and for each abstraction site. A risk matrix is used to rank the risks (Figure 5). Compared to the risk matrix from Beuken et al. (2008), one extra level is introduced in order to create more difference between the classified risks. Based on this classification, priorities will be set for the protection of each well site, and action and management plans (including cost analysis) will be defined for hazards with an unacceptable and possible unacceptable risk.

At the moment the presented approach is being performed as a pilot study on two extraction sites, and several initiatives, such as a dynamic groundwater monitoring strategy and the implementation of a drought indicator, tracer tests and 3D hydrogeological modelling, are taken by De Watergroep to enlarge its knowledge of the water catchments and to improve the risk analysis. In a next phase the necessary management actions will be taken to implement the strategy for all catchment areas and for the entire drinking water supply chain (Figure 2).



Risk matrix			Consequence				
			Limited consequence	Standard	Not wanted	Long term consequence on human health	Urgent consequence on human health
			Unimportant	Small	Intermediate	High	Catastrophic
			1	2	4	8	16
Likelihood	Very Unlikely - has never happened and it is very unlikely that this will happen	1	1	2	4	8	16
	Unlikely - is possible and can not be completely ruled out	2	2	4	8	16	32
	Predictable - can happen under certain circumstances	3	3	6	12	24	48
	Very likely - already happened in the past and can happen again	4	4	8	16	32	64
	Almost certain - is happened in the past and will happen again	5	5	10	20	40	80

Risk assessment	Risk classification
< 5	Acceptable risk
>5 <12	Possible risico
>16 <24	Possible unacceptable risico
> 24	Unacceptable risk

Figure 5: Risk matrix used for ranking of the identified hazards (adapted from Beuken et al. 2008)

Advantages of the risk based approach

The advantages of using the presented approach for the protection of the catchment areas are the following:

- General as well as site specific risks will be identified.
- Every pumping site will be evaluated according to the same approach
- The actions will focus on the hazards with the highest risks.
- The risk analysis and the resulting actions will be kept up to date periodically.
- The presented approach focuses on groundwater quality as well as groundwater quantity.
- The approach will lead to an increasing awareness of the importance of groundwater protection.
- The cooperation with governmental administration is strengthened.
- This approach will lead to a well organised protection of the groundwater catchments and to decreasing treatment costs.
- As the evaluation of the hazards is a continuous process, new risks for drinking water quality and quantity will be detected in an early stage.

CONCLUSIONS

For the protection of the catchment areas of the drinking water wells of the Watergroep in Flanders (Belgium), a workable and practical risk based approach is presented. This approach forms an important part of the water safety plans that will be developed for the drinking water supply in Flanders. First a general descriptive file of the well sites and its catchment area is put together. An important part of this file is the delineation of the attention zones, whose outer boundary forms the capture zone of the pumping wells. These attention zones were based on a particle tracking analysis with a large-scale hydrogeological model of Flanders. All possible hazards for groundwater quality and quantity were listed, resulting in 82 hazards that were brought together into 13 elementary groups. In a next step a framework for a risk analysis was set up. Risk analysis will be performed on the identified risks in the defined attention zones. When the risk based approach is followed for the 80 extraction sites supplying the drinking water, this will lead to a well organised protection of the groundwater, will reduce the costs for treatment and will support a sustainable abstraction.

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Introduction of specific pesticide-degrading bacteria into waterworks sand filters

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Contamination of groundwater with organic micropollutants like pesticides, solvents, and pharmaceuticals forces waterworks in many areas of the world to either close down abstraction wells or to purify the water before it is distributed to the consumer. BIOTREAT is a new EU project initiated 1st January 2011 aiming at developing new technologies for bioremediation of polluted drinking water resources. The basis of the proposed technologies is bioaugmentation, which in the present context is the introduction of specific degrading microorganisms or microbial consortia into existing sand filters at waterworks. 2,6-dichlorobenzamide (BAM), a degradation product of the herbicide dichlobenil, is one of the target compounds in BIOTREAT. BAM has closed down numerous abstraction wells due to its presence above the 0.1 µg/L threshold limit set by the European Union. BAM is a highly recalcitrant compound, but recently a BAM-degrading bacterium, *Aminobacter* sp. MSH1, was isolated. In BIOTREAT we are currently investigating the possibility of using this bacterium to degrade BAM at waterworks during their normal simple water purification process in sand filters. Laboratory experiments have shown that MSH1 can degrade and mineralize BAM rapidly at concentrations below the threshold limit, and column experiments have shown that the strain adheres well to common filter materials like sand and expanded clay. The strain has been tested in a number of small- and large-scale laboratory filters at realistic conditions and in all cases BAM was either fully or partly degraded with only traces of degradation products formed. A field experiment using a pilot-scale waterworks is currently being performed. Results from these experiments will be presented along with the current available data, and finally the general possibility of using added bacteria for removal of organic micropollutants during water purification will be discussed.

Pesticide mineralization in sand filter material taken from drinking water production facilities

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Sand filters are used in drinking water production plants for removing iron and manganese oxides. The water that flows through these sand filters often contains low concentrations of pesticides which might cause growth of microorganisms adapted to degrade pesticides or their degradation products. Therefore, mineralization of bentazone, 2-methyl-4-chloorphenoxyacetic acid (MCPA) and 2,6-dichlorobenzamide (BAM) was evaluated in sand filter material from eight different drinking water production plants. Mineralization was examined by following the production of $^{14}CO_2$ from ^{14}C-labelled pesticides in laboratory microcosms. MCPA was mineralized in all samples while BAM and bentazone were only mineralized in sand filter material from respectively two and three drinking water production plants treating water with a long history of pesticide contamination. After 50 days, mineralization of BAM, bentazone and MCPA reached up to 65%, 21% and 57% respectively. When comparing samples from different sampling dates and different sand filters at the same site, no differences were observed. Mineralization kinetics were different per compound and per drinking water production site. Furthermore, the BAM mineralization capacity in sand filter material from Kluizen could be transferred to non-active sand. In conclusion, biodegradation of persistent pesticides and pesticide metabolites like BAM at low concentrations can be established in sand filters and is consistent in both time and space. This is the first observation of MCPA, BAM and bentazone biodegradation in drinking water systems, showing a great potential for bioremediation strategies.

INTRODUCTION

The wide use of pesticides has led to the contamination of surface and groundwater which compose the main sources of drinking water worldwide. In drinking water production plants, sand filters are used for removing iron and manganese oxides. Although the concentrations of pesticides in environmental waters are typically within the µg/L range, the large volumes of water passing through these sand filters might cause growth of microorganisms adapted to degrade pesticides or their degradation products. To test this hypothesis, mineralization of bentazone, 2-methyl-4-chloorphenoxyacetic acid (MCPA) and 2,6-dichlorobenzamide (BAM) was examined in sand filter material sampled at eight Belgian drinking water production plants differing in water source, water flow rate and contamination level. Next, the cumulative mineralization curves were modelled using different nonlinear kinetic models. Comparing mineralization kinetics can yield insight in the underlying degradation processes. Differences in kinetics can for instance be due to different species of degrading microorganisms, e.g. single species versus consortia; different enzymes and pathways, e.g. metabolic versus cometabolic processes; the number of degrading cells and the availability of other carbon sources and nutrients. Last, the transfer of BAM mineralizing sand to sand with no BAM mineralization activity was tested as a bioaugmentation strategy.

MATERIAL AND METHODS

Determination of pesticide mineralization capacity

Sand filter material was sampled at eight different Belgian water works between 2011 and 2013. Samples were taken from the upper 20 cm of the sand filter. Sample characteristics and pesticides contaminating the treated water are shown in Table 1. The pesticide mineralization capacity of the endogenous bacterial sand filter community was studied by adding ^{14}C-labelled bentazone (carbonyl ring labelled or aromatic ring labelled), MCPA (aromatic ring labelled) and BAM (aromatic ring labelled) to 2.5 g of sand filter material at concentrations of 100-200 µg/L. The produced CO_2 was captured in 1 ml 0.5 M NaOH, which was replaced regularly. The captured radioactivity was then measured by liquid scintillation counting.

Table 1: Overview of sand filter samples used in this study and their origin.

	Location	Company	Water source	Type of sand filtration	Sampling date	Contamination
K1	Kluizen SF24	VMW	SW + GW	Rapid	8/11/2011	BAM, bentazone
K2 SF21	Kluizen SF21	VMW	SW + GW	Rapid	12/06/2012	BAM, bentazone
K2 SF22	Kluizen SF22	VMW	SW + GW	Rapid	12/06/2012	BAM, bentazone
K2 SF26	Kluizen SF26	VMW	SW + GW	Rapid	12/06/2012	BAM, bentazone
K3 SF21	Kluizen SF21	VMW	SW + GW	Rapid	03/04/2013	BAM, bentazone
K3 SF26	Kluizen SF26	VMW	SW + GW	Rapid	03/04/2013	BAM, bentazone
E1	Eeklo SF2	VMW	GW	Rapid	9/11/2012	BAM, bentazone
E2 SF1	Eeklo SF1	VMW	GW	Rapid	13/06/2012	BAM, bentazone
E2 SF2	Eeklo SF2	VMW	GW	Rapid	13/06/2012	BAM, bentazone
E2 SF3	Eeklo SF3	VMW	GW	Rapid	13/06/2012	BAM, bentazone
Z1	Zele	VMW	GW	Rapid	10/05/2011	BAM
Z2	Zele	VMW	GW	Rapid	28/06/2012	BAM
Si0	Sinaai	VMW	GW	Rapid	10/05/2011	Bentazone
Si1	Sinaai	VMW	GW	Rapid	10/11/2011	Bentazone
Si2	Sinaai	VMW	GW	Rapid	28/06/2012	Bentazone
Sn	Snellegem	VMW	GW	Rapid	28/06/2012	BAM, bentazone
DB1 SF1	De Blankaart SF1	VMW	SW	Rapid	27/06/2012	Bentazone
DB1 SF3	De Blankaart SF3	VMW	SW	Rapid	27/06/2012	Bentazone
DB1 SF4	De Blankaart SF4	VMW	SW	Rapid	27/06/2012	Bentazone
DB2 SF1	De Blankaart SF1	VMW	SW	Rapid	02/04/2013	Bentazone
DB2 SF3	De Blankaart SF3	VMW	SW	Rapid	02/04/2013	Bentazone
DB2 SF4	De Blankaart SF4	VMW	SW	Rapid	02/04/2013	Bentazone
StL	Saint Léger	VMW	GW	Rapid	13/06/2012	none
AWW	Antwerp	AWW	SW	Slow	13/06/2012	Bentazone

SF = sand filter VMW = De Watergroep GW = groundwater
AWW = Antwerpse Waterwerken SW = surface water

Modelling of mineralization kinetics

Mineralization curves were determined as percentage captured ^{14}C as $^{14}CO_2$ of the total amount of added radioactivity as a function of incubation time. To evaluate the kinetics of mineralization, several non-linear models, as reviewed by Fomsgaard (1997), were fit to the curves. Of these, two models were selected that best described the kinetics of most mineralization curves. The two-compartment model consists of two simultaneously occurring first order processes:

$$P = c_1\left(1 - e^{-k_1 t}\right) + c_2\left(1 - e^{-k_2 t}\right) \qquad \text{eqn.1}$$

where P is the fraction of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$), c_1 and c_2 are the total fractions of pesticide converted to $^{14}CO_2$ by two first order degradation processes and k_1 and k_2 are the corresponding degradation rate constants. The second model used is a three-half-order model, which combines a first and zero order degradation process with linear growth of the degrading microorganisms:

$$P = c_0\left(1 - e^{-k_1 t - \left(\frac{k_2 t^2}{2}\right)}\right) + k_0 t \qquad \text{eqn. 2}$$

where P is the fraction of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$), c_0 is the total fraction of pesticide converted to $^{14}CO_2$ by first order metabolism, k_0 and k_1 are the degradation rate constants for the zero and first order process respectively and k_2 is the linear growth rate constant. Since not all mineralization curves could accurately be fit by the last two models, one extra model described by Zwietering et al. (1990) was used. The modified Gompertz model describes a lag phase and combines logistic growth of microorganisms with zero order degradation. An extra degradation term was added to this model to describe endogenous mineralization:

$$P = c_0 . e^{\left(-e^{\left(\frac{e}{c_0}(k_1 t_0 - (k_1 - k_2)t) + 1\right)}\right)} + k_2 t \qquad \text{eqn. 3}$$

where P is the fraction of pesticide mineralised at time t (% ^{14}C as $^{14}CO_2$), t_0 is the lag time, c_0 is the total fraction of pesticide converted to $^{14}CO_2$ by the logistic degradation process, k_1 is the logistic degradation rate constant and k_2 is the endogenous degradation rate constant.

Transfer of BAM mineralization capacity to non-active sand

Sand with no BAM mineralizing capacity was inoculated with sand filter material from Kluizen to evaluate the transfer of BAM mineralizing sand filter material as a bioaugmentation strategy. As non-active sand, material from samples Si1 and DB1 SF3 (Table 1) was used. In addition, both were sterilized by autoclaving two times at 120 °C for 21 minutes with resting periods of 24 h, to exclude interactions with microorganisms without BAM degrading activity. Furthermore, sterile sand with the same particle size, but no previous use in drinking water production (Sibelco) was used. Material from sample K3 SF26 (Table 1) was mixed with non-active sand at 20%, 40% and 60% ratios to a total of 2.5 g. As non-inoculated controls, 2.5 g non-active sand was used. Furthermore, 0.5 g, 1 g, 1.5 g and 2.5 g pure sand from sample K3 SF26 were used as positive controls. ^{14}C-labelled BAM was added and mineralization curves were determined as described before.

RESULTS

Pesticide mineralization capacity in sand filter material

The extent of mineralization after 50 days for the tested samples and compounds is given in Table 2. Mineralization of BAM was only found in sand filter material from Kluizen and Eeklo. Bentazone was mineralized in sand filter material from Kluizen, Eeklo, Antwerp and Snellegem. In contrast, all tested samples, except samples from De Blankaart, showed mineralization of MCPA. A total cumulative mineralization of 65%, 24% and 57% was reached after 50 days for BAM, bentazone and MCPA, respectively. Mineralization of the tested compounds was constant over time for the sand filter systems of Kluizen, Eeklo, Zele and Sinaai. Moreover, the extent of mineralization and mineralization rate appear to have increased in time in samples from Kluizen, when comparing mineralization curves for sample K1, K2 SF26 and K3 SF26 (Figure 1). To assess whether the sand filter samples show complete mineralization of bentazone, the experiments were repeated with aromatic ring labelled bentazone instead of carbonyl ring labelled bentazone. The resulting mineralization curves did not differ markedly from those with carbonyl ring labelled bentazone (data not shown).

Modelling of mineralization kinetics

To determine whether the underlying degradation processes were comparable for different compounds and different sand filters, three non-linear models were fit to the mineralization curves. The model with the best fit was selected based on the sum of squared errors (SSE) (data not shown). In case of BAM, all mineralization curves were best fit with the three-half-order model. All bentazone mineralization curves were best fit with the three-half-order model, except bentazone mineralization in samples E1 and E2 SF1. Differences in SSE were however small. In case of MCPA, mineralization kinetics were different per drinking water production site. Samples from Kluizen, Eeklo, Zele and Snellegem showed two compartment kinetics. For samples from Sinaai and De Blankaart, MCPA mineralization curves were best fit by the three-half-order model and for samples from Saint Léger and Antwerp by the modified Gompertz model. Different samples from the same drinking water production site generally showed the same type of kinetics for the same compound, with only few differences between kinetic parameters (data not shown).

Table 2: Extent of mineralization of BAM (% ^{14}C as $^{14}CO_2$), bentazone and MCPA after 50 days of incubation. Values are average values (± st.dev.) of 3 replicates.

	BAM	Bentazone	MCPA
K1	34% ± 4%	10% ± 1%	37% ± 1%
K2 SF21	65% ± 4%	20% ± 1%	39% ± 7%
K2 SF22	58% ± 13%	21% ± 2%	41% ± 8%
K2 SF26	62% ± 7%	18% ± 1%	48% ± 3%
K3 SF21	64% ± 3%	24% ± 3%	55% ± 8%
K3 SF26	62% ± 3%	23% ± 3%	53% ± 5%
E1	6% ± 1%	11% ± 3%	48% ± 2%
E2 SF1	7% ± 1%	14% ± 0%	47% ± 4%
E2 SF2	6% ± 1%	11% ± 2%	42% ± 2%
E2 SF3	8% ± 0%	14% ± 1%	52% ± 4%
Z1	ND	ND	39% ± 3%
Z2	1% ± 0%	3% ± 1%	40% ± 3%

ND = not determined

	BAM	Bentazone	MCPA
Si0	ND	ND	27% ± 5%
Si1	ND	ND	27% ± 1%
Si2	2% ± 1%	3% ± 0%	29% ± 1%
Sn	8% ± 6%	5% ± 1%	57% ± 2%
DB1 SF1	2% ± 1%	2% ± 1%	43% ± 7%
DB1 SF3	ND	ND	4% ± 1%
DB1 SF4	ND	ND	4% ± 1%
DB2 SF1	1% ± 0%	2% ± 0%	3% ± 0%
DB2 SF3	ND	ND	1% ± 0%
DB2 SF4	ND	ND	3% ± 0%
StL	1% ± 0%	2% ± 0%	14% ± 1%
AWW	4% ± 1%	8% ± 0%	45% ± 5%

ND = not determined

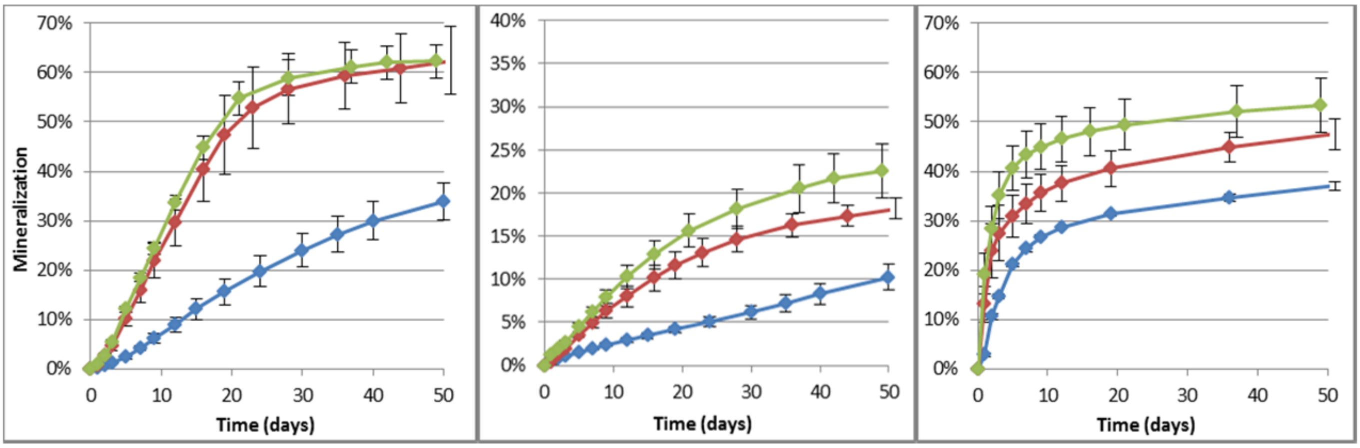

Figure 1: Mineralization (% ^{14}C as $^{14}CO_2$) versus time in sample K1 (blue line), K2 SF26 (red line) and K3 SF26 (green line) for BAM (left), bentazone (middle) and MCPA (right). Error bars indicate standard deviation.

Transfer of BAM mineralization capacity to non-active sand

Next to pure cultures of xenobiotic compound degrading strains, environmental matrices with degrading activity can be used as inoculum for bioaugmentation purposes (Sniegowski *et al.* 2011). In this view, sand filter material from Kluizen was mixed with sand showing no BAM mineralization, at ratios of 20%, 40% and 60%, to evaluate whether the BAM mineralizing capacity can be transferred to non-active sand. No mineralization was found in non-inoculated controls. In all conditions, mineralization rates were slower in sand mixtures than for pure sand from Kluizen. The maximal extent of mineralization was however often higher for mixtures compared to the same amount of pure sand from Kluizen. Only at 60% ratios, the same extent of mineralization was reached as for 100% pure sand from Kluizen (2.5 g) after 90 days (Figure 2). Best results were obtained for sterile sand with no previous use in drinking water production and sterilized sand from sample DB1 SF3. Sterilization of sand from De Blankaart thus resulted in higher mineralization, indicating a negative effect of interactions between BAM mineralizing microorganisms and microorganisms endogenous to sand from De Blankaart. In contrast, this was not the case for sand from Sinaai, in which better results were obtained for non-sterile sand. This could be due to positive interactions with the endogenous bacterial community from Sinaai. Another possible explanation is that compounds inhibiting BAM mineralization could have been formed by autoclaving the sand.

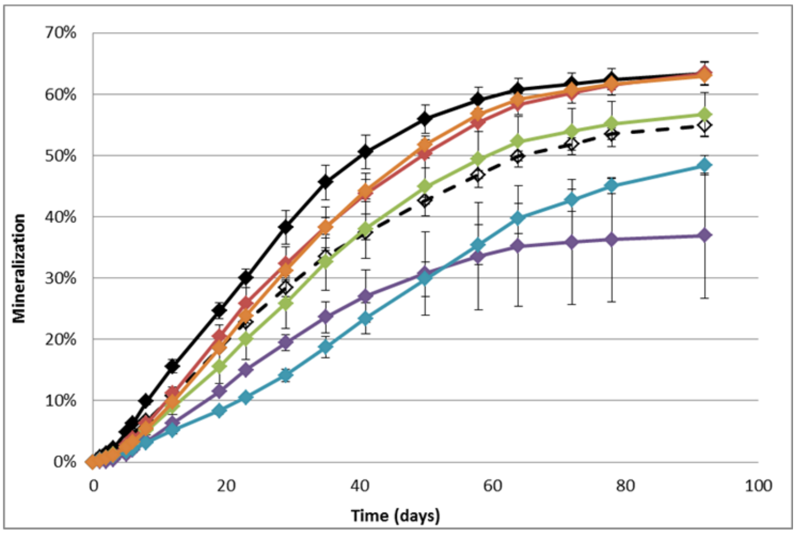

Figure 2: Mineralization (% ^{14}C as $^{14}CO_2$) versus time for material from sample K3 SF26 mixed with sand from sample Si1 (green line) and DB1 SF3 (blue line), sterilized sand from sample Si1 (purple line) and DB1 SF3 (orange line) and sterile sand with no previous use in drinking water production (red line) at a 60% ratio. Black lines indicate positive controls with 1.5 g (60%, dashed line) and 2.5 g (100%, full line) pure sand from sample K3 SF26. Error bars indicate standard deviation.

CONCLUSIONS

We conclude that adaptation to the presence of BAM and bentazone in sand filters used for drinking water is possible, but not evident. Especially the occurrence of bentazone mineralization is of interest since complete mineralization of bentazone is scarcely reported. MCPA proved to be easily degradable in all sampled sand filters. Mineralization kinetics differed per site and per compound, but were constant in time. Sand filter material from Kluizen is of particular interest since its ability to degrade all tested compounds. The BAM mineralization capacity in sand filter material from Kluizen is transferable to non-active sand. The next step is to enrich, isolate and/or identify the pesticide degrading strains using conventional and less conventional enrichment techniques.

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An unmanned surface vessel with environmental mapping services for drinking water reservoirs

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Increasing pressure on water quality necessitates adequate management and availability of monitoring data to detect changes, to indicate problems (early warning), to improve understanding of the water system functioning and to plan or evaluate measures. There are plenty of instruments and technologies on the water sensing market providing a wide range of data at very different scales and resolutions. The most simple and straightforward approach is to perform measurements and collect samples at the locations of interest. This allows for detailed information but lacks temporal and spatial resolution.

The use of automated instruments allows for much higher frequency data collection. Spatial resolution can be increased by installing a network of fixed in-situ sensors. A major shortcoming of the sensor network strategy is the large number of sensors (and corresponding investments) needed to assess the water quality over larger areas with sufficient spatial resolution.

This limitation can be overcome by using mobile sensor platforms; i.e. manned or unmanned vehicles equipped with automated sensors and smart samplers. An example of such a vehicle is the Aqua Drone®, an unmanned surface vessel (USV) for 3D monitoring of large inland water bodies. The Aqua Drone® can be used to map the water quality of water bodies, both to establish their natural condition as well as to investigate the extent and spatial distribution of chemical contamination events or microbiological events, such as blooms of toxic algae. The high density data, collected with the Aqua Drone®, will provide valuable information for target measures to mitigate harmfull effects of such events.

The case study that will be presented describes the use of the Aqua Drone® in performing autonomous water quality measurements on a drinking water reservoir. The survey included both a spatial mapping exercise as well as depth profiling using the sensor winch on the platform. Algal monitoring sensors results will be presented within the VITO sensorview application.

Poster Presentations

Assessment of a series of NF membranes and process for the treatment of the waste water of IEX-step for NOM removal from drinking water

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Natural organic matter (NOM) in drinking water is responsible for colour, odour and taste and it gives rise to the formation of disinfection byproducts and impairs the biological stability of the produced water. NOM should therefore be (partly) removed during drinking water treatment. This can be done by coagulation, activated carbon filtration, oxidation, membrane filtration and/or anion exchange (IEX). The most common method used to remove NOM from surface waters is by coagulation. The surface water from the storage reservoirs of the production plant Kluizen contains high levels of NOM and alkalinity and requires high amounts of coagulants and sulfuric acid to obtain an acceptable NOM removal during coagulation and subsequent floc separation. A prior reduction of the NOM level by IEX will reduce operation costs by saving coagulant and neutralization chemicals and by reducing sludge production. The IEX resin is regenerated with a NaCl brine. The waste water contains high salt and organics concentrations and is only 0.05% of the treated flow. After coagulation with $FeCl_3$, the organics are separated from the liquid by means of a filter press. The liquid is reused in the brine (zero liquid discharge). The filter cake with a dry solid content of 32% contains a high concentration of humics (NOM), the valorization of these cakes is difficult because of their high salt content.

Currently, an innovative treatment concept for solving the problem of the high salt content of the filter cake is under investigation. This concept consists of using low salt rejection NF membranes followed by a diafiltration step. The so-formed NF permeate can be used again “as such” for the regeneration of the IEX resin. The generated diafiltrate from this step could be further treated by RO to boost its NaCl content back up again, whereas the resulting concentrate is a concentrated suspension of the desalted organics. To “harvest” the desalted organics from this suspension a coagulation with $FeCl_3$ will be used followed by dewatering in a sludge dewatering press.

The presentation will primarily focus on the selection of a suitable NF membrane based on laboratory tests using seven different membranes. The used NF membranes/modules which are both in spiral and tubular configuration, are either commercially available or interesting developmental ones. They were characterized for pure water permeability, their cut-off value and their rejection for NaCl and Na_2SO_4. Moreover, they were assessed for their NOM retention, their potential for brine passage, their process flux and their potential for volume reduction. We hope to be able to give also more details of the pilot experiments onsite with the two selected membranes which are planned to start from September 2013.

Session 2
New Developments

Oral presentations

Enhanced groundwater bioremediation using microbial fuel cell concepts

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ABSTRACT: The *in situ* biodegradation of organic contaminants in groundwater is often limited by a lack of electron acceptors for microbial metabolism. Laboratory studies show that microbial fuel cells (MFCs) can enhance biodegradation of organic contaminants by providing electrodes as electron acceptors. This study focused on bioremediation of groundwater contaminated by phenolic compounds (phenol, cresols, xylenols) using MFCs. The MFCs were operated for 24 days. Electricity up to 2.0 mW/m^2 of electrode surface area was produced in an H-type dual-chamber MFC treating contaminated groundwater. The microbial community present in the groundwater used the electrode as an electron acceptor; thus enhancing the degradation of total phenols by 17% in comparison with open circuit control. The electrodes of MFCs installed in the ground have a potential to serve as an inexhaustible electron acceptor for enhanced *in situ* groundwater bioremediation.

INTRODUCTION

Organic contaminants in groundwater can be biodegraded by bacteria when electron donors, electron acceptors and nutrients are available. Natural attenuation of organic compounds (electron donors) under anaerobic conditions is often limited by a lack of readily available electron acceptors, such as oxygen and nitrate for bacterial metabolism (Lovley, 2006). Engineered *in situ* bioremediation technologies e.g. biosparging or nitrate addition, which supply bacteria with electron acceptors, may not be cost-effective, energy efficient or may even cause more environmental pollution (Zhang et al., 2010).

Recent laboratory studies report that bioremediation of petroleum hydrocarbons (Mohan and Chandrasekhar, 2011; Morris et al., 2009; Morris and Jin, 2012; Wang et al., 2012); phenol (Huang et al., 2011; Luo et al., 2009); benzene, toluene, naphthalene, phenanthrene and pyrene (Yan et al., 2012; Zhang et al., 2010) can be enhanced by microbial fuel cells (MFCs). The electrodes of MFCs provide bacteria with a long-term continuous electron acceptor.

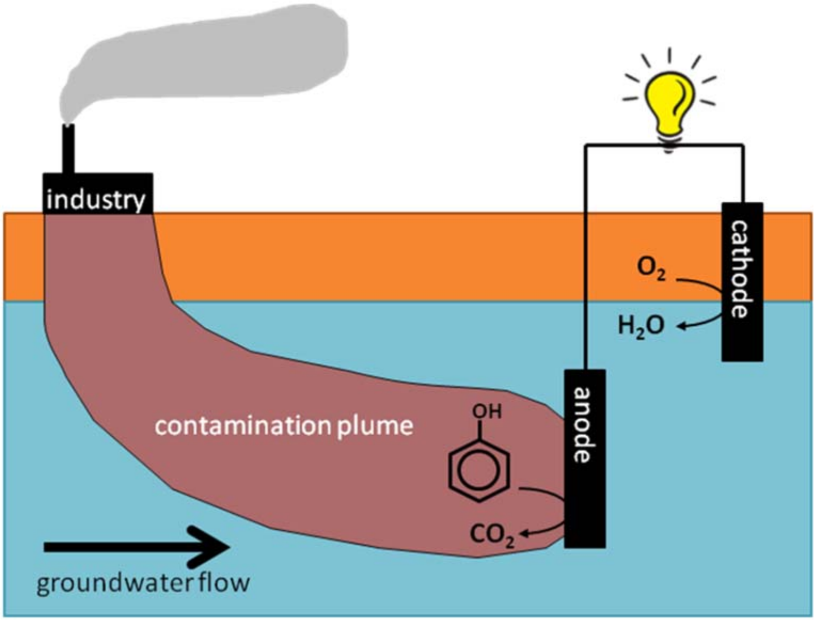

Figure 1: Conceptual model of enhanced in situ groundwater bioremediation using a microbial fuel cell.

Figure 1 shows a conceptual model of an MFC used for enhanced bioremediation in groundwater (bioremediation-MFC). The anode is inserted within the contaminated, oxygen-depleted groundwater and serves as an electron acceptor for biodegradation of organic compounds; phenol is used as an example here. The anode is connected via the wire to the cathode, which is placed in oxygenated uncontaminated groundwater. Electrons released by bacteria at the anode are transported to the cathode and reduce oxygen to water. Electricity is produced during this process, which makes this technology potentially sustainable, considering power consumption. The anode and cathode in the laboratory MFCs can be placed in different chambers separated by a semi-permeable membrane, to simulate the conditions in the aquifer; anode and cathode in the contaminated and uncontaminated groundwater, respectively.

To our knowledge, laboratory experiments, which explored groundwater bioremediation by MFCs, have to date used groundwater amended with nutrients (Morris and Jin, 2008; Morris et al., 2009). Phenolic compounds (e.g. phenol, cresols, xylenols) mainly occur as mixtures in contaminted groundwater (Thornton et al., 2001). However, current research focused on the bioremediation of phenolic compounds using MFCs has only evaluated phenol biodegradation (Huang et al., 2011a; Luo et al., 2009). The aim of this research is to explore the potential of MFCs to enhance bioremediation of groundwater contaminated by coal tar, which contains a mixture of phenol, cresols and xylenols, without any addition of nutrients.

MATERIALS AND METHODS

Groundwater

Groundwater was collected in July 2013 from a multilevel sampler installed within a plume of mixed phenolic contaminants at a site in the UK, using methods described in Thornton et al. (2001). Uncontaminated groundwater was sampled at a depth of 7 meters below ground level (mbgl), whereas contaminated groundwater was sampled from 12 mbgl. This is within a zone defined as the upper plume fringe where dissolved oxygen is below detection, total dissolved phenolic compounds are ca. 200 mg/l, total cell count is 10^7 (Rizoulis et al., 2013; Thornton et al., 2001) and 25% of the microbial population consists of *Goebacter* sp. (unpublished data), a well-known exoelectrogen. Groundwater samples were collected in 2.5-l sterilized bottles filled with nitrogen until all the headspace was removed and then sealed. Samples were stored at 4°C prior to experimentation.

MFC set up

H-type dual-chamber MFCs were constructed using two 250-ml Schott bottles joined by a 7.5 cm long glass tube (1.5 cm diameter), which enables a proton exchange membrane, Nafion^{TM} 117 (DuPont), to be inserted between the chambers. Both electrodes were made of carbon cloth (H2315, Freudenberg FCCT SE & Co. KG), with a working surface area of 50 cm^2 and connected to each other using a copper wire and 1 kΩ resistor. The anode chamber was equipped with sampling ports to maintain anaerobic conditions in the anode chamber. The ports were covered by 0.22 μm sterile filters to keep the anode chamber aseptic. All equipment was sterilized by autoclaving (121°C, 0.1 MPa, 20 min.) prior to experimentation.

Three different MFCs were set up, a closed circuit MFC (CC-MFC), an open circuit control MFC (OC-MFC) and a sterile control MFC (S-MFC). The anode chamber of the CC-MFC and the OC-MFC contained 200 ml of contaminated groundwater (12 mbgl). In the S-MFC, 200 ml of filtered (tangential flow filtration unit, 0.1 μm, Pall) contaminated groundwater (12 mbgl) with 2 g/l of sodium azide was added into the anode chamber. All three cathode chambers were filled with 200 ml of uncontaminated groundwater (7 mbgl) sterilized by autoclaving and covered by wooden pulp stopper to allow aeration and prevent contamination by airborne bacteria. The circuits of CC-MFC and S-MFC were closed with a 1 kΩ resistor, whereas the OC-MFC operated under open circuit conditions. All MFCs were placed on a shaker (85 rpm) to support mixing within the chambers and operated for 24 days. The open circuit and closed circuit voltage (across the resistor) were monitored daily. Polarization and power curve measurements were made using a potentiostatic discharge technique when the closed circuit voltage, i.e. electricity production by MFCs, reached its maximum value.

Chemical analysis

Samples for chemical analysis were taken every 5-7 days from the anode and cathode chamber and filter-sterilized through a 0.22 μm filter. Samples were stored at -20°C prior to analysis. The concentration of total phenols (phenol, isomers of cresols and xylenols) in the anode and cathode chamber was determined by high performance liquid chromatography (HPLC) using a Perkin Elmer instrument and UV detector. The detection limit was 1 mg/l and precision of this analysis was ±7% (Thornton et al., 2001).

RESULTS AND DISCUSSION

Electricity production

The open circuit voltage (OCV) of CC-MFC, OC-MFC and S-MFC reached 137 mV, 165 mV and 76 mV, respectively, at the beginning of the experiment (Figure 2A). Similarly, as in sediment-MFCs (Reimers et al., 2001), the non-zero OCV at time zero was caused by the natural difference in redox potential between contaminated and uncontaminated groundwater. The OCV value of biologically active MFCs increased up to 550 mV and 590 mV in CC-MFC and OC-MFC, respectively, while OCV of S-MFC decreased to -18 mV. The OCV of CC-MFC decreased after 16 days of operation to 330 mV (Figure 2A). The closed circuit voltage (CCV) (Figure 2B) started increasing in biologically active MFCs after 3 days of operation, reaching a maximum value 82 mV in the CC-MFC and 29 mV in the OC-MFC. The CCV of the CC-MFC decreased to 14 mV after 16 days (Figure 2B). The CCV of control sample S-MFC remained at 0 mV, suggesting that the electricity production was due to biological activity in the CC-MFC and OC-MFC.

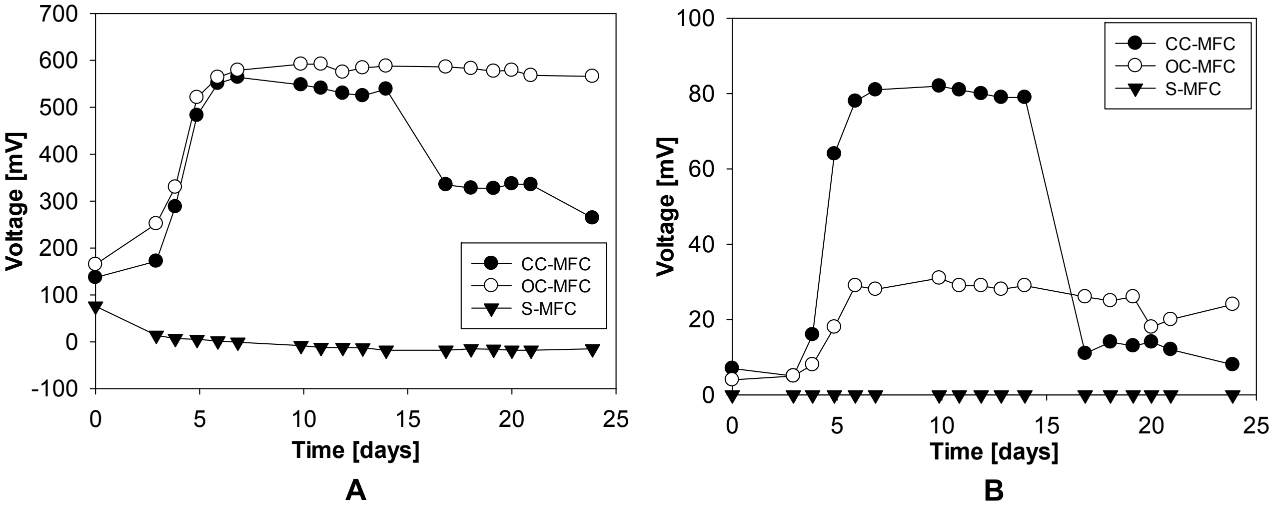

Figure 2: Open circuit voltage (A) and closed circuit voltage (B).

Figure 3 shows the results of polarization and power curve measurement for the CC-MFC and OC-MFC. The OC-MFC voltage decreased more rapidly with increasing current density than for the CC-MFC, resulting in a lower power density (1.2 mW/m^2 in the OC-MFC, 2.0 mW/m^2 in the CC-MFC). The OC-MFC generates a lower maximum current density (10.3 mA/m^2) than the CC-MFC (20.8 mA/m^2). The internal resistance of the CC-MFC was calculated using Ohm's law at the highest power production point, resulting in 2270 Ω. The measured values of electrical efficiency correspond with the values of power density and internal resistance for H-type dual-chamber MFC published previously (Logan, 2008).

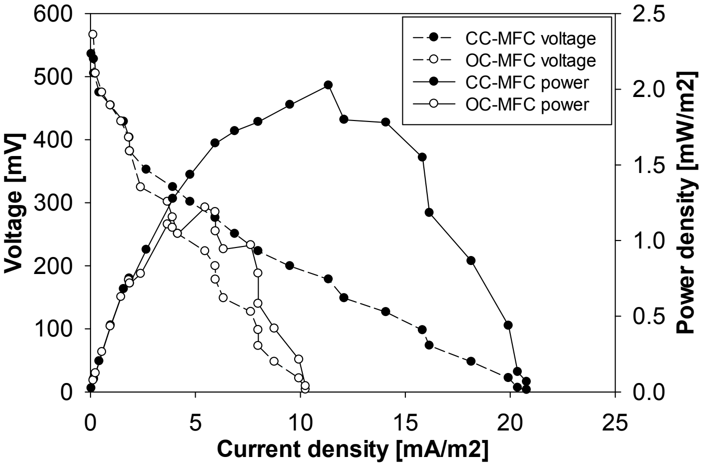

Figure 3: Polarization and power curve for the CC-MFC and OC-MFC.

The results demonstrate that no electricity can be produced in the absence of bacteria (S-MFC), indicating that microbial activity contributed to the electricity generation. In this study, although there is no significant difference in the OCV between the CC-MFC and OC-MFC, the CCV produced and the maximum power density show that the CC-MFC can produce more electricity than the OC-MFC (2.0 mW/m^2 and 1.2 mW/m^2, respectively). This is likely due to the adaptation of bacteria in the CC-MFC for electricity generation. The closed circuit set up creates a selection pressure in the CC-MFC microbial community. The community develops the ability to transfer electrons to the anode electrode and uses it as an electron acceptor. The OC-MFC bacteria, growing under open circuit conditions, are not adapted for this. A previous study on bioremediation-MFC by Yang et al. (2013) confirms this hypothesis. The authors observed a significant difference between the microbial community of the CC-MFC and OC-MFC with increased number of exoelectrogens in the CC-MFC (Yang et al., 2013).

Biodegradation of phenolic compounds

Phenolic compounds diffused from the anode chamber to the cathode chamber through the Nafion membrane (Figure 4), decreasing the concentration of total phenols in the anode chamber from 158 mg/l to 93 mg/l at the end of the experiment. The concentration of phenolic compounds in the cathode chamber of the S-MFC was 72 mg/l, due to phenol diffusion from the anode chamber. The diffusion coefficient for the total phenols was calculated using data from the S-MFC. The mass balance of total phenols for the sterile system can be expressed as

$$m_{an,0} + m_{cat,0} = m_{an,t} + m_{cat,t} \qquad (1)$$

$$c_{an,0}V + 0 = c_{an,t}V + c_{cat,t}V \text{ or } c_{an,t} = c_{an,0} - c_{cat,t} \qquad (2)$$

$$\frac{dc_{cat,t}}{dt} = \frac{D_{phenols} \cdot A}{L \cdot V}(c_{an,0} - 2c_{cat,t}), \qquad (3)$$

where m is mass, c is concentration, V is volume, $D_{phenols}$ is the average diffusion coefficient of total phenols through the membrane, A is the membrane surface area, L is the membrane thickness, an,0 and cat,0 are anode and cathode chambers at the beginning of the experiment, and an,t and cat,t are the MFC chambers at time t (Kim et al., 2007). The diffusion coefficient of phenolic compounds can be calculated after integration,

$$D_{phenols} = -\frac{VL}{2At} ln\left[\frac{(c_{an,0} - 2c_{cat,t})}{c_{an,0}}\right]. \qquad (4)$$

The diffusion coefficient $D_{phenols} = (1.280 \pm 0.017) \cdot 10^{-6}$ cm^2/s was calculated from measured data applying Equation 4.

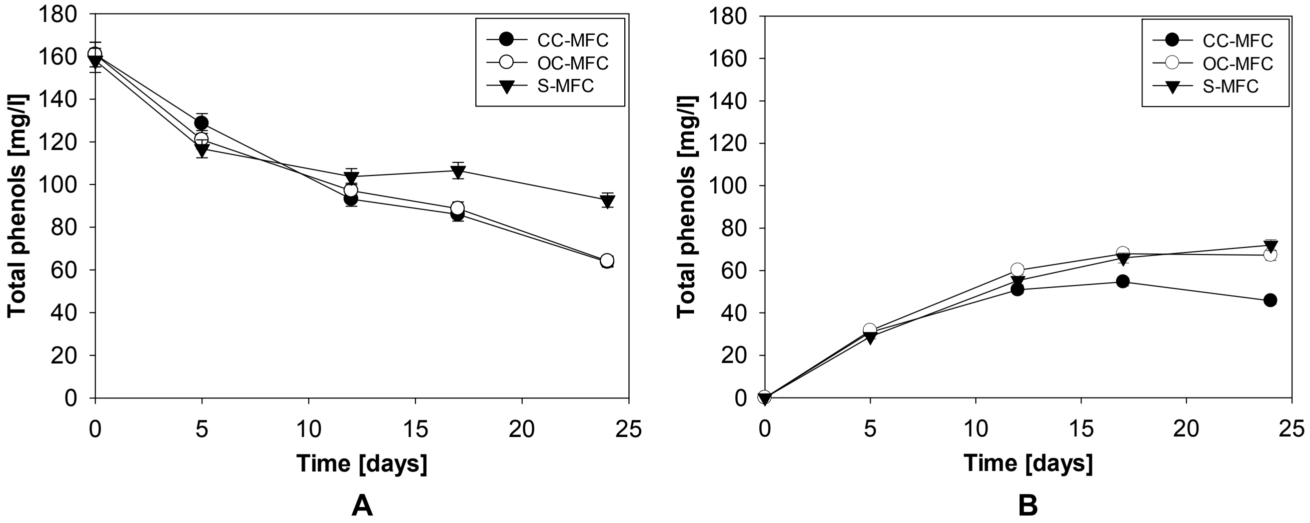

Figure 4: Concentration of total phenols in the anode (A) and cathode (B) chamber.

The concentration of phenolic compounds in the anode chamber of the OC-MFC decreased from 161 mg/l to 64 mg/l which is due to diffusion into the cathode chamber and biodegradation. The final concentration of total phenols in the cathode chamber is similar to the S-MFC (67 mg/l). It was previously reported that oxygen can be transported from the cathode chamber via the Nafion membrane to the anode chamber ($D_{O2} = 2.4 \cdot 10^{-6}$ cm^2/s) (Kim et al., 2007). It is likely that oxygen served as the main electron acceptor for biodegradation of the phenolic compounds in the OC-MFC. Total phenols in the anode chamber of the CC-MFC decreased from 161 mg/l to 64 mg/l. It is the same rate of decrease as in the OC-MFC. This change was also caused by diffusion and biodegradation. Considering the concentration of phenolic compounds in the anode chamber, there's no significant difference between the CC-MFC and OC-MFC. However, the concentration of total phenols in the cathode chamber of the CC-MFC starts decreasing after 16 days of operation and reaches 46 mg/l at the end of the experiment. It is likely that the phenols were transported back to the anode chamber and then biodegraded, supporting further electricity production. Electricity production in the CC-MFC decreased after 16 days of operation (Figure 2), which is likely due to the limited mass transfer of phenolic compounds from the cathode chamber to the anode chamber.

Table 1: Biodegradation of phenolic compounds.

Time [days]	CC-MFC	OC-MFC	S-MFC
	Biodegradation [%]		
0	0	0	0
5	0.87	5.14	9.54
12	10.48	2.27	1.20
17	12.65	2.67	-7.17
24	32.04	18.35	-2.36

The total mass of phenolic compounds, considering the anode and cathode chamber, does not decrease in the S-MFC (Table 1), but decreases in comparison with S-MFC by 18% in the OC-MFC and by 32% in the CC-MFC after 24 days of operation. The microbial community in the CC-MFC used two types of electron acceptors: oxygen transported to the anode chamber and the anode electrode. The presence of the anode electrode as an electron acceptor enhanced the biodegradation of the phenolic compounds by 17% compared with the OC-MFC.

CONCLUSIONS

Electricity was produced in a dual-chamber MFC using groundwater contaminated by phenolic compounds. The maximum power generation reached 2.0 mW/m^2. Bacteria already present in the groundwater were able to biodegrade the phenolic compounds, using the anode electrode as an electron acceptor. Bioremediation of the total phenols was enhanced by approximately 17% in comparison with an open circuit control system. Phenolic compounds diffused through the Nafion membrane at the rate $(1.280 \pm 0.017) \cdot 10^{-6}$ cm^2/s, which must be taken into account to correctly interpret the biodegradation rate and performance of the MFC design concept. Future research will explore the mass transfer processes, electron acceptors and microbial community present in the system in more detail.

ACKNOWLEDGEMENTS

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Evaluation of solid polymeric organic materials to stimulate the degradation of chlorinated ethenes in bioreactive caps

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In situ bioreactive capping is a promising technology for mitigation of surface water contamination in which contaminants are transformed into harmless products through microbially mediated reactions. Stimulation of dechlorination of chlorinated ethenes in bioreactive caps can be achieved through incorporation of solid polymeric organic materials (SPOMs) in order to provide a sustainable electron source for organohalide respiring bacteria. In this study, five different SPOMs, i.e. wood chips, hay, straw, tree bark and shrimp waste, were assessed for their long term applicability as an electron donor for reductive dechlorination of *cis*-dichloroethene (cDCE) and vinyl chloride (VC) in sediments originating from a river stretch affected by a cDCE/VC contaminated groundwater plume. The initial fast release of fermentation products, such as acetate, propionate and butyrate led to the onset of extensive methane production especially in microcosms amended with shrimp waste, straw and hay, while no considerable stimulation of VC dechlorination was obtained in any of the SPOM stimulated microcosms. However, in the longer term, accumulation of short chain fatty acids (SCFAs) decreased as well as methanogenesis, whereas high dechlorination rates of VC and cDCE were established with concomitant increase of *Dehalococcoides mccartyi* and corresponding catabolic genes *vcrA* and *bvcA* both in the sediment and on the surface of the SPOMs. Of all SPOMs, the rapid and persistent colonization of tree bark by *Dehalococcoides mccartyi* combined with the lowest stimulation of methanogenesis singled out tree bark as a SPOM of interest for use in bioreactive caps for long-term stimulation of cDCE/VC organohalide respiration.

Aerobic cometabolic bioremediation of trichloroethylene- and 1,1,2,2-tetrachloroethane-contaminated groundwater in a packed bed bioreactor

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The aim of this study was to develop a packed bed reactor (PBR) process for the on-site aerobic cometabolic bioremediation of a groundwater contaminated by trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (TeCA).

With regard to the growth substrate selection, the comparison of the CAH degradation performances obtained with 5 candidate substrates led to the selection of butane and to the development from the site's indigenous biomass of a suspended-cell consortium capable to degrade TCE (TCE first-order constant = 96 L $g_{protein}^{-1}$ d^{-1} at 30 °C and 4.3 L $g_{protein}^{-1}$ d^{-1} at 15 °C) with a 90% mineralization of the organic Cl.

Based on PCR-DGGE analysis of the 16S rRNA genes followed by band excision and sequencing, the microbial consortium enriched was mainly composed of Bacteroidetes and Alpha- and Beta-Proteobacteria that were distantly related to known CAH-cometabolizing bacteria. The low TeCA degradation rate by the developed consortium suggested the introduction of a chemical pre-treatment based on the TeCA to TCE conversion via β-elimination, a very fast reaction at alkaline pH.

The choice of the best-performing carrier was made by means of a 2-level procedure: the 1st level consisted of batch tests, operated both at 30 and 15 °C, whereas the 2nd level consisted of continuous-flow tests, operated at 30 °C. A porous ceramic carrier named Biomax resulted the best-performing one.

On the basis of the kinetic parameters relative to TCE aerobic cometabolic biodegradation by the selected consortium, a 31-L packed-bed reactor, consisting of 14 columns connected in series, packed with Biomax and immerged in a temperature-controlled bath, was designed and set-up. The preliminary data, obtained by operating the plant with a 4-day residence time, indicate the attainment of a 0.1 mg L^{-1} d^{-1} TCE biodegradation rate.

INTRODUCTION

Chlorinated aliphatic hydrocarbons (CAHs) represent a widespread cause of water contamination and some of them are proven or suspected carcinogens. CAH-contaminated waters are usually treated by means of physical-chemical methods which simply transfer the contaminants to a different matrix.

On the other hand, several scientific studies have indicated that aerobic cometabolism (AC) can present significant advantages over the alternative technologies, such as reduced costs, short treatment times and the possibility to completely dechlorinate a wide range of CAHs (Kim et al., 2000; Tiehm et al., 2008).

In-situ AC presents remarkable challenges, such as the risk of clogging the aquifer porosity and of attaining a very short bioreactor zone; conversely *on-site* implementation of AC is a valid alternative (Goltz et al., 2001).

Different types of bioreactors can be used to treat contaminated groundwater. Among them, packed bed reactors (PBRs) represent an interesting solution for biodegradation processes, in particular in the presence of recalcitrant and toxic compounds. In the PBRs cells grow attached to the surface of suitable carriers. PBRs present specific advantages over suspended-cells bioreactors, such as higher biomass concentrations, higher cell retention times, the elimination of the biomass settling step, a partial protection of cells against toxic substances, and lower inhibition due to high substrate concentrations (Singh et al., 2006). Furthermore, AC implementation in PBRs in in general not characterized by the risk of clogging the packed bed, even when the growth substrate is fed continuously (Ciavarelli et al., 2012).

The goal of this study was to develop a procedure for the design of a PBR AC process for the bioremediation of a groundwater contaminated by trichloroethylene (TCE) and 1,1,2,2-tetrachloroethane (TeCA). More specifically, the study was aimed at selecting the best growth substrate and the best carrier for the aerobic cometabolic process, and at scaling-up the process to a 31-L PBR.

MATERIALS AND METHODS

Experimental scheme

The studied site, located in Northern Italy, is contaminated by a mixture of TCE (0.04-5.8 mg L^{-1}) and TeCA (0.2-4.0 mg L^{-1}). Groundwater was sampled from four wells, screened in the confined aquifer or in the shallow one.

The tests were conducted in 119-mL glass vials (batch bioreactors), containing 60 mL of site groundwater, closed with Teflon-lined septa and maintained in agitation (125 rpm). Most experiment was work was performance both at 30°C (temperature that allows a rapid initial screening) and 15°C (average site's temperature).

The selection of the best-performing substrate and groundwater was made through a two-step method. In the 1st step 25 suspended-cell tests were set up by exposing 5 groundwaters sampled from different site's wells to 5 candidate growth substrates: methane (M), propane (PR), butane (B), pentane (PE) and phenol (F). At the end of the 60-day monitoring period, the 25 vials were compared in term of the normalized degradation rates $r_{TCE,30}/C_{TCE}$ and $r_{TCE,30}/C_{TeCA}$. In the 2nd step, the 8 best-performing vials were then compared by means of a kinetic test; the selection of the best combination of groundwater and growth substrate, and therefore of the best microbial consortium, was made on the basis of the first-order constants $k_{1,TCE,30}$ and $k_{1,TeCA,30}$, obtained by dividing the values of $r_{TCE,30}/C_{TCE}$ and $r_{TCE,30}/C_{TeCA}$ by the biomass concentration evaluated at the beginning of each pulse.

A preliminary screening based on the previous experience of the research group led to the pre-selection of four candidate biofilm carriers (porous materials specifically designed for biofilm processes): Biomax, Biomech, Biopearl and Cerambios.

The choice of the best-performing carrier was made by means of a 2-level procedure. The 1st level consisted of batch tests, operated both at 30 and 15°C, whereas the 2nd level consisted of continuous-flow tests, operated at 30°C. The reason for the 2-level procedure is that, while the 119-mL batch tests allow a more precise evaluation of the CAH degradation rates and an easier operation of the 15 °C tests, the continuous-flow tests allow the investigation of fluid-dynamic aspects not considered in the batch tests.

The 30°C continuous-flow tests were conducted in four 1-L packed columns, connected to a feeding system designed so as to attain a pulsed feed of both oxygen and the selected growth substrate (butane). The pulsed feed of oxygen and butane aims at minimizing the substrate competitive inhibition on CAH cometabolism, and at distributing biomass growth over the entire bioreactor length. The four columns were operated in continuous mode for about 100 days.

The selected enriched culture grown both under suspended (liquid sample) and attached cells (biofilm on biomass carrier) at 30°C and 15°C were characterized using the PCR-DGGE (Denaturing Gradient Gel Electrophoresis) analysis of the 16S rRNA genes.

On the basis of the kinetic parameters relative to TCE AC biodegradation by the selected consortium, a 31-L packed-bed reactor, consisting of 14 columns connected in series, packed with the selected carrier (Biomax) and immerged in a temperature-controlled bath, was designed and set-up.

RESULTS

Selection of the best-performing substrate and groundwater

On the basis of the results (see Figure 1), the coupling of butane and groundwater n. 4 (B4) was identified as the best-performing one, thanks to its high $k_{1,TCE,30}$ ($96\ L\ g_{protein}^{-1}\ d^{-1}$).

The selected consortium was used to inoculate a further bioreactor that was placed in a shaker at 15°C (average site's temperature). After a three month period characterized by periodic additions of oxygen, substrate, TCE and TeCA, the bioreactor was subjected to a kinetic test, in order to compare the CAH degradation performances at 15 and 30°C. The kinetic test conducted at 15°C resulted in a marked decrease of the first-order constant (4.3 L $g_{protein}^{-1}$ d^{-1}) in comparison with the value obtained at 30°C.

Considering that $k_{1,TeCA,30}$ was significantly lower than $k_{1,TCE,30}$ and that, in a pre-treatment step, TeCA can be rapidly converted into TCE via β-elimination, $k_{1,TeCA,30}$ was not included in the criteria of consortium selection (Joens et al., 1995). The inclusion of an abiotic pre-treatment aimed at converting TeCA into TCE was selected as the best option for the remediation of the studied groundwater.

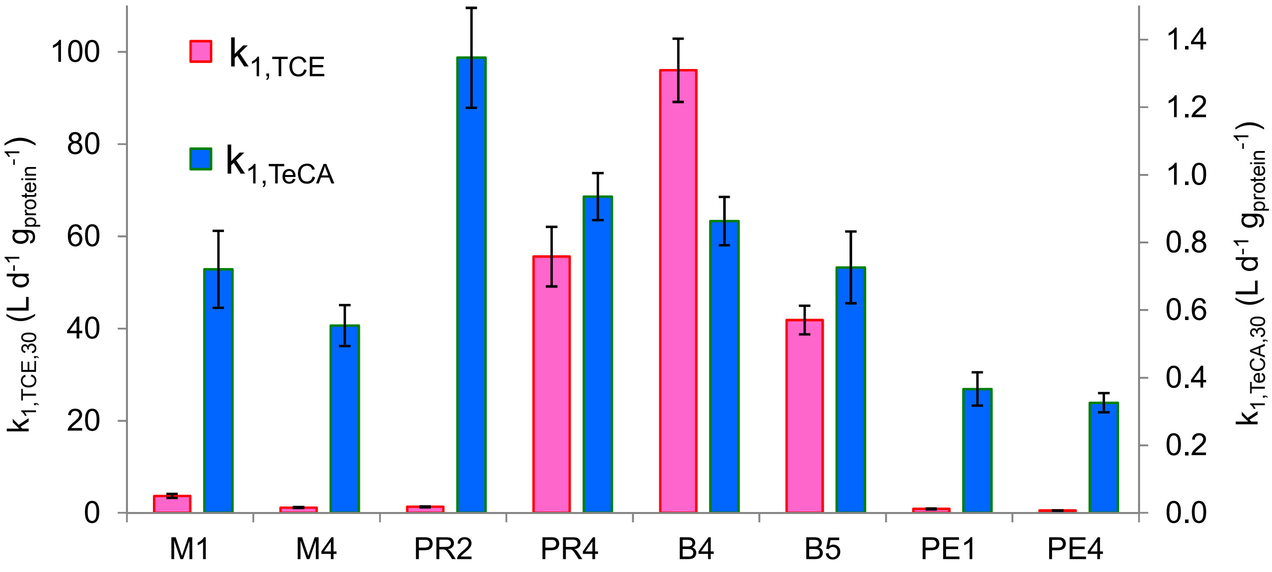

Figure 1: First order degradation constants.

Based on PCR-DGGE analysis of the 16S rRNA genes, consortium B4 was composed of one unclassified bacterium that represented the most abundant phylotype, four phylotypes belonging to the Bacteroidetes, Betaproteobacteria and Alphaproteobacteria. None of detected phylotypes was related to known butane oxidizing or chlorinated solvent cometabolizing bacteria. Further details on the microbiological characterization are described by Frascari et al. (2013c).

The ratio of Cl^- moles released to TCE moles depleted increased during the initial weeks, and rapidly attained a stable value corresponding to a 90% ± 1% mineralization of the organic chlorine. This result is in agreement with several studies of CAH AC that demonstrate a very high degree of mineralization (Frascari et al., 2013a).

Selection of the best-performing biofilm carrier

The results of the attached-cell tests were compared on the basis of the TCE normalized degradation rate ($r_{TCE,15}/C_{TCE}$ and $r_{TCE,30}/C_{TCE}$) and of the attached cell concentration attained, at the two temperatures, at the end of the biofilm development process (see Figure 1).

On the basis of both the batch and the continuous-flow tests, Biomax resulted the best-performing biofilm carrier. The effect of biomass attachment on $k_{1,TCE}$ depended on temperature: at 15°C the attached consortium performed slightly better than the suspended one, whereas at 30°C an opposite trend was noticed.

Scale-up of the process to a 31-L packed-bed reactor

On the basis of the kinetic analysis relative to TCE aerobic cometabolic biodegradation by the selected consortium (Frascari et al., 2013b), a 31-L PBR was designed and set-up, consisting of 14 glass columns of 1.25 meters of length, connected in series and immerged in a temperature-controlled bath (see Figure 2). The columns were filled with the selected biofilm carrier (Biomax) and inoculated with 20 L of a highly-concentrated suspension of the selected consortium (B4).

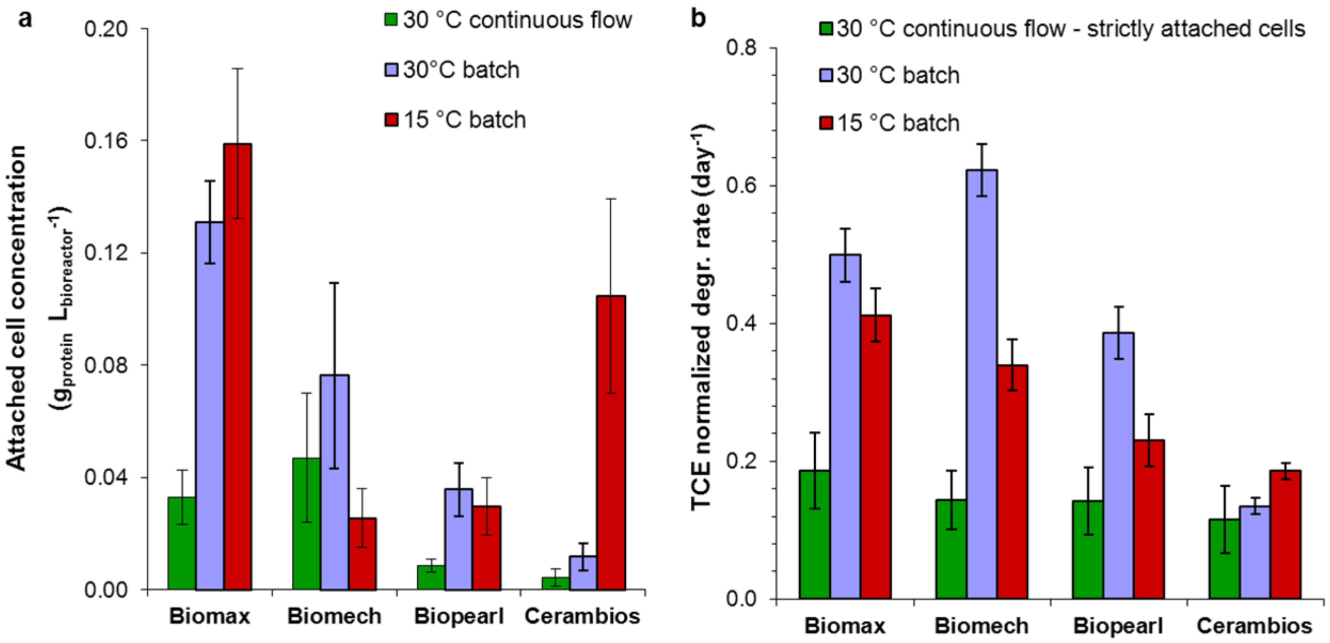

Figure 2: Attached cell concentration (a) and TCE normalized degradation rate (b).

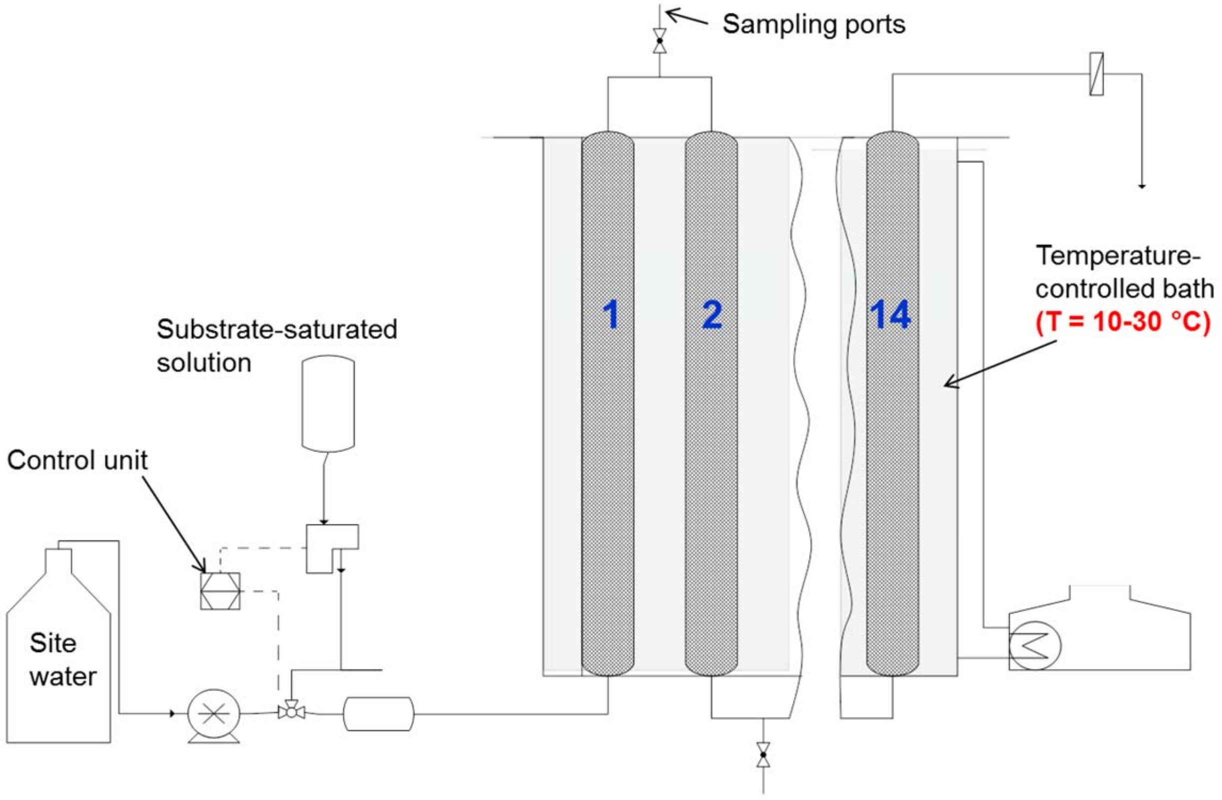

Figure 3: Flow sheet of 31-L pilot plant.

A substrate pulsed feed was set up to avoid excessive inhibition between butane and TCE, and to attain an homogeneous distribution of biomass concentration along the columns. Different pulsing schedules were tested (see Table 1): the first to increase biomass, the other to increase the performance. The plant was operated with a 4-day residence time in continuous mode for about 170 days.

Table 1: Schedules of pulsed substrate/oxygen supply tested in the 31-L PBR.

Phase n°	Time d	t_{cycle}[a] d	t_B[b] h	t_{TCE}[c] h	t_B*[d] %	$c_{B,IN}$[e] mg L^{-1}	$c_{TCE,IN}$[f] mg L^{-1}	r_{TCE}[g] mg L^{-1} d^{-1}	TCEconv[f] %
1	0-15	1	3	21	13%	56	0,8	-	-
2	15-25	2	4,8	43,2	10%	32	0,7	0,12	50%
3	25-39	2	9	39	19%	35	1,1	0,11	49%
4	39-55	3,5	15,8	68,3	19%	31	1,3	0,11	44%
5	55-61	3,5	10	74	12%	40	1,2	0,09	35%
6	61-99	3,5	10	74	12%	37	0,4	0,03	18%
7	99-153	1	6	18	25%	36	0,4	-	22%
8	153-159	1	8	16	33%	40	0,3	-	-
9	159-174	2,5	9	51	15%	41	0,4	0,16	79%

[a] cycle time; [b] time of butane pulse in the t_{cycle}; [c] time of TCE pulse in the t_{cycle}; [d] t_B/t_{cycle}; [e] inlet butane concentration; [f] inlet TCE concentration; [g] TCE degradation rate; [f] TCE conversion.

Preliminary data indicated the attainment of a TCE biodegradation rate of about 0.1 mg L^{-1} d^{-1}, and a 50% TCE conversion. However, after about 60 days of plant operation, the TCE rate decreased significantly, probably due to cell lysis or inactivation. The degradation performance improved only in response to a further inoculation of the plant, performed with 20 L of a highly-concentrated suspension of the selected consortium. During the last period of operation, the TCE rate attained 0.16 mg L^{-1} d^{-1}, and the TCE conversion was equal to about 80%.

An optimization of the feed pulsation schedule and operational conditions is in progress to increase the TCE degradation performance. A plot of TCE, butane and oxygen concentration versus PBR length representative of the performance of the PBR during the last operational phase is shown in Figure 4.

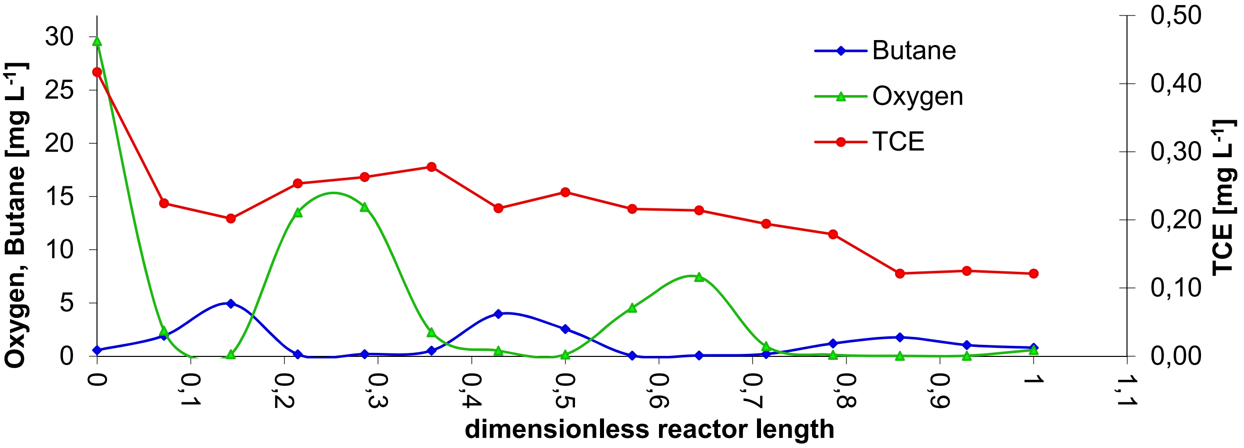

Figure 4: Results obtained in the seventh phase: butane pulsed feed = 25%, HRT = 4.66 d, TCE inlet concentration = 0.4 mg L^{-1}, T = 30 °C.

CONCLUSIONS

In this work, a procedure for the development of a PBR AC process was applied to the groundwater of a site contaminated by TCE and TeCA.

- Butane was selected among 5 tested substrates, and a suspended-cell consortium capable to degrade TCE was developed from the site's indigenous biomass.
- The attachment of the selected consortium to 4 porous biofilm carriers led at both 15°C and 30°C to satisfactory TCE degradation performances, and to the selection of a ceramic porous carrier (Biomax).
- A 31-L packed-bed reactor, consisting of 14 columns connected in series, was designed, set-up, inoculated and operated for 170 days with satisfactory results; a substrate pulsed feed was set up to avoid excessive inhibition between growth substrate and TCE.

ACKNOWLEDGEMENTS

Project co-funding by the European Commission under Grant Agreement no. 265946 (Minotaurus project, 7th FP) is acknowledged. The authors acknowledge Askoll Due for kindly supplying the Biomax biofilm carriers.

NOMENCLATURE

c_i	Aqueous phase concentration of compound *i* at the beginning of a given pulse ($mg_i\ L^{-1}$)
$k_{1,I,30}$	First order constant of net biodegradation of compound *i*, obtained by dividing r_i / c_i by the biomass concentrations evaluated at the beginning of the pulse ($L\ d^{-1}\ g_{protein}^{-1}$)
$r_{i,30}$	Net initial biodegradation rate of compound *i* in a given pulse at 30°C, obtained by subtracting the abiotic contribution to the overall depletion rate ($mg_i\ L^{-1}\ d^{-1}$)
$r_{i,30}/c_i$	Ratio of the net initial biodegradation rate of compound *i* in a given pulse to the aqueous phase concentration of *i* at the beginning of the pulse (d^{-1})

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MIP-IN device for combined detection of pollutants and injection of microscale zerovalent iron – pilot test

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ABSTRACT: The innovative MIP-IN detection-injection device was used for implementing guar gum stabilized zerovalent iron in a contaminated subsurface for treatment of a CAH-contamination in the groundwater at an industrial site in Belgium. The device facilitates (1) the detection of pollutants by a membrane interface probe (MIP) and (2) a simultaneous correlated injection (IN) during direct push of the device using a Geoprobe®. MIP-logs showed that chlorinated pollutants were present in the subsurface at distinct depths between 2 and 12 meter below ground surface, but the exact depths altered from spot to spot. The MIP-IN injection approach was used to inject guar gum stabilized microscale zerovalent iron slurry in a challenging sandy subsurface using high injection pressures, high flow and relatively low injection volumes. In parallel, also the classical injection approach was followed where the injection depths were fixed based on prior MIP-measurements or soil profile characteristics. After the injection, undisturbed soil samples were taken to verify the distribution of the injected material. It was shown that the MIP-IN device is able to inject guar gum stabilized zerovalent iron at depths where CAHs were detected, and that the MIP-IN approach has potential. To deliver the reagent at the injection depth, a targeted radius of influence of 0.5 m was found suitable.

INTRODUCTION

In-situ remediation technologies are considered more sustainable and cost-efficient compared to many ex-situ technologies like pump and treat (US EPA, 2001). To stimulate pollutant removal in the subsurface, different kinds of reagents are being injected, comprising electron donors, nutrients, chemical oxidants, reductants and combinations of these. A crucial aspect for the success of in-situ remediation technologies is the contact between reagents and pollutants. One of the difficulties is often the lack of knowledge about the exact location (x, y, z) of the contaminants in the subsurface. This implies that reagents may be injected in areas where no pollution is present, while other parts with significant contaminant concentrations are not treated.

Within the FP7 project UPSOIL, an innovative device (MIP-IN) was developed combining (1) detection of pollutants by a membrane interface probe (MIP) and (2) a simultaneous correlated injection (IN) during direct push of the device using a Geoprobe®. The MIP-IN device is the basis for a new detection-injection technology with the main advantage of the nearly simultaneous coupling of detection of pollutants at a certain depth and injection of a suitable amount of reactive agent at that precise spot (Figure 1). Thus, the injected reagent is more targeted towards the real location of the pollution with reduced remediation time and cost. The MIP-IN prototype was tested for permanganate injection at pilot scale during a field test at a site in the port of Antwerp, Belgium. Results proved that the MIP-IN device has potential for simultaneous detection of contaminants and injection of reagents for contaminants removal (Uyttebroek et al., 2012).

Recently, as part of the FP7 AQUAREHAB project (EU GA 226565), the first prototype version of the MIP-IN device was used also for injection of a different reagents type into a sandy aquifer. More specifically, guar gum stabilized microscale zerovalent iron (ZVI) particles were injected in the subsurface to degrade chlorinated aliphatic hydrocarbons (CAHs) in the groundwater). Zerovalent iron is known for its ability to degrade CAHs like tetrachloroethylene (PCE) and trichloroethylene (TCE) abiotically to harmless ethane and ethane (Gillham, 1996; Velimirovic et al., 2013), and has been used for in-situ groundwater remediation purposes for more than a decade (Gillham, 1996). To be injectable, fine sized ZVI-particles such as nanoscale particles or lower microscale particles are required. In our study, microscale ZVI (mZVI) was used as it combines some advantages of granular iron (storage as dry material, significant life-time and lower price) and of nanoscale particles (high reactivity, injectable, etc.). However, sedimentation of mZVI due to gravity when suspended in water is a point of attention and needs to be prevented during the injection. Earlier, the green biopolymer guar gum was reported to be a good stabilizer for small particles like mZVI (Tiraferri et al., 2008; Tiraferri and Sethi, 2009; Xue and Sethi, 2012). Lab scale experiments proved that guar gum stabilized mZVI has opportunities for in-situ remediation as the reactivity of mZVI is completely recovered after guar gum degradation and removal of guar gum breakdown products (Velimirovic et al, 2012; 2013).

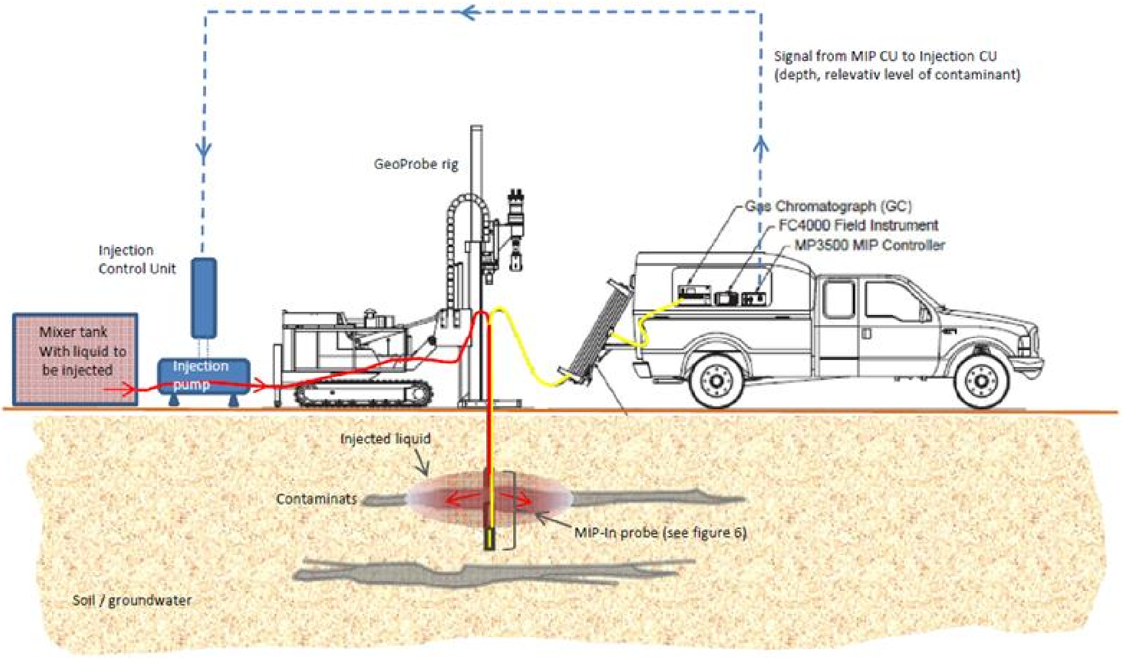

Figure 1: Schematic representation of the MIP-In detection-injection device.

The aim of the current study was to evaluate the MIP-injection device for delivery of guar gum stabilized mZVI in the subsurface. The results were compared with a classical injection approach to evaluate the benefits of the MIP-IN device. Based on the obtained results, a potential scenario for a full scale application has been worked out.

EXPERIMENTAL SET-UP

Site information

The injection of guar gum stabilized mZVI was performed at an active industrial site in Belgium. The main pollutant at the site is PCE, detected at concentration ranging from 8.1 to 72.6 mg/L. The selected test location is located near but outside the area where DNAPL is known to be present. A map of the test area is given in Figure 2.

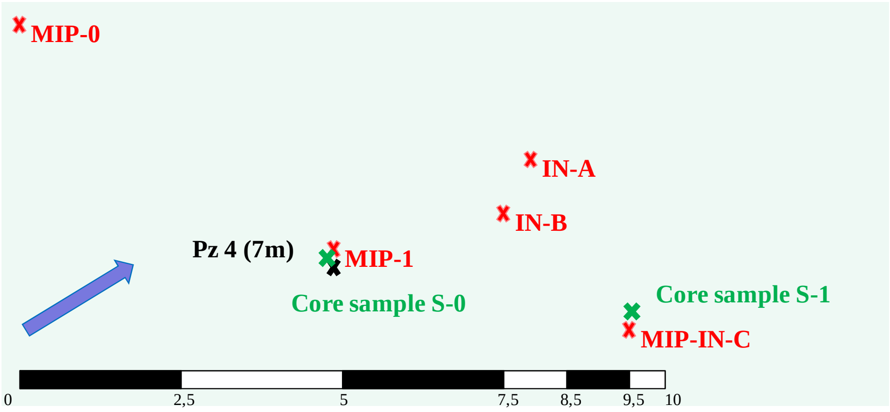

Figure 2: Schematic overview of the test site.

The hydrogeological structure of the site consists of various tertiary and quartier sand (fine, light loamy sand 0-20 m bgs) combined in certain cases with sporadically clay layers. Empirical approximation of hydraulic conductivity was based on available data on grain size distribution (GSD). According to the GSD data, from 4.3-6.5 m bgs the estimated average K is 6.0×10^{-5} m/s, the hydraulic gradient is 0.000681 and the groundwater flow velocity is 7.4 m/year. The water table is located approximately 2 m bgs.

MIP-IN device and injections

For the injection, microscale ZVI from Höganäs (Sweden) with d_{50} of approximately 56 µm was used. The mZVI was suspended in a 0.45 % guar gum suspension as described by Velimirovic at al. (2013b).

The field test consisted of several “top-down” injections at high pressures performed using a Geoprobe 7822DT and the patented MIP-IN device (Figure 1; Bastiaens and Stupdrup, 2012). The MIP-IN probe used herein has a diameter of 6.35 cm and comprises (1) a membrane interphase section which is connected with a GC-device and (2) an injection section. The injection section is located 60 cm above the detection section. The probe used in the current pilot test was equipped with 5 injection openings divided radially (1 for each 72° section). They were connected via an injection tube to an one m^3 reagent storage vessel above ground. Compared to the pilot test described by Uyttebroek et al (2012), a wider injection tube was used to transport the viscous guar gum stabilized mZVI suspension. While the probe was drilled down, data were analyzed with three detectors: the photoionization detector (PID) for detection of components with an ionization potential <10.2 eV (e.g. benzene, toluene, ethylbenzene and xylene, and some chlorinated hydrocarbons), the flame ionization detector (FID) for detection of aliphatic and aromatic hydrocarbons, and the halogen specific detector (XSD) for detection of halogenated components (Bronders et al., 2009). When the injection part reached a depth where pollutants were detected, the whole MIP-IN probe was hold in position and a certain volume of mZVI was injected using high pressure (50-70 bar), high flow and low volume injections (50-100L). When larger volumes were found necessary at a certain depth, more injection events were performed at the same depth.

Core samplings and analyses

Immediately after the injection, core samples were taken up to 12 m bgs to evaluate the distribution of injected mZVI in the subsurface. In the lab, the core samples were dismantled and aliquots of aquifer material were taken along the whole profile. The presence of mZVI in the subsamples was determined by quantifying the iron concentration indirectly via hydrogen measurements after acid digestion (Velimirovic et al., 2012).

RESULTS

Pre-injection analyses

In March 2012, a MIP-probing (MIP-0 in Figure 1) was performed at about 8 meter distance from the MIP-IN injection area. MIP-0 results indicated the presence of chlorinated compounds around 6,5 and 9,5 m below ground surface (bgs).

Undisturbed core samples, taken in January 2013 near Pz4 up to a depth of 7 m, were analysed and confirmed the presence of CAHs. Very high concentrations of PCE (> 600 mg/kg DM) were found around 5 m bgs (Table 1). Also between 6 and 7 m bgs, and to a less significant extent between 3 and 4 m bgs, peak concentration of PCE were measured. The grain size distribution for the different sections were determined via laser diffraction (ISO 13320:2009) and are summarized in Table 1. The data indicated that the subsurface was less homogeneous than anticipated based on available site data. A thin clay layer was found present between 3 and 4 m bgs, which may explain the higher PCE concentration at this depths. Also in the thin section around 5 m bgs where the very high amounts of PCE were found, finer aquifer material was found. The pollutant concentrations seem to be higher in layers with a lower permeability. On the other hand, this correlation was less obvious between 6 and 7 m bgs.

In April 2013, the day before the injection, another MIP-probing was made near Pz4 (MIP-1). The Xsd-detector indicated peak concentrations of CAHs between 3 and 4 m bgs and between 6 and 7,5 m bgs (results not shown).

All these data show, that the pollutants are distributed heterogeneously in the subsurface, also within the small test area.

Table 1: Pre-injection analyses performed on undisturbed core sample taken near well pz4.

Depth	PCE	TCE	Texture	d_{10}	d_{25}	d_{50}	d_{75}	d_{90}
m bgs	**mg/kg**	**mg/kg**		µm	µm	µm	µm	µm
1-2 m	0.44	0.04	Sand	154	195	270	392	514
2-3 m	0.68	<DL	Sand	154	191	242	312	406
3-4 m	6.00	0.10	Clay	2	7	25	48	214
4-5 m	0.04	<DL	Sand	15	159	277	384	503
5 - 5.1 m	**639.47**	1.06	Sand	3	10	81	199	294
5,1 - 6 m	1.96	<DL	Sand	7	73	166	263	400
6-7 m	28.52	0.03	Sand	50	119	200	296	408

Injection of mZVI following the classical approach

Injection 1 (IN-A). Based on the pre-injection site data, it was decided to inject mZVI between 4 and 7 m bgs, with 50 cm intervals. At each depth, 50 to 75 L of mZVI was injected, except at 5,5 and 6 m bgs. At the latter depths, a higher injection volume (175 L) was implemented because of (1) the high concentration of PCE around 5 m bgs (Table 1), and (2) the expected upwards migration of the injection fluid. During the IN-A injection, the simultaneously recorded MIP-logs were not used to adjust the injections. When comparing the injected volumes with the XsD-profiles (Figure 3), It seems that the peak concentration expected at 5 m bgs, is present at the IN-A location at 4 mbgs. As such the highest quantities may have had a higher impact on the pollution when injected 1 m less deep.

Injection 2 (IN-B): The second injection was performed at about 1 m distance from the IN-A spot. It was decided to inject the reagents between 4,25 and 7,25 m bgs, again with 50 cm intervals. The injection depths were shifted 25 cm as compared to IN-A, to realize a more homogeneous mZVI distribution. The injection volumes were adapted prior to the injection based on the MIP-logs of location IN-A, explaining the higher injection volumes between 4 and 5,5 m bgs. Again, the simultaneously recorded MIP-logs at IN-B were not used to adjust the injections. Data summarized in Figure 3 confirm the heterogeneous distribution of PCE. MIP-profiles at IN-A and IN-B appeared to differ significantly, despite the only 1 m distance. PCE concentration at the IN-B spot peaked rather between 6-7 m bgs. These observations illustrate the challenges associated with injecting reagents at depths where the pollutants are present, even when more detailed site information is available.

Injection of mZVI following the MIP-IN approach

Injection 3 (MIP-IN-C): At about 4,5 m distance of the IN-B location, a third injection was performed (Figure 2). For this injection the MIP-IN approach was followed: injection depths and injection volumes were determined based on the nearly simultaneously recorded MIP-data. The MIP-logs and injection data are summarized in Figure 4 and show that the guar gum stabilized mZVI was effectively injected at depths where CAHs were found present.

Fate of the injected mZVI: After the MIP-IN-C injection, the location of the implemented mZVI was checked via 1 set of core sampling taken at 30 cm distance from the injection spot. The ZVI-concentration profile based on indirect iron measurements is given in Figure 4. Whereas mZVI was injected between 5,5 and 8 m bgs, ZVI was detected between 5 and 7,5m bgs. A slightly upwards migration was observed. The lower volumes of mZVI injected deeper in the subsurface (11 m bgs) were not found in the core samples. In contrast to an earlier pilot test where a large radius of influence was envisioned (Velimirovic et al., 2012b), the high pressure, high flow and low volume approach applied in the current study targeting a lower radius of influence was found to have a better control of the delivered mZVI.

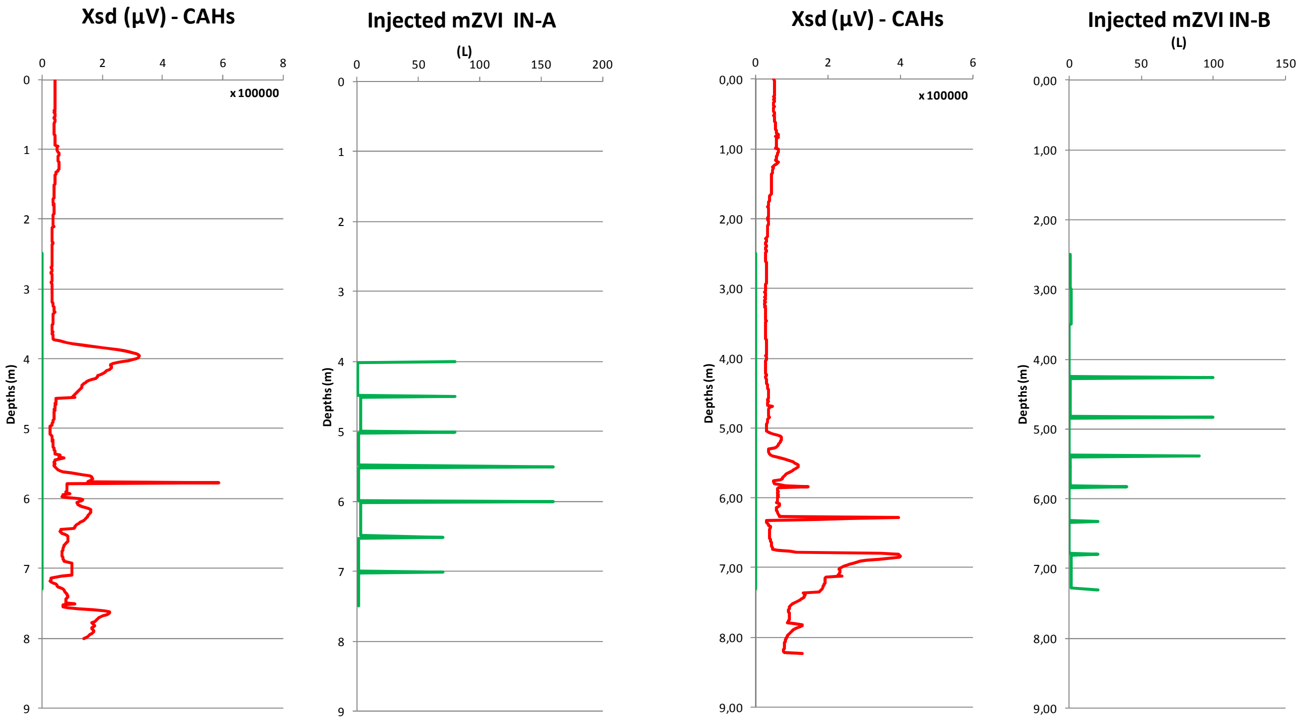

Figure 3: Summery of pollutants detected (MIP) and injected volumes when following the classical approach for IN-A (left) and IN-B (right) injection.

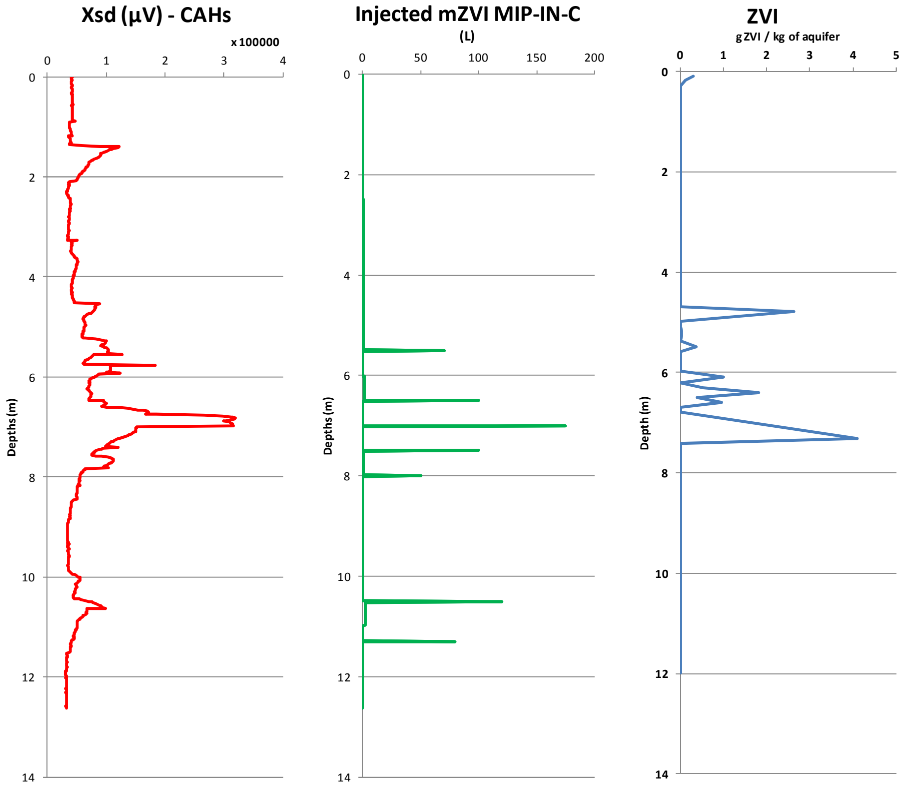

Figure 4: Results obtained following the MIP-IN approach:

(left) CAH-profile as detected via MIP-Xsd;

(middle) injected volumes based on mip-data;

(right) ZVI-concentrations measured in the aquifer after injection at a distance of 0,30 m.

CONCLUSIONS

The MIP-IN injection device combined with the MIP-IN injection approach was found to be suitable to introduce guar gum stabilized mZVI at depths where the pollutants were detected. Injection up to a depth of 12 m was demonstrated to be feasible. Automatic logging of injection parameters (volumes, times, depths, etc.), not yet available for the used prototype MIP-IN version, was identified as a crucial aspect for further improvement of the device and the injection.

To bring the reagent into contact with the pollutant, not only the injection depth, but also the fate of the injected reagent in the subsurface is important. High pressure injection does create preferential flow-paths, but the high flow rate and low volume approach was found to control the delivery of mZVI better than high volume injections. To create reactive barriers able to prevent further spreading of CAH-contamination plumes, 4 injection rows of 1 m spaced injections may be a good option.

ACKNOWLEDGEMENTS

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Poster Presentations

Passive treatment of acid drainage followed by electricity generation

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Acid drainage waters generated in a heap of low-grade copper ore were subjected to treatment by passive system consisting of an anaerobic limestone drain and a permeable reactive multibarrier (intended for microbial dissmilatory sulphate reduction, biosorption and additional chemical neutralization), connected in a series.

The multibarrier effluents were free of non-ferrous metals but still contained iron and manganese (although in lower concentrations) and were enriched in dissolved organic compounds and heterotrophic microorganisms from the multibarrier. Most of these effluents were efficiently treated by an aerobic wetland. However, a small portion of them were directed to a microbial fuel cell located near to the multibarrier.The flow rate of this small portion varied within the range of 20-80 ml/h and the organic content (expressed as the relevant COD – Chemical Oxygen Demand) varied within the range of 0.5-3.0 g COD/L. The continuous operation of the microbial fuel cell was connected with continuous generation of current values within the range of 0.02-0.2 mA depending mainly on the composition of the waters being treated, the temperature and the flow-rate. The maximum power density achieved by this system was 268 mW/L.

Assessment of the distribution of micro-scale iron in Field Studies via an in-situ susceptibility sensor

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ABSTRACT: Within the AQUAREHAB project WP5 focused on the development of groundwater rehabilitation technologies with injectable Fe-based particles. The assessment of the distribution of the particles during and the fate of the particles after the injection posed new challenges which were tried to meet with two strategies: (a) innovative sensor systems which are based on the measurement of the magnetic susceptibility were installed directly in the vicinity of the injection points; (b) classical liner samples were taken after the injection in order to proof the presence of the particles. In this paper the strategy, problems, solutions and the results of the sensor systems will be presented.

STRATEGY TO MEASURE THE DISTRIBUTION AND THE FATE OF IRON PARTICLES IN THE SUBSURFACE

Design of Sensors

There are several commercial measurement systems available which are based upon susceptibility measurements and are able to quantify zero valent iron. However, no such system could be used directly in the subsurface as an in-situ device. Thus, in cooperation with the Institute of Theory of Electrical Engineering (ITE) VEGAS developed in-situ sensors which can be installed in the subsurface by direct push techniques. In contrast to the available systems which are based on the measurement of susceptibility changes inside a coil, the in-situ sensors have to be able to measure changes outside the coils. In addition the size of the sensors was restricted such that its diameter had to fit into a direct push driving rod (i.d. 65 mm). Therefore, a great number of numerical simulations had to be made (see Figure 2) and prototypes were produced to verify the simulation results (see Figure 2).

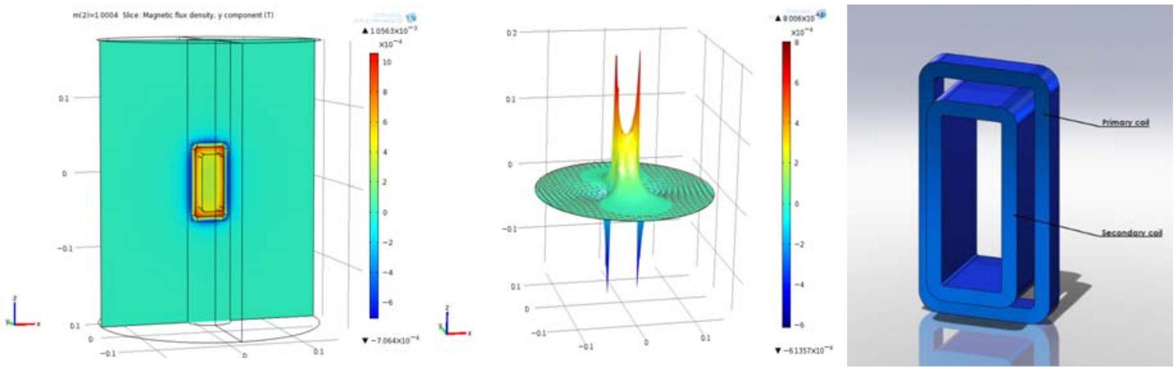


Figure 1: Simulation and final sensor geometry

From Sensors to Field Arrays

In order to measure in a field situation, a couple of additional possibilities have to be considered:

- To increase the sensitivity of the coils a reference measurement was foreseen such that the difference between two coils was measured, one of which was located in the area of injection, the second one near the surface, where no suspension was expected.
- To distinguish between the carrier fluid and the suspension including the particles a temperature measurement was added to each sensor.

- To include the possibility of taking samples special sampling ports were added to the measurement systems.
- A specific electronic had to be developed where several measurement systems could be controlled with and the data could be stored. The electronics was designed to work without additional infrastructure (electrical energy).
- The electronic was designed to measure the susceptibility for an extended period of time. With this it was hoped to be able to detect the decline of the particle concentration caused by the reaction with the contaminants or corrosion processes.

The final layout of the monitoring arrays consisting of 4 iron sensors, 5 temperature sensors and 3 sampling ports is shown in Figure 3. Several of these arrays can be installed in certain distances to cover the area of injection.

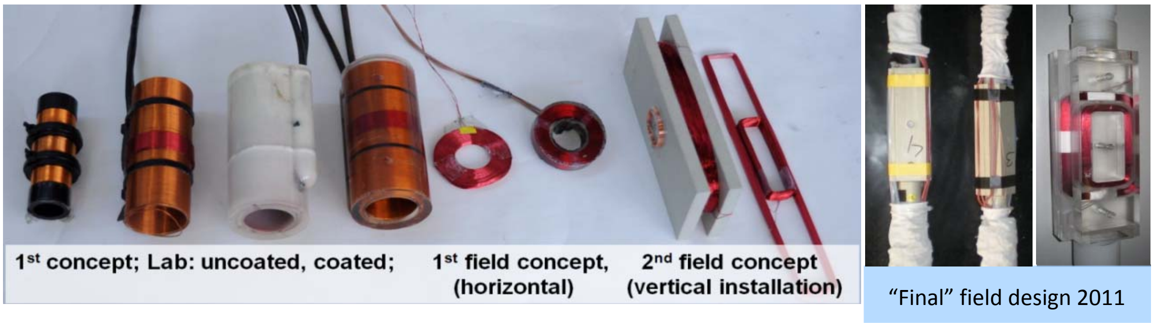


Figure 2: Prototypes of different sensor shapes

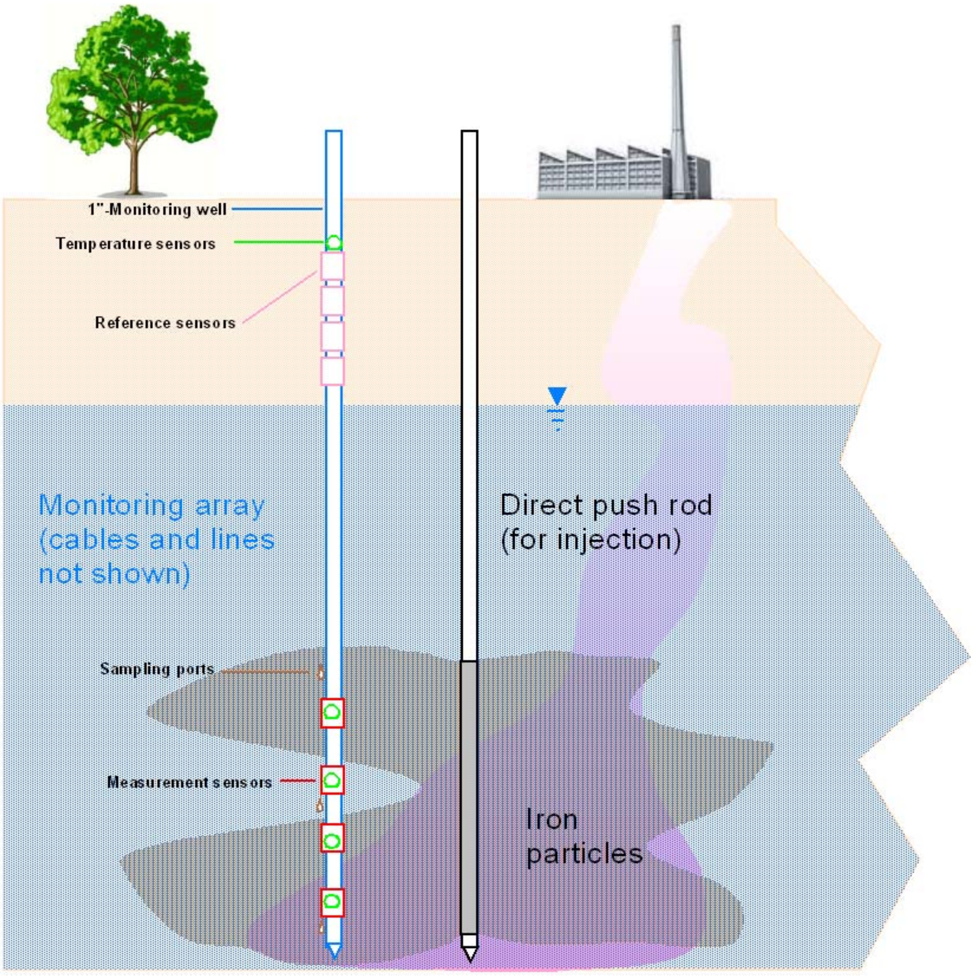


Figure 3: Layout of monitoring arrays and intended use

The electronics is based on a bus system which allows for the integration of numerous slave systems that are connected to a master system and each of which controls one array with up to 8 iron sensors and 16 temperature sensors. The master system switches the slaves on and off to save energy and records and stores the data. The principle composition is shown in Figure 4.

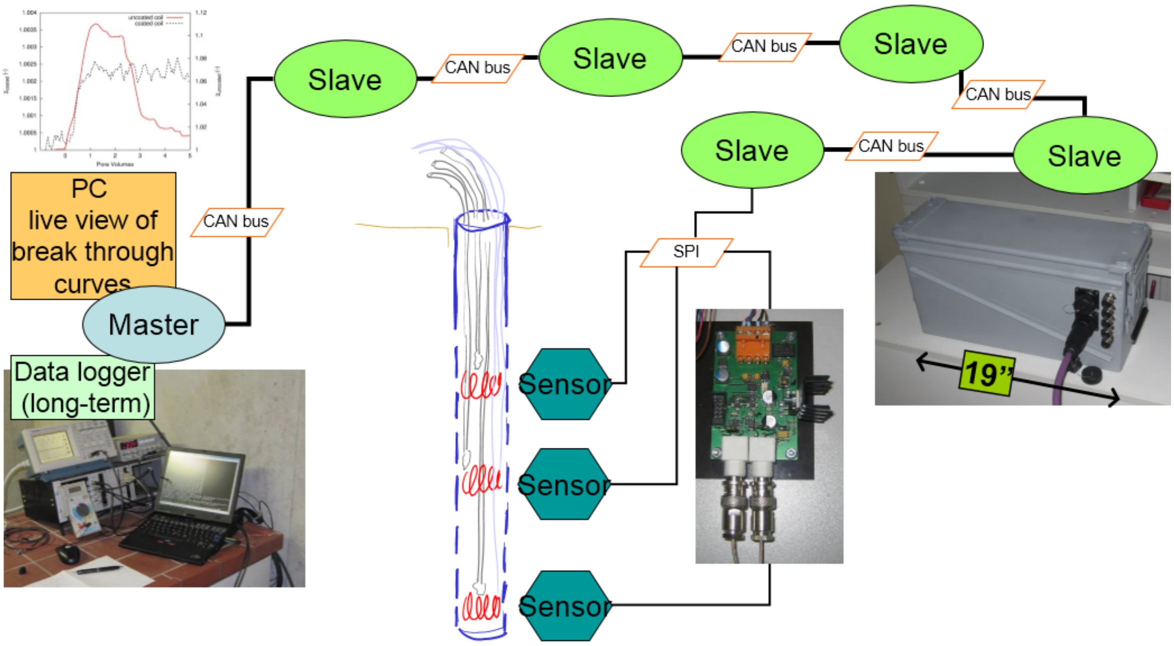


Figure 4: Composition of the electronics

FIELD WORK

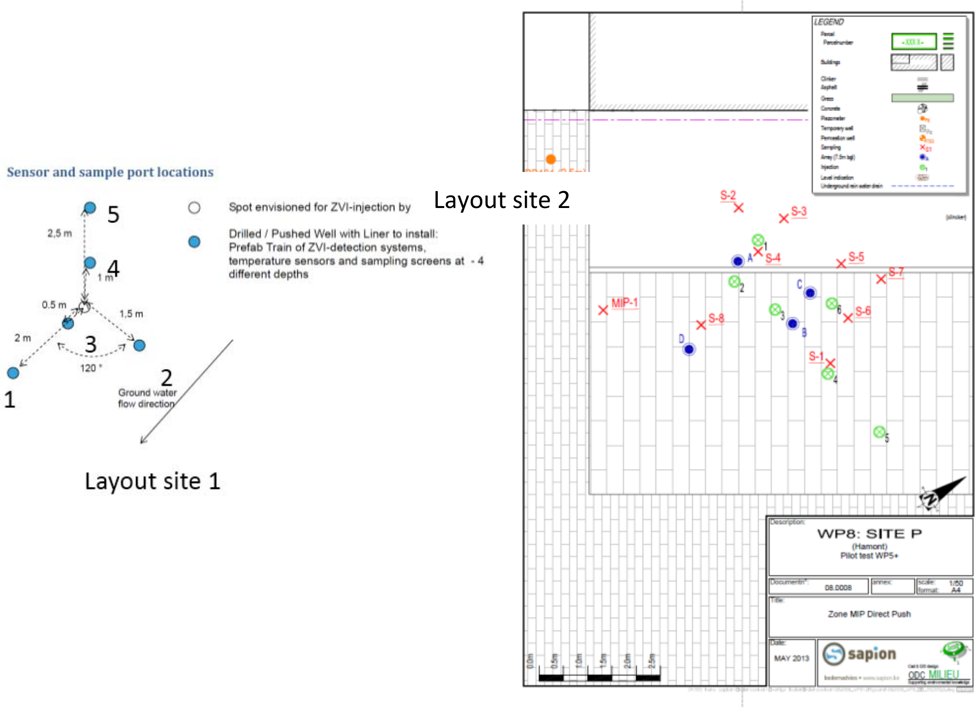


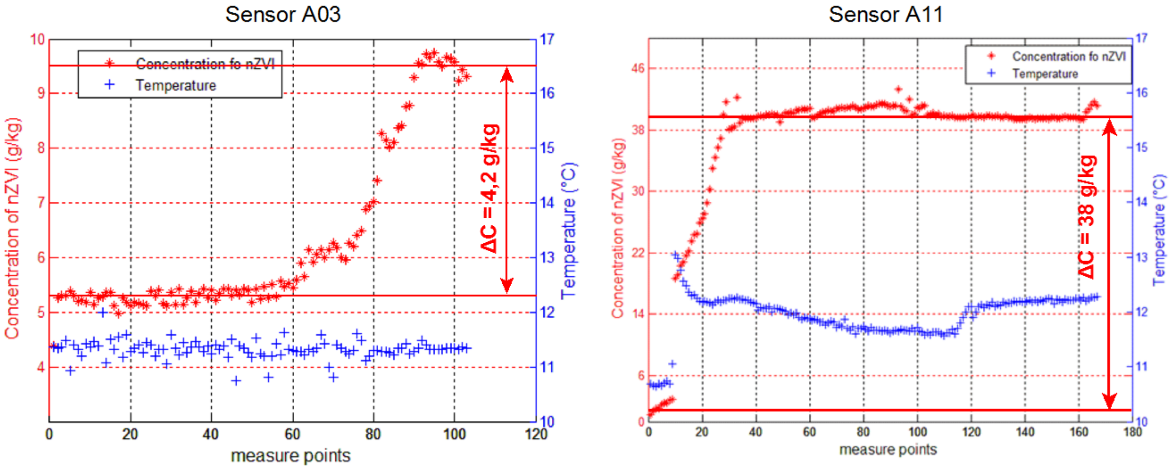
Figure 5: Layout of pilot sites

Within the scope of the AQUAREHAB project two pilot sites have been equipped with the sensor arrays. At the first site one injection location was planned and 5 sensor arrays were installed around it (see Figure 5, left). The sensors were located at a depth between 12 and 14 m bgs (Velimirovic et al. 2012).

At the second site three sensor arrays were installed in a test area where 6 injections were done (Figure 5, right). A fourth array was installed upstream as reference and consisted of temperature sensors and sampling ports only. The depth of the sensors at this site was between 5 and 7 m bgs (Velimirovic et al. 2013).

RESULTS

Unfortunately severe electronic problems were encountered and no reasonable data could be obtained at the first pilot site. Before the measurement systems were installed at the second site, the electronics was completely redesigned. Even with this redesigned electronics some stability issues occurred at the second site. Some of the sensors ran into saturation within the background measurement period before the injection. But at two locations clear and unambiguous signals could be detected, which coincide with the depth, time and location of the injection. An evaluation of the sensor signal yielded iron concentrations in the vicinity of the sensors.


Sensor A03

Sensor A11

Figure 6: Sensor signals and corresponding iron concentrations

SUMMARY AND OUTLOOK

Despite the electronic problems, which occurred in the field, the measurement principle could be demonstrated successfully. Currently, the circuit is optimized by intensive simulations and the arrays will be installed at further sites. There they will be used to follow the injection of iron particles and the consumption of the particles by the reaction with the contaminants in the course of time.

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Is it possible to distinguish abiotic and biotic degradation of cDCE via chlorine and carbon isotopes?

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ABSTRACT: *In situ* chemical oxidation (ISCO) followed by bioremediation might be a cost-effective option to remove chlorinated aliphatic hydrocarbons (CAHs) and to achieve contaminant concentrations below regulatory limits in the subsurface. This study is related to an injection of sodium permanganate (PM) at a field site with a very heterogeneous distribution of contaminants in the subsurface. This study is related to injection of sodium permanganate (PM) at a field site with a very heterogeneous distribution of the contaminants in the subsurface, with cDCE the main pollutant. To distinguish between dilution, chemical oxidation and biological degradation, compound specific stable isotope analyses (CSIA) were performed. The specific aims were to (i) identify the mechanisms involved in the changes in cDCE concentrations and (ii) to examine the possibility of biodegradation of leftover pollutants after PM oxidation. Firstly, based on lab scale batch experiments, carbon and chlorine isotope enrichment factors for cDCE oxidation by PM were determined as ε_C = -26.2‰ ± 0.9‰ and ε_{Cl} = +0.2‰ ± 0.02‰, respectively. Similarly, lab scale anaerobic biodegradation tests performed with aquifer and groundwater from the site revealed isotope enrichment factors for cDCE of ε_C = -17.9‰ ± 0.6‰ and ε_{Cl} = -3.3‰ ± 0.1‰. The observed inverse chlorine isotope effect of the oxidation by PM was an important tool to distinguish biodegradation and chemical oxidation of cDCE. The field data, collected before and after a pilot PM injection, showed that chemical oxidation and anaerobic biodegradation of cDCE could be distinguished via carbon and chlorine isotope measurements.

INTRODUCTION

Contamination of groundwater caused by chlorinated aliphatic hydrocarbons (CAHs), like trichloroethene (TCE) and *cis*-1,2-dichloroethene (cDCE), is a common environmental problem as these compounds pose a serious health threat due to their toxicity and potential carcinogenicity. Although *in situ* bioremediation has recently become a promising technique to remediate these compounds at contaminated sites, the success of this technology in heterogeneous field environments remains challenging (Lee at al., 2007). A combination of *in situ* chemical oxidation (ISCO) followed by bioremediation might be a cost-effective approach to remove CAH contamination in the subsurface and reduce their concentrations below regulatory limits (Richardson et al., 2011; Doğan et al., 2013). Sodium permanganate (PM) has been shown to be an effective oxidant for treating CAHs in contaminated soil and groundwater systems (Schnarr et al., 1998).

When applying ISCO in the field, decreases in the concentrations of CAHs could either be due to degradation or transformation processes, but also to for instance dilution by displacement of contaminated ground water by the injected permanganate solution (Hunkeler et al., 2003). Compound specific stable isotope analysis (CSIA) has been shown to be a promising tool to distinguish between these processes (Ewald et al., 2007) since dispersion, sorption, or volatilization of CAHs are not influenced by the isotope content of the pollutants (Schmidt et al., 2004). On the other hand, transformations like biodegradation (Hunkeler et al.,1999; Abe et al., 2009; Fletcher et al.,2011) and chemical oxidation (Hunkeler et al., 2003) do lead to enrichment of heavy carbon isotopes in the original, not yet reacted substrate because of the stronger and less reactive molecular bonds formed by heavier isotopes in comparison to lighter isotopes (Lee et al., 2007; Elsner, 2010). This enrichment can be used as evidence for the occurrence of degradation process and can be quantitatively expressed by the isotope enrichment factor (ε), that can be determined for a specific compound and a specific degradation process in laboratory experiments based on the Rayleigh equation (Milosevic et al., 2013). A next step is to distinguish between different transformation mechanisms that may occur in remediation processes, which is of paramount importance for field data interpretation (Hunkeler et al., 1999).

In this study, we evaluated the possibility to use multiple stable isotope analyses ($^{13}C/^{12}C$, $^{37}Cl/^{35}Cl$) to distinguish between (1) dilution and (2) degradation by chemical oxidation using PM and (3) biodegradation of cDCE. The research was linked to an industrial area near Antwerp, Belgium that underwent *in situ* PM injection.

MATERIALS AND METHODS

Laboratory Experiments

To determine the carbon and chlorine isotope enrichment factor for cDCE during oxidation by permanganate, batch experiments were set up in duplicate in closed 250 mL bottles equipped with Mininert valves (Supelco, Bellefonte, Pennsylvania, USA). Each bottle contained 150 mL distilled water with a final cDCE concentration of 60 mg/L (99%, Acros Organics). Forty percent(w/v) of sodium permanganate solution (same solution as used for *in situ* injection) was added to each bottle with a final concentration of 240 mg/L. Control bottles were filled with 150 mL of aqueous cDCE solutions (240 mg/L) without PM addition. Ten mL subsamples were taken every two minutes for 20 minutes and subdivided in 2 mL samples into 2 mL GC vials containing 0.1 mL of a quenching solution (0.5 M sodium thiosulfate and 0.06 M calcium nitrate, used to stop the reactivity of the PM) for the analyses of CAHs and carbon and chlorine isotope.

Microcosms were prepared in 160-mL glass serum bottles containing homogenized 40 g (wet) aquifer material and 70 mL anaerobic groundwater from the field and sealed with Teflon-lined butyl rubber stoppers. All the preparations were performed in a glove box and under anoxic conditions. All the bottles were purged with a N_2/CO_2(80/20%) mixture to remove all other contaminants and then 15 mg/L cDCE was injected into each bottle. cDCE concentration in microcosms was monitored over time by a GC equipped with a flame ionization detector as described in Doğan-Subaşı et al. (2013) and sub-samples were taken for carbon and chlorine isotope measurements when the concentration of cDCE was dropped to 10, 7, 5, 2 and 1 mg/L.

Field Test

The site is located in an industrial area near Antwerp, Belgium. At this site, a heterogeneous geology has been documented with dredged sand from 0 to 3 m below ground level (bgl), alluvial deposits of loamy sand and sandy loam with shells from 3 to 8 m bgl, sand with glauconite from 8 to 25 m bgl and a non-permeable clay layer at 25 m bgl (Uyttebroek et al., 2012). The groundwater flow direction is irregular but it flows mainly southwards and a mixture of pollutants was detected in the groundwater. The cDCE concentrations detected in the groundwater ranged from 41 to 18,000 µg/L in all the wells. Via direct push technology, 1896 L and 900 L of a 83 kg PM/m^3 solution were injected at two locations (IN1 and IN2, 2 m apart), between 2.1-5.1 m bgs and 5.1-6.0 m bgs, respectively. As high injection pressures were used, preferential flow paths were created (Uyttebroek et al., 2013). The injection spots were surrounded by monitoring wells as summarized in Table 1. Some of them were directly impacted by PM based on visual observations of the groundwater which turned purple due to PM injection (Table 1).

Table 1: Monitoring wells the depth of the filters and distance from the two injection points

Well	Filter depth	Distance from inj. point-1(m)	Distance from inj. point-2(m)	Degree of impact by PM
MW5a	2-3 m bgs	1.0	3.0	+++
MW5b	5-6 m bgs	1.0	3.0	-
MW6b	5-6 m bgs	1.5	0.5	+++
MW7b	5-6 m bgs	2.0	3.5	-
MW8b	5-6 m bgs	3.0	2.0	++

RESULTS

Carbon and chlorine isotope enrichment during oxidation by permanganate and in anaerobic biodegradation

Batch experiments were performed to determine the carbon and chlorine isotope enrichment factor of cDCE during oxidation by permanganate and during anaerobic biodegradation. The obtained carbon and chlorine isotope values of cDCE were plotted according to the Rayleigh equation and the calculated isotope enrichment factors are presented in Figure 1. Negative controls (without permanganate) did not show any cDCE concentration decreases nor change in their carbon and chlorine isotope signatures (data not shown).

The carbon isotope enrichment factor of cDCE during anaerobic biodegradation was estimated as ε_c= -17.9 ‰ ± 0.6‰ (Figure 1A) which was in agreement with previous studies where ε_c ranged from -16.9‰ to -31.9‰ (Lee et al., 2007; Carreon-Diazconti et al., 2009; Abe et al., 2009; Fletcher et al., 2011). On the other hand, during PM oxidation of cDCE values of ε_c = -26.2± 0.9 ‰ were calculated in our test (Figure 1A), which is in line with the average values range (ε_c = -17 to -31.9‰) reported before for the oxidation of different chlorinated ethenes by PM (Poulson and Naraoka, 2002; Hunkeler et al., 2003). When looking at chlorine enrichment factors, the shift observed during anaerobic biodegradation (ε_{cl} = -3.27 ‰ ± 0.1‰, Figure 1B) was significantly larger than reported by Abe et al. (2009) (ε_{cl} = -1.6 to -1.4‰), indicating the underlying differences in cDCE reductive dechlorination between organisms. On the other hand, our study provides the first data on chlorine isotope enrichment of cDCE during oxidation by PM. Here the observed enrichment ε_{Cl}= 0.2 ± 0.02 ‰ was insignificant (Figure 1B).

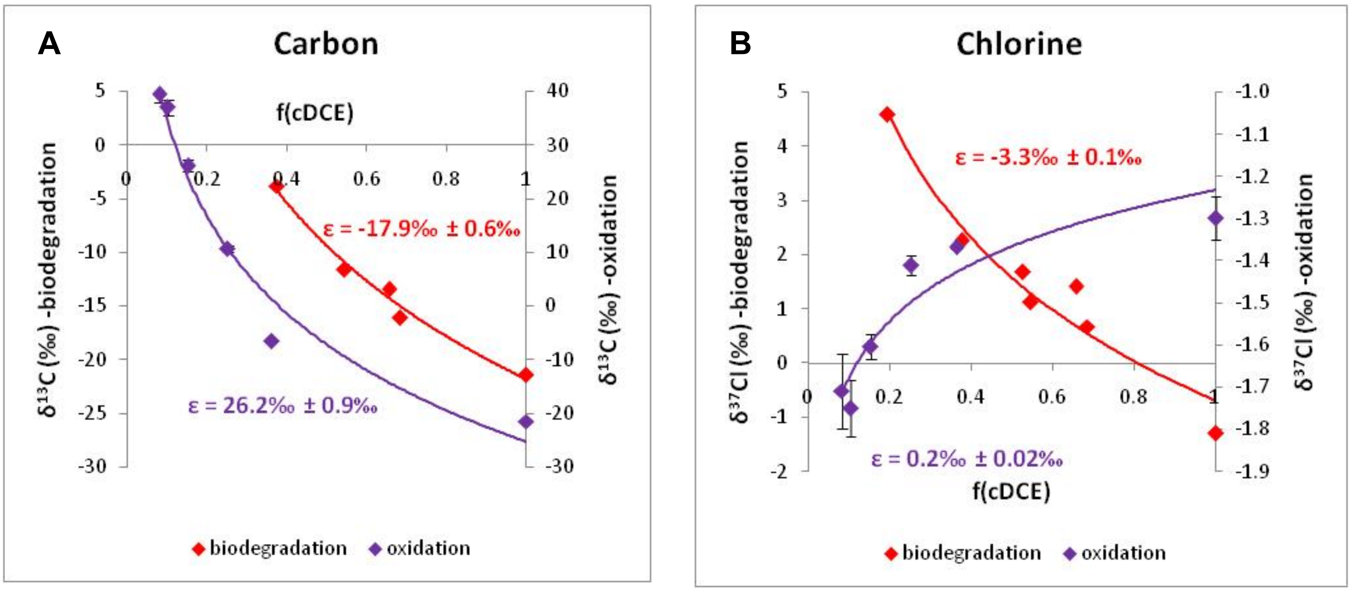

Figure 1: Isotope fractionation patterns in cDCE of δ^{13}C (A) and δ^{37}Cl (B) measured during degradation by biodegradation and chemical oxidation. Data points are from duplicate batches per experiment.

In situ carbon and chlorine isotopic shift

The average of the stable isotope values of cDCE obtained during the first 82 days for not directly impacted monitoring well MW5b (δ^{13}C = -29.6‰ ± 0.2 and δ^{13}Cl = 5‰ ± 0.1) were considered the reference isotopic signature of the field throughout the test (data not shown).

After PM injection, isotopic shifts in the groundwater collected from the directly PM impacted wells MW5a, MW6b and MW8b were studied (Figure 2). In MW5a, there was a significant decrease in cDCE concentration from 30 µM to 6 µM after 15 days of PM injection with relatively constant values of δ^{37}Cl (from 5.0 ± 0.1 to 4.8 ± 0.2‰) and δ^{13}C (from -29.9 ± 0.2 to -28.3 ± 0.2‰), however, pointing rather in the direction of dilution by the injected permanganate solution than degradation of cDCE. On the other hand, the carbon and chlorine isotope ratios changed from -26.7‰ to -24.1‰ and from 4.1‰ to 6.1‰, respectively in MW5a between day 33 and 55 suggesting that the degree of anaerobic biodegradation increased. These δ^{37}Cl and δ^{13}C values were in agreement with the field study of Hunkeler et al. (2011) in which anaerobic reductive dechlorination was recorded as the removal mechanism.

Different from well MW5a, a 0.6 ‰ decrease in δ^{37}Cl and 3.1‰ increase in δ^{13}C ratios for well MW6b on day 15 indicates that the reduction of cDCE from 186 µM to 160 µM might predominantly be attributed to the chemical oxidation near that well at that time. From day 33 onwards, when PM was no longer reactive, isotopic signatures that were closer to the pre-chemical condition were again recorded, although the slightly increased average δ^{13}C value (-28.11‰) in this well may indicate some slowly ongoing biodegradation as compared to the pre-injection values (-29.5‰) (Figure 2).

Lastly, in well MW8b, in which strong indication for cDCE biodegradation was found based on isotope ratios (-20.8‰ for δ^{13}C and 6.0‰ for δ^{37}Cl) before the injection, 1.8‰ decrease in δ^{37}Cl value 15 days after PM injection was recorded. As time proceeded, the isotopic values in MW8b bounced back to the values of -28.8‰ and 5.0‰ for δ^{13}C and δ^{37}Cl, respectively (Results not shown).

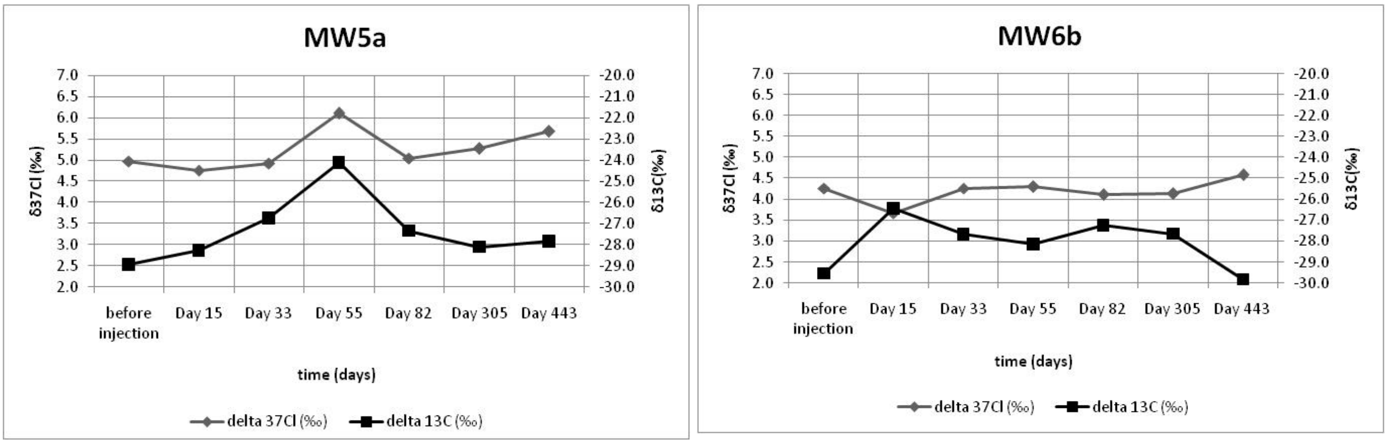

Figure 2: Carbon and chlorine isotope ratios in the monitoring wells (Note that for the Y axes, different concentration scales are used).

In well MW5b, which was not directly impacted by PM, δ^{13}C values were constant until day 82 (used as reference values), although cDCE concentration decreased from 302 to 250 µM between day 15 and day 82. Yet, significant increases in δ^{13}C (from -29.4‰ to -7.3‰) and δ^{13}Cl values (from 5.1‰ to 7.0‰) were measured at day 305, giving strong prove of the occurrence of anaerobic degradation of cDCE. Change in cDCE concentration from 250 µM to 53 µM followed by production of VC and ethene supported this fact (results not shown).

CONCLUSIONS

The ratio between carbon and chlorine isotope enrichment is significantly different for anaerobic reductive dechlorination and permanganate oxidation of cDCE which enables us to distinguish these two mechanisms using a dual isotope approach. Evidence was found for chemical oxidation of cDCE in 2 out of 3 directly impacted wells 15 days after the injection. Pre- and post- biodegradation of cDCE was also proved, but not at all time points. Decreases in cDCE concentrations did not always end up with significant isotopic shifts, pointing towards dilution.

ACKNOWLEDGEMENTS

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Assessing Secondary Environmental Impacts and Sustainability of In situ Thermal Remediation Technologies

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INTRODUCTION

SRI Biochim is a 2 ha site located in the 250 ha industrial zone of Vilvoorde-Machelen just north east of Brussels. The SRI Biochim site was used as a solvent recycling facility until it burned down in 1993. The storage tanks that were destroyed by the fire in 1993 leaked a toxic mix of chlorinated volatile organic compounds, benzene, toluene, ethylbenzene, xylene (BTEX) compounds, mineral oil, polychlorinated biphenyls (PCB's), chlorophenols, phenols and cresol into the subsurface which have formed a large light non-aqueous phase liquid (LNAPL) smear zone. The estimated contaminant load is 520 tons of insoluble contaminants.

Figure 1: SRI Biochim site, north of Brussels. 1 hectare smear zone that will be remediated on SRI site outlined in red.

Four feasible remediation technologies have been identified for the remediation of SRI Biochim, two of which have already been piloted (*excavation under controlled atmosphere* and *in situ multiphase extraction*) and two of which are currently being piloted (*in situ thermal desorption via conduction* and *in situ radio frequency heating*). The pilot studies will determine the resource requirements of the four technologies for remediating this site and from there each technology will be evaluated in terms of its overall sustainability.

The CO_2 Calculator and the Life Cycle Assessment (LCA) method will be used to compare the alternatives. The CO_2 Calculator is a carbon footprint calculator that provides an estimation of carbon dioxide emissions emitted during the remediation process. It is an easy-to-use tool that allows for CO_2 emissions comparisons between remediation technologies and has been recently introduced as part of the Flemish MCA. The LCA method has proven to be useful in determining the extent of secondary impacts brought about by remediation technologies, on a site by site basis (Diamond et al., 1999; Lemming et al., 2010d; Morias and Delerue-Matos, 2010; Owsianiak, 2013; Suer et al, 2004) The LCA method is far more comprehensive than the standard tools used to perform sustainability appraisals since it considers the entire life-cycle of the equipment, material and resources consumed by the remediation process (Beames et al., 2014).

TECHNOLOGY PILOTS COMPLETED FOR SRI BIOCHIM

The results from the two technologies that have already been piloted at SRI Biochim will be presented here.

Excavation Under Controlled Atmosphere

SRI presents unique challenges in applying an excavation alternative. It is not possible to excavate in open air since the soil vapors are highly toxic and contain high concentration of hydrogen cyanide (HCN) amongst other hazardous volatiles. The excavation will therefore be performed under a shed with a controlled atmosphere. A blower is used to ensure that the concentrations of the volatiles inside the shed are kept below the explosion thresholds. Site workers will use compressed air breathing apparatus and the contaminated air inside the shed will be purified with granular activated carbon (GAC). The groundwater-table needs to be lowered in order to remove the NAPL and the extracted groundwater will also be treated with GAC.

Once the soil is excavated, it needs to be transported to a thermal treatment facility at Moerdijk, in the Netherlands (near Rotterdam). The soil can either be transported by truck or by ship to Moerdijk.

The excavation alternative is by far the treatment with the shortest duration (6 months), however it is relatively energy intensive.

Multiphase Extraction (MPE)

When a contaminant is released into the soil, it spreads into four phases: bulk liquid, adsorption to soil particles, vapor phase and dissolution into soil moisture. Multiphase extraction (MPE) is a soil remediation technique which can treat the different phases at the same time. MPE allows liquid flow rates to be increased around the extraction well, due to the increased pressure gradient from the groundwater being drawn downward below the groundwater table and then extracted. Lowering the atmospheric pressure around the well also allows the non-aqueous phase liquid (NAPL) to volatize more easily. The volatized contaminants are also removed from the subsurface via soil vapor extraction wells.

The extracted soil vapor and groundwater are treated on the surface of the site by being put through gas and liquid treatment trains. Clean air, carbon dioxide (CO_2) and clean water are then emitted at the end of the treatment train.

MPE is a far slower technology in terms of duration (20 years for this case) but is less energy intensive than any of the other alternatives.

RESULTS

The results for the CO_2 Calculator and Simapro for the two piloted technologies are presented below and compared.

CO_2 Calculator

According to the CO_2 Calculator, the most energy intensive process in the excavation alternative is the thermal treatment of the soil *ex situ*, accounting for 13,855.1 tons of CO_2 (76% of the total CO_2 from this alternative). The next largest contributing process is the transport of the contaminated soil and backfill to and from Moerdijk. The excavation itself and materials have a very small carbon footprint compared to the *ex situ* thermal soil treatment.

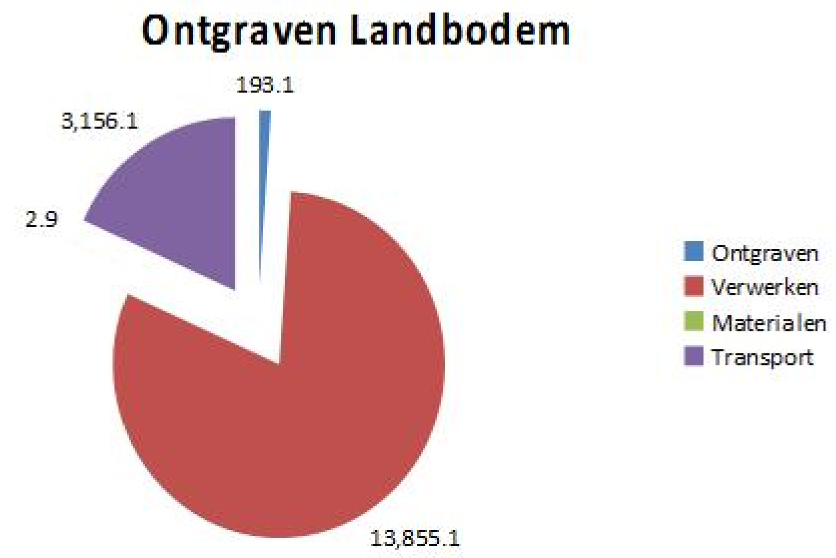

Figure 2: Contribution of CO_2 emissions for processes in excavation alternative according to the CO_2 Calculator

The *in situ* MPE alternative produces far less CO_2 emissions than the excavation alternative. The largest contributing process is the energy consumed by the extraction and treatment of soil vapor, groundwater and pure product on site (80%).

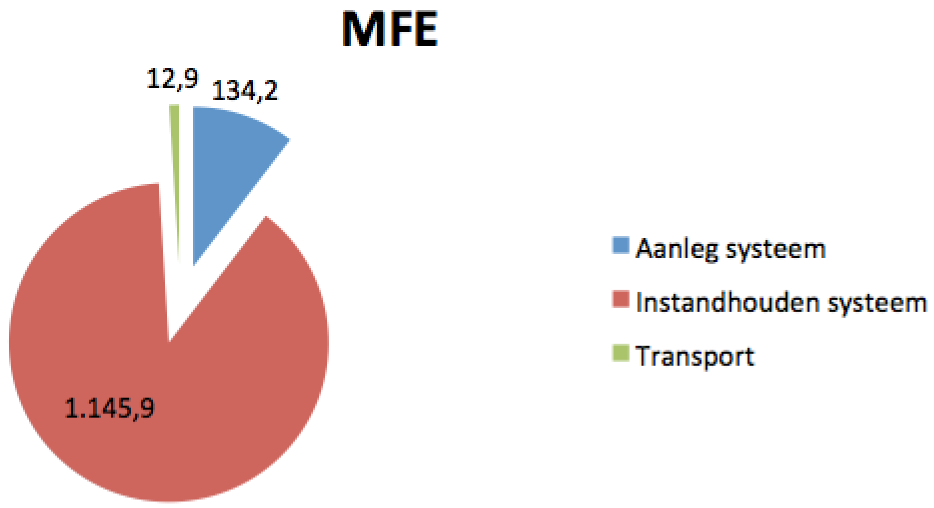

Figure 3: Contribution of CO_2 emissions for processes in multiphase extraction alternative according to the CO_2 Calculator

LCA Method

The results from Simapro (LCA software) confirm that the environmental impacts from the excavation alternative are far larger than the MPE system. LCA impacts go beyond only accounting for CO_2 production and include an extensive inventory which is translated into a broad range of impacts. The LCA method also shows that energy consumption and in particular fossil fuel consumption have the largest impact in terms of overall the normalized impacts. This is illustrated in the graph in Figure 4.

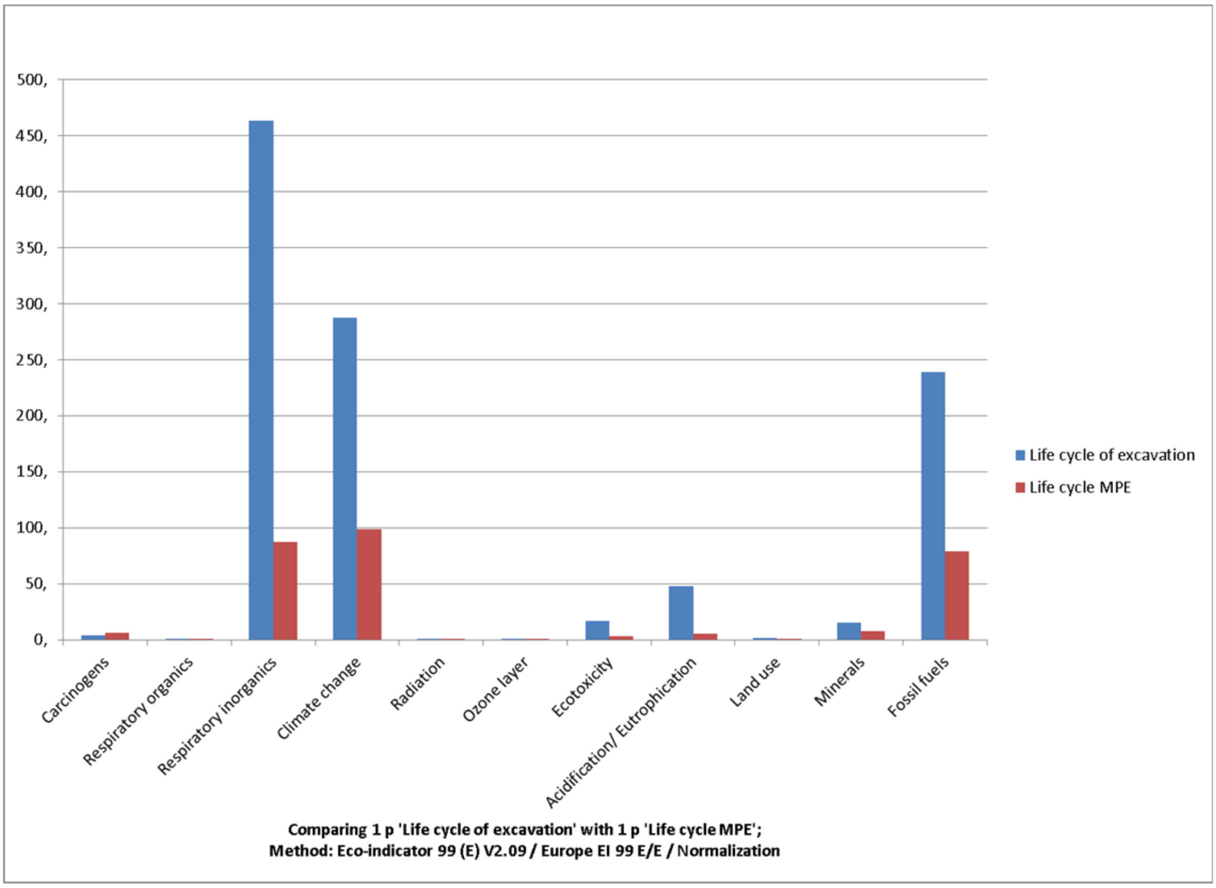

Figure 4: Normalized impacts from LCA method for both alternatives. Y-axis is equivalent impact caused by number of European citizens per year.

According to the LCA method, the process that contributes most to CO_2 emissions in the excavation alternative is the thermal treatment of the soil, reflecting the results from the CO_2 Calculator. Similarly, the largest contribution to CO_2 emissions in the MPE alternative is from the energy required by the on-site air and groundwater treatment system during treatment.

The results from the CO_2 Calculator and LCA method do however differ in terms of quantities of CO_2 emissions produced by the two alternatives. Table 1 shows the total CO_2 emissions results from both alternatives. The difference in CO_2 emissions between the alternatives is far larger in the CO_2 Calculator.

The next step in the research presented here is apply the method to the two *in situ* thermal treatments currently being piloted. The function used to measure energy and emissions will then be to carefully analyzed and compared.

Table 1: CO_2 emissions results from CO_2 calculator compared to those from the LCA method (Simapro)

Remediation Alternative	CO_2 Calculator	Simapro
Excavation	18,124.90	10,772.02
MPE	1417.93	3549.88
ISTD	?	?
RFH+MFE	?	?

Values in tons of CO_2 emitted

The functional unit used for the LCA applied here is the removal of 520 tons of contaminant mass from 42550 m3 of soil. This is a standard functional unit approach used in remediation technology evaluation with the LCA method. It is interesting to note, that the way in which the LCA method is applied allows the land-use impact to be insignificant in both alternatives even though the difference in the duration of treatment between alternatives is over 19 years. The costs and benefits brought about by the shorter duration of the excavation alternative are not accounted for in either tool, although land-use is an impact factor in the LCA method.

CONCLUSIONS

The *in situ* MPE alternative performs better than the excavation alternative in both tools. This is not however due to the transport of soil and is rather from the soil treatment facility. The results between the two assessment methods do however differ. The *in situ* thermal treatments currently being piloted on SRI Biochim will also be compared and evaluated and the functions used to calculate the carbon footprint will be reviewed. When applied to the soil remediation technologies the land-use indicator in LCA method should account for the duration of treatment and the costs and benefits of having the site made available sooner.

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MTBE/TBA-degrading bacterial M-consortium as beating heart for Inoculated bioreactor technology

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ABSTRACT: Methyl tertiary-butyl ether (MTBE) and tertiary butyl-alcohol (TBA) are synthetic car fuel additives. Removal of these compounds from contaminated groundwater is challenging because of the high water solubility and low sorption tendency. However, biodegradation by specialised bacteria was identified as a promising technology. In the framework of FP7 MINOTAURUS project (GA 265946), lab scale bioreactor tests (7L) were set-up with two different carrier materials and were operated under ideal as well as periodically non-ideal conditions (pH, changing influent concentration, oxygen limitations, ...). The bioreactor was degrading MTBE as well as TBA from the influent during more than 1 year after a single inoculation event. The extent of contaminant removal did vary over time and could be linked to stress situation that were applied to the system. The fate and behaviour of the inoculated M-consortium in the non-sterile bioreactor system was followed using specific molecular detection techniques that were designed for the M-consortium, being FISH (fluorescence in situ hybridisation) and q-PCR (Quantitative Polymerase chain reaction). The M-consortium was found present through-out the more than 1 year test period and was shown to behave dynamically.

INTRODUCTION

To be mature for the commercial market, technologies need to be reliable and robust. For bioreactor technologies aiming at remediation of groundwater, reliability refers to good performance of the technology (1) during longer time periods under targeted test conditions and (2) in different and repeated experiments. Robustness, on the other hand, can be defined as the capacity of the technology (1) to function in real conditions and (2) return to its original steady state within a reasonable time period after non-ideal experiments conditions.

At VITO an inoculated bioreactor technology has been developed for removing fuel oxygenates (MTBE, TBA) from groundwater. A bacterial consortium (M-consortium), selected for its capacity to use MTBE and TBA (and BTEX) as sole carbon source (Moreels et al., 2004; Bastiaens et al, 2005, 2008; Debor et al., 2010), is the beating heart of the technology. Numerous lab scale tests have been performed where the performance of the system was followed and results proved that the system performed well under ideal conditions.

Here we report on a lab scale long term test that was performed in a 7L bioreactor to evaluate the reliability and robustness of bioreactors. The fate of the inoculated M-consortium during the test was monitored via FISH (fluorescence in situ hybridisation) and q-PCR (Quantitative Polymerase chain reaction).

MATERIALS AND METHODS

Lab scale inoculated bioreactor

A 7L-bench scale bioreactor (Figure 1, down scale model of the pilot bioreactor) was filled with biochips as carrier material and was inoculated with the M-consortium (93,24 mg DW) .

The bioreactor was firstly operated in batch mode, implying no influent and effluent, only recirculation at 300 mL/hour. MTBE and TBA were spiked in the system and the following parameters were monitored: MTBE, TBA, pH, DO, visual appearance. MTBE and TBA were spiked again when they were completely degraded and the DO/pH was adjusted when necessary. During the experiment, the liquid phase and the carrier material was samples at several time points for characterization and quantification of the biomass.

In a next phase, the reactor was operated under in a continuous mode. An overview of the different phase of the long term bioreactor test is given in Table 1. During the continuous operational periods, influent was pumped into the lower part of the bioreactor, and effluent was discharged at the top of the bioreactor. Real groundwater was used as influent and was de-ironed before use by precipitation of the dissolved iron by aeration. In function of time, liquid samples were taken from the influent, the effluent and the bioreactor compartment for monitoring MTBE and TBA concentrations, pH, and DO. In addition, larger amounts of effluent were collected for characterization and quantification of the biomass, and to evaluate the outflow of biomass. The applied hydraulic retention times were reduced over time from 12-14 hours to 5 hours to test the performance and robustness of the system under conditions that are more closely related to the ones required in the field. During the test, temporarily stress-conditions and changes of the test conditions were applied to the bioreactor systems, which occurred as a consequence of the process itself (reduction of pH) or were applied by purpose.

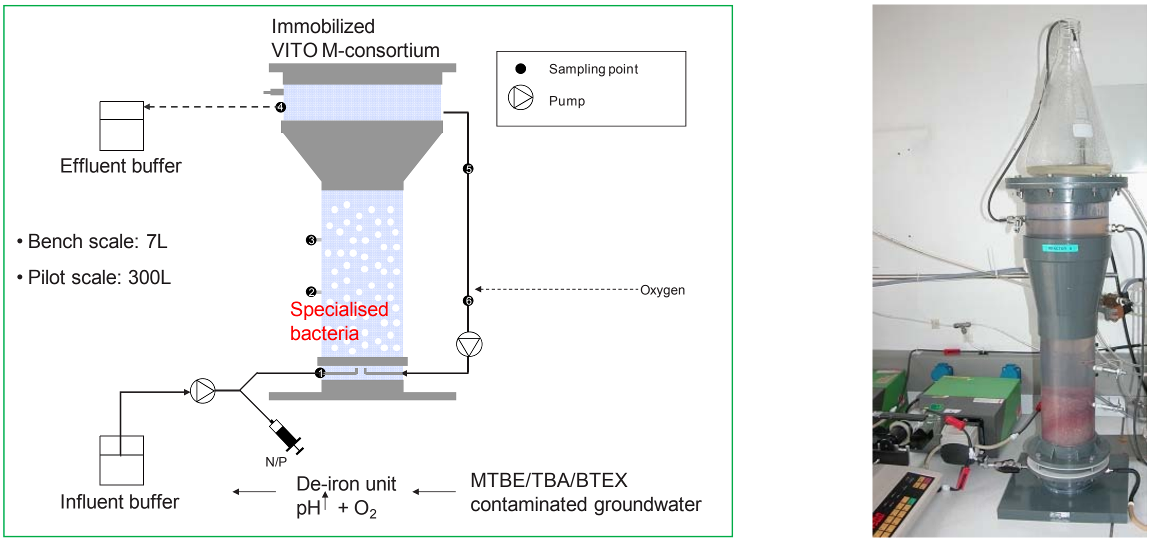

Figure 1: Schematic representation (left) and picture (right) of the 7L-lab-scale bioreactor

Table 1: Overview of operational phases of the long term 7L lab scale bioreactor experiment (BR1).

Phase	Operational mode	Influent	Duration	Tim indication
Phase 1	Recirculation mode	None (spikes of MTBE & TBA)	220 days	Day R1-R220 (R160)
Phase 2A	Continuous mode	Real groundwater from a contaminated site	128 days	Day 1-day 340
Phase 2B	Continuous mode	Artificially contaminated (MTBE & TBA) real groundwater	130 days	
Phase 3	Recirculation mode	None (spikes of MTBE only)	20 days	
Phase 4	Continuous mode	Artificially contaminated (MTBE only) real groundwater	60 days	
Total			**Total duration BR1: 560 days**	

Microbial and chemical analyses

Efforts were made to study in more detail the fate and dynamics of the inoculum. Specifically, the fate of the three key-organisms involved in the MTBE and TBA-removal in the M-consortium (*Methylibium* sp. LD3, *Hydrogenophaga* sp. LD1, and *Mycobacterium* sp. LD6) were followed using detection tools that were specifically designed for these isolates. These detection tools comprise specific FISH probes and specific q-PCR probes (unpublished results). In this paper, the fate of the M-consortium is expressed as the sum of the three key-organisms relative to all bacteria that were detected by means of unspecific probes. Analyses were performed on liquid samples as well as on carrier material retrieved from the columns.

Remaining concentrations of BTEX and MTBE/TBA were determined with an Interscience GC 800 Top gas chromatograph with headspace injection connected to a Voyager MS detection system.

RESULTS

Recirculation mode

The bioreactor was operated during 220 days. The results of the chemical analyses during the recirculation mode are summarized in Figure 2. After addition of the inoculum, which was cultivated on MTBE as carbon source, degradation of MTBE started immediately. TBA-degradation was observed after a lag-phase of about 1 week. Afterwards, each re-spike of MTBE (10-20 mg/L) and TBA (5-10 mg/L) was degraded completely, which was considered as the main criterium for a reliable biodegradation. The decline of the MTBE/TBA concentration after each re-spike (= observed degradation rate) was not always identical. Reasons for this observation are (1) sampling frequency, (2) frequency and amount of MTBE/TBA re-spikes, so the condition of the reactor before the spike, (3) biomass growth in the system during the experiment, and last but not least (4) fluctuations in test conditions. In respect to the latter, Figure 1 shows that the dissolved oxygen concentration and the pH do fluctuate somehow during the test. A pH-value below 6,5 (day R60 till day R100) clearly decreased the degradation rate of both MTBE and TBA. Adjustment of the pH returns the system back to an efficient MTBE/TBA-removal which is an indication of the robustness of the system. Generally, TBA-degradation is faster than MTBE degradation, which is in line with earlier findings based on batch degradation experiments (Debor et al., 2010).

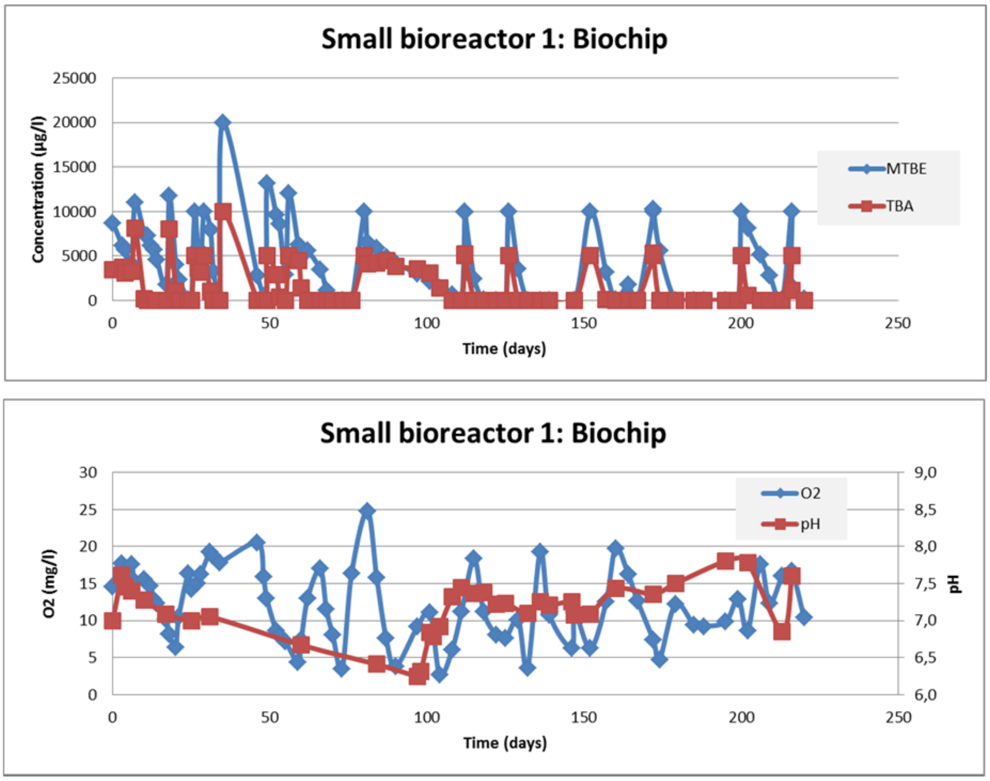

Figure 2: Performance of bioreactor 1 (Biochips) during recirculation mode

Continuous mode

During phase 2A (day 0-day 128) TBA was the main pollutant in the influent that was retrieved from a real contaminated site (Figure 3). From day 1 on, TBA-degradation was observed and the removal percentage in the bioreactor (HRT = 15,5h) increased from about 50% till 97-100 % within 12 days. Similar results were obtained for MTBE. After a 1 month non-operational phase (day 15-46), TBA was nearly immediately totally removed, while a short lag phase was observed for MTBE. A three weeks period was needed to reach the 100 µg/L MTBE discharge limit again in the effluent. A reduction of the HRT from 13,5 to 9,5 hours at day 82 did not influent the removal percentages of TBA and MTBE. After the second non-operational period (day 88-104), again a fast total removal of TBA was observed, while 10 days were needed to reach the discharge limit for MTBE. Short oxygen concentrations above 10 mg/L were not found to have a significant negative influence on the performance. Further reduction of the HRT to 4,7 hours resulted in only a small increase of the TBA and MTBE effluent concentrations. The higher MTBE and TBA-load in the reactor led to a pH-decrease below pH 6,3.

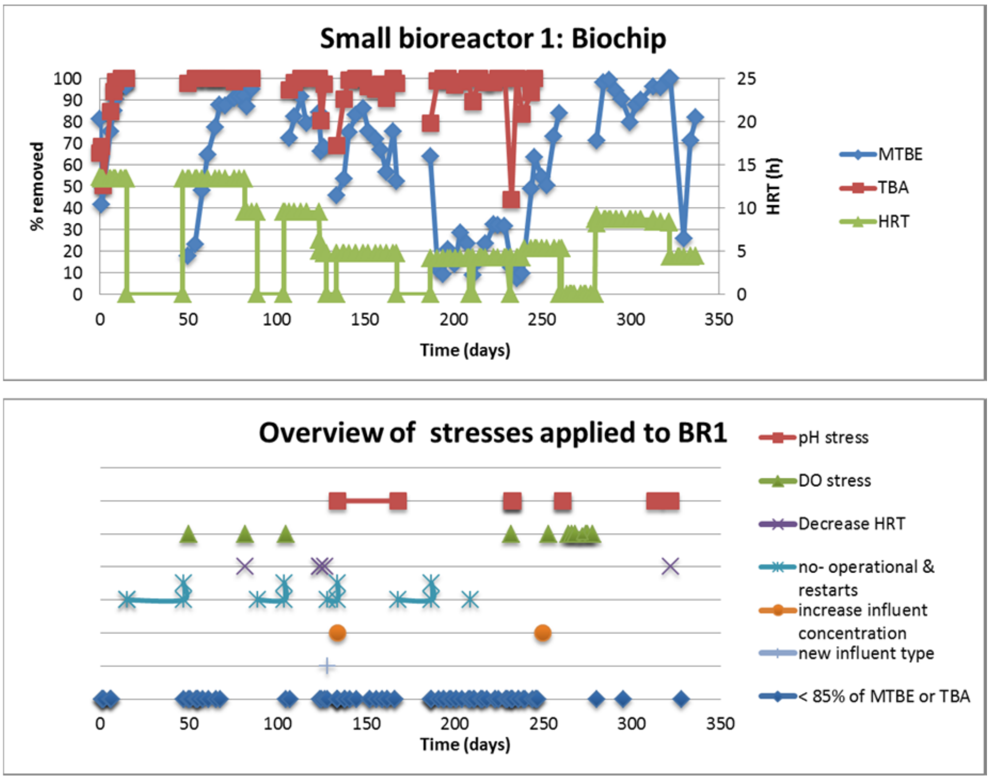

Figure 3: Performance of bioreactor 1 (Biochips) during continuous mode.

In phase 2B (day 128-day 258) groundwater from the VITO site was used and artificially polluted in cubitainers targeting 8 mg/L TBA and 1,5 mg/L MTBE. When restarting the reactor with the new influent at day 133 after a short (5 days) non-operational period, the initial removal of TBA and MTBE was reduced to 46% and 69%, respectively. Improved removal degrees were observed within 3 and 6 days, respectively. This temporarily decreased reactivity was larger than the restart at day 104, explicable by (1) the lower HRT, (2) adaptation of the M-consortium in the bioreactor to the switched influent, and (3) the decreased pH values. A lower buffer capacity of the new influent may have been responsible for the low pH-values which decreased till values as low as pH 5,9. The low pH is expected to be responsible for the partial MTBE removal from day 150 on. After the fourth non-operational period, the TBA-degradation restarted as was observed around day 133. But for MTBE, a clearly different removal percentage was obtained. Effluent concentrations were only slightly lower than the influent concentrations. Re-inoculation at day 211 did not improve the situation until day 250.

Phase 3 (day 259-day 278) starts at day 259 when the bioreactor system was switched to a recirculation mode with only MTBE-spikes. The aim was to evaluate whether an MTBE-biodegradation potential was still present due to preferential substrate use of TBA. The results clearly indicate that the MTBE-biodegradation potential was still present. The addition of new inoculum at day 268 was not strictly necessary but was performed to increase the biomass.

In phase 4 (day 279-Day 340) the system was operated again under continuous conditions but with MTBE as sole pollutant. A good removal was obtained as shown in Figure 3. Renewal of the influent vessel elevated the influent concentration back to normal values at day 328. This event together with the lowering of the HRT to 4.5 hours, resulted in a temporarily lower removal percentage.

Fate of the M-consortium inoculum

Efforts were made to quantify the biomass in the effluent of the bioreactor. For this purpose, larger volumes (0.5-2 L) of effluent were taken and subjected to dry weight analyses, protein measurements, q-PCR and FISH-analyses. Data based on q-PCR were used to calculate the results presented in Figure 4.

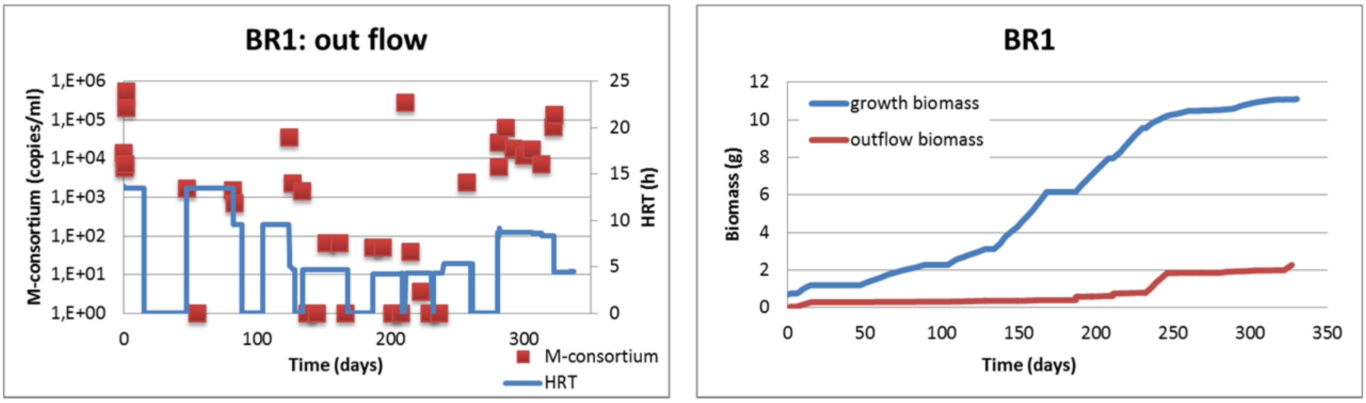

Figure 4: (Left) M-consortium (dots) in the effluent of the bioreactor 1 (BR1) in function of time and HRT(bleu curve); (Right) comparison of measured outflow and estimated growth of the M-consortium.

The amount of M-consortium in the effluent was mostly between 10^2 and 10^4 cells per ml, with a maximum below 10^6 cells per ml, just after (re-)inoculation. A lower HRT, and as such high flow rate, did not result in a higher concentration of the M-consortium in the effluent. Rather the opposite trend was observed (Figure 3, left).
The cumulative outflow of M-consortium from the bioreactors (based on measured and extrapolated q-PCR data) is given in Figure 4 (right). The q-PCR data were converted from copies/ml to g assuming that (1) one copy of the 16S RNA-gene per bacteria and (2) a weight per bacterium of 10^{-12} g. The growth of biomass in the bioreactors was calculated based on the amounts of MTBE and TBA that were removed from the passing water taking into account yield factors reported by Debor et al. (2010). Based on these calculations, the outflow of M-consortium from the bioreactor systems was significantly lower than the growth. This suggest that biomass is accumulating to a certain extend in the bioreactor, which was confirmed by visual observations. This approach can not reveal whether all biomass in the column is still alive and active.

FISH-analyses can be used to detect and quantify active microbial populations. In bioreactor BR1 the M-consortium represented 45-62% of the total bacteria present on the carrier material 56 days after inoculation (recirculation phase). By the end of the recirculation phase, this percentage dropped to about 20%. During the continuous phase, the % of M-consortium increased initially till 50%, and decreased below 5% later on. In the bottom part of the bioreactor, the % of M-consortium remained constant between day 170 and 400, and dropped later on also below 5%. Although the percentages decreased, the absolute amount of M-consortium in the reactor was still in the order of 10^7 cells per g carrier material. It is assumed that bacteria are entering the system via the groundwater that is pumped through the column also colonise the bioreactor.

CONCLUSIONS

In general it was concluded that the bioreactor system inoculated with the M-consortium is robust and can be operated with a single inoculation event for quite a long period. The extent of contaminant removal did vary over time and could be linked to stress situation that were applied to the system. Temporarily high DO concentrations were not found to influence the removal rates negatively. After non-operational periods, the system did restarted MTBE/TBA removal within reasonably time frames (mostly within 0-14 days). Reduction in HRT caused a temporarily slow reduction in the removal percentage, but a fast adaptation of the system was observed for the applied HRT (5 hours and above). A further reduction of the HRT to 1-2 hours was not possible due to practical constrains to prepare larger amount of ‘stable’ influent. The pH was identified as the most sensitive parameter for the system, but the system could mostly be regenerated. In pilot systems and full scale installation, pH is a parameter that can be regulated automatically, whereby long periods of unfavourable pH-values can be avoided. The results showed that MTBE and TBA can be removed simultaneously, where it was confirmed that (1) TBA is degraded faster than MTBE, and (2) TBA is preferred as substrate above MTBE. A decrease of the MTBE-degradation capacity when feeding a system predominantly with TBA is a point of attention, but no loss of MTBE-degradation potential in the current systems was observed. The need for a occasional re-inoculation events cannot be excluded totally, but, when necessary, it can be made in a relatively easy way.

ACKNOWLEDGEMENTS

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Session 3
Nano & Micro-technology for Water treatment

Oral presentations

The Nano4water cluster: boosting European research on nanotechnology for water treatment

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Worldwide problems associated with the lack of clean, fresh water are well-known: 1.2 billion people lack access to safe drinking water, and 2.6 billion have little or no sanitation. In addition, water is a scarce resource, and for many countries supplies already fall short of demand. As consequences, water treatment is undoubtedly amongst one of the most important topics in the environmental technologies. Conventional methods of water treatment can address many of these problems, but these treatment methods are often chemically, energetically and operationally intensive. Intensive chemical treatments and co-products or waste resulting from treatment (e.g. sludge, toxic waste) can add to the problems of contamination.

In this context, nanotechnologies may offer significant opportunities for water treatment. Looking at the nanoscale has stimulated the development and use of novel and cost-effective technologies for remediation, pollution detection, catalysis and others.

At the European level, a number of relevant research activities has been funded by the EC in the scope of FP7 concerning the application of nanotechnology for water treatment. To facilitate dissemination and information exchange, the Nano4water cluster (http://nano4water.eu/) was initiated. The Nano4water cluster started with six collaborative projects following a Joint Call on nanotechnologies for water treatment (FP7-ENV-NMP-2008-2). In 2013, the cluster has expanded to 17 finishing, ongoing and starting FP7 projects dealing with nano approaches to water treatment. The aim of this action is to support research and technological development in the field of water treatment by applying developed or adapted engineered nanomaterials to promising separation, purification and detoxification technologies.

Projects of the nano4water cluster focus on (i) nanostructured membranes and nanocatalysts, (ii) bioinspired membranes and processes, (iii) nanotechnology, materials and process innovations.

Low pressure injection of guar gum stabilized microscale zerovalent iron particles: a pilot study

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ABSTRACT: In the framework of the research project AQUAREHAB (FP7 - G. A. Nr. 226565), a pilot injection test of guar gum stabilized microsized zerovalent iron (mZVI) was designed and performed under low pressure in a CAHs contaminated site in Belgium.

Since the injection regime of iron slurries depends on subsurface geotechnical parameters, aquifer hydraulic conductivity, and fluid properties, a specifically designed injection well was installed and a monitoring set-up developed in order to achieve high discharge rates and radii of influence, and a likely homogeneous distribution of the iron particles through low pressure injection.

The injection well was designed and sealed in order to sustain average to high discharge rates, preventing the daylighting of the product. Moreover it was hydraulically tested by means of innovative water and guar gum step rate injection tests in order to determine the most suitable injection rate for the iron slurry.

A subsequent injection of 50 kg of microsized iron particles (BASF, Germany), dispersed in 5 m^3 of a 2 g/l guar gum suspension, was performed at a discharge rate of 1.5 m^3/h. The monitoring of the process was conducted measuring injection rate and pressure as well as iron concentration by means of a magnetic susceptometer. After the injection, the iron distribution in the subsurface was determined through liners extraction and the iron concentration measured both via non-invasive magnetic susceptibility measurements and chemical analysis.

The field test was specifically designed to inject in a permeation regime, or on the threshold between permeation and fracturing. A radius of influence in the order of 1 m was obtained. The presence of mZVI particles was detected up to 1.7 m from the injection point.

INTRODUCTION

The ability of zerovalent iron to degrade a wide range of groundwater contaminants has been largely studied and results obtained make the technology one of the most promising in the context of groundwater remediation. In particular permeable reactive barriers filled with granular zerovalent iron is a consolidated technology for the reclamation of CAHs polluted groundwater (Di Molfetta and Sethi 2006, Orth and Gillham 1996). Nevertheless, high excavation costs and technical difficulties (Di Molfetta and Sethi 2006) often hinder its application. Moreover the technology allows only the treatment of the contaminated plume without remove the contamination source.

In order to overcome these technical issues, smaller iron particles, suitable for being transported through porous media, have been studied. .Both microscale and nanoscale zerovalent iron particles (mZVI and nZVI) can be injected as aqueous slurries in the subsurface directly in the contaminated area, hereby avoiding excavation operation, reducing costs (Elliott and Zhang 2003, Zhang 2003). Further, mZVI and nZVI are more reactive due to the high specific surface area, allowing to degrade a wider range of contaminants (He and Zhao 2005, Lien and Zhang 2001, Liu et al. 2005, Zhang 2003). However, despite these advantages, the realization of full scale applications is hindered by mZVI-based slurries instability, which due to strong interparticles forces lead to aggregation and sedimentation, significantly reducing reactivity and affecting mobility in the porous media.

An effective strategy to stabilize particles and enhance their mobility without irreversibly affecting reactivity (Velimirovic 2012) consists in the use of a green biopolymer as dispersing fluid, such as guar gum, which is characterized by a shear-thinning behavior and can be easily degraded by enzymes to restore ZVI reactivity. Both laboratory scale experiments (A.Tiraferri and Sethi 2008, Cantrell et al. 1997, Dalla Vecchia et al. 2009, Hydutsky et al. 2007) and field scale applications (Elliott and Zhang 2003, He et al. 2010, Johnson et al. 2013, O'Carroll et al. 2013, Quinn et al. 2005, Su et al. 2012) proved that the use of green-biopolymers is able to stabilize and sensibly improve particles mobility.

The main issue concerning full scale application depends on the selection of the injection technology. From a theoretical point of view permeation injection, characterized by low discharge rate and low pressure and therefore able to assure an homogenous reactive zone, is preferable. However, due to limiting factors (such as low aquifer hydraulic conductivity, particles size distribution compared with aquifer grain size distribution, and the necessity to inject in a time shorter than the slurry sedimentation time), is often necessary to increase the injection pressure, thus exceeding the porous medium critical value and giving rise to the generation of preferential flow paths. Field scale injection reported in literature usually adopt high injection pressure (Chang 2010, Sprinkle 2004).

The design of field scale injection of ZVI slurries needs a deep knowledge of the geology and hydrodynamic conditions of the aquifer as well as the characterization of iron slurries. Moreover the injection process has to be monitored in order to understand occurring phenomena, and iron distribution in the subsurface needs to be determined.

The paper here presented describes the design, the realization and the monitoring results of a field scale mZVI particles injection, which was performed in a regime on the threshold between permeation and fracturing aiming to generate a large and likely homogenous reactive zone.

The objectives of the test were (i) to deliver particles in the subsurface with sufficiently high Radius of Influence (ROI) and with a fairy uniform distribution in order to improve the contact between reagent and contaminants, (ii) design an injection well and (iii) develop an innovative and efficient monitoring set-up.

TEST SITE DESCRIPTION

The site selected for the pilot test injection, herein denominated Site P, is an industrial site located in Belgium, contaminated by CAHs. For the pilot injection the test area (Figure 1) was selected since the characterization of contaminants showed a high PCE concentration (up to 73 mg/l) from 4.5 to 7 m-bgl in the test area. From a hydro-geological point of view the site is characterized by fine sand with several local heterogeneities; the subsoil average bulk density is 1850 kg/m^3 and the effective porosity was estimated equal to 0.2. The average depth of the water table is 2 m, the hydraulic gradient is 0.07% and the groundwater flow direction from South to North. Concerning the hydrodynamic characterization, slug tests were performed in order to assess aquifer hydraulic conductivity and provided an horizontal hydraulic conductivity equal to $1.8 \cdot 10^{-5}$ m/s (Butler 1997), which leads to an effective velocity equal to 0.005 m/day.

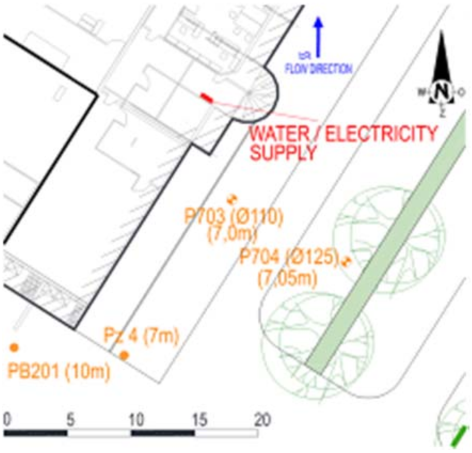


Figure 1: Map of the test area

INJECTION WELL DEISIGN, PUMPING SYSTEM AND MONITORING SET-UP

A tailor made injection well was designed for the pilot test in order to sustain average to high discharge rates and properly sealed on the top to avoid product daylighting. The well is characterized by a PVC pipe of inner diameter of 110 mm with a screen length equal to 2,5 m (from 4,5 to 7 m-bgl). Fluids were injected in the subsurface with a lobe pump (Jabsco 24-A1, Germany), recommended for the injection of viscous fluids. The pump is characterized by a maximum injection pressure equal to 15 bar and a maximum flow rate equal to 95 l/min for water.

The injection process and the fluid properties were monitored by means of a set-up specifically designed. The injection pressure was measured in real time with two pressure transducers (one inside the injection well and the other connected to the injection pipe) and a digital manometer (Delta Ohm, Italy). The discharge rate was continuously measured with and electromagnetic flowmeter (Endress+Hauser, Switzerland) as well as the total injected volume. Slurry viscosity and concentration were periodically assessed through a Marsh Funnel and a

magnetic susceptibility sensor respectively (Bartigton, UK). After the mZVI injection test, liners were extracted around the injection well at different radial distances (Figure 2) with a Geoprobe at depths ranging from 2.4 to 8 m-bgl and the presence of iron was detected via magnetic susceptibility measurements each 10 cm using a susceptibility sensor (Bartigton, UK). Chemical analyses (i.e. H_2 measurements after acid digestion of the mZVI particles) were performed on some portions of soil from the dismantled soil cores for comparison.
Two weeks before the injection groundwater samples were collected from the injection well P704 to obtain baseline concentrations. About 2, 4, 8 and 12 weeks after injection more groundwater samples were collected (1) to measure redox parameters, (2) to quantify chlorinated ethenes and (3) degradation products.

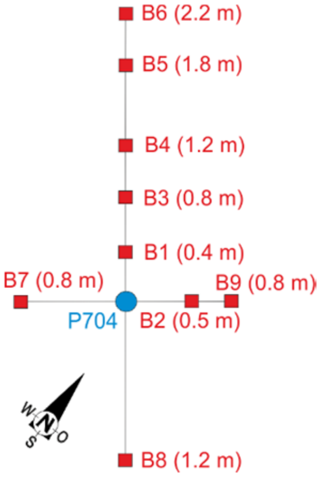


Figure 2:Liners position around the injection point P704

PRELIMINARY TESTS

Laboratory tests

The mZVI selected for this application (HQ from BASF, Germany) is characterized by a very fine granulation (d_{10}, d_{50}, d_{90} < 3 μm) and batch reactivity tests results showed that the proper concentration of iron particles in the slurry must be equal to 10 g/l. With the purpose to stabilize the particles, in order to reduce the sedimentation rate, the highly hygroscopic polysaccharide guar gum was chosen (HV700 by RANTEC, Ranchester - United States). The commercial product was provided as dry powder with a medium to fine granulation (nominal maximum grain size equal to 75 μm). Basing on sedimentation and rheological experiments the proper guar gum concentration able to stabilize the selected iron particles for 3h (the average injection time was estimated to be equal to 2h) is equal to 2 g/l.

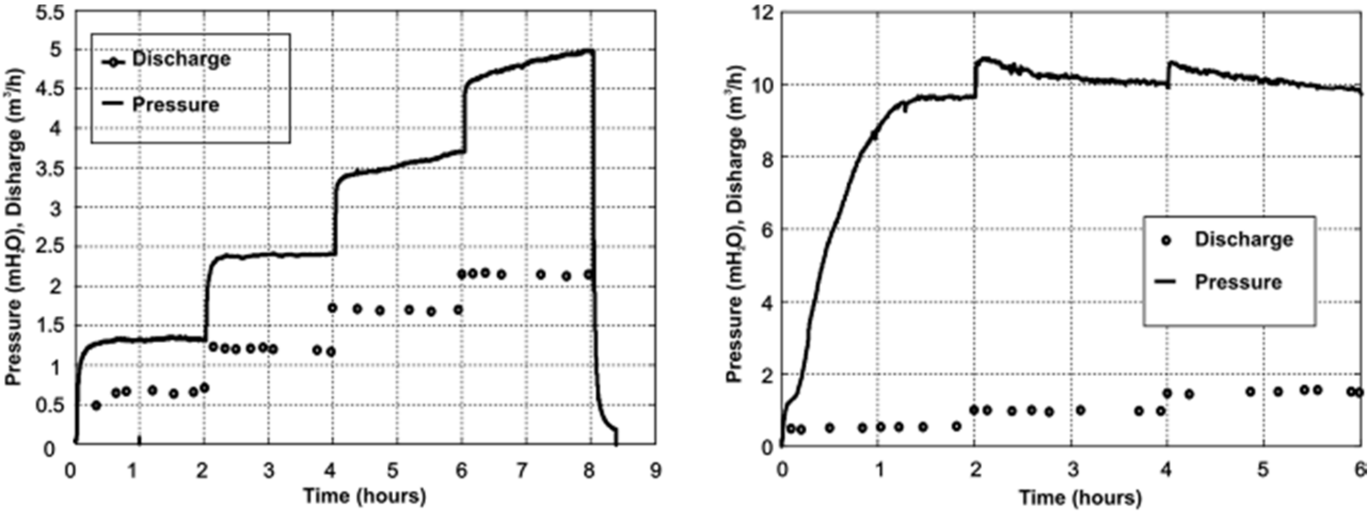
Water injection step test

The first preliminary field injection test consisted in injecting water at different discharge steps. Four discharge rate steps were conducted, each of them lasting 2 hours, injecting at 0.6, 1.2, 1.7 and 2.15 m^3/h. The discharge and the water level were continuously monitored respectively trough an electromagnetic flowmeter and a pressure transducer placed inside the well below the water table. Test results (Figure 3a) allowed to verify that the injection pressure is always lower than the critical value (104 kPa or 10.4 mH_2O) in the investigated discharge range.

Guar gum injection step test

In order to assess the injectability of non-Newtonian viscous fluids, to evaluate the pressure built up which can be generated during the mZVI injection and to select the proper discharge rate for the slurries injection, a guar gum injection step rate test was carried out injecting the solution at the selected polymer concentration (2g/l). Differently from the previous test, three lower discharge steps were performed (0.5, 1 and 1.5 m^3/h) since higher injection pressure were expected due to higher fluid viscosity; each step lasted 2 hours and discharge rate, injection pressure and water level in the injection well were continuously monitored.
As shown in Figure 3b, in the second and third steps the injection pressure increased until a peak value and then slightly decreased reaching an asymptotic lower value. This profile and the peaks values (which overcomes the

critical pressure), can be explained with the generation of preferential flow paths, which means that the injection occurred in a regime on the threshold between permeation and fracturing.



(a) *(b)*

Figure 3: (a) water and (b) guar gum injection step rate tests: pressure and injection discharge rate over time

FIELD SCALE INJECTION

The injection volume for the pilot test was roughly estimated on the basis of the ROI (Radius of Influence) of the fluid in the subsurface and the geometry of the injection well and resulted equal to 5 m^3.

Firstly 5 m^3 of 2 g/l concentration guar gum solution was prepared by means of a rotor-stator dispersing unit (YTRON, Ben Endorf, Germany) and transferred into a 1 m^3 conic vessel, directly connected to the injection circuit, where the iron particles were dosed and properly dispersed using a high speed rotor-stator based dispersing unit. The slurry was continuously recirculated before injection. The iron concentration in the injected slurries was equal to 10 g/l, which means that 50 kg of mZVI particles were delivered in the subsurface.

In order to find a compromise between the necessity to avoid sedimentation of the iron particles and to achieve a uniform distribution, the injection discharge was fixed equal to 1.5 m^3/h and allowed to inject 5 m^3 of ZVI slurry in a time almost equal to the sedimentation time of the slurry (t_{50} ~ 4 hours). Since the discharge rate was higher than the one which gave rise to fractures during guar gum injection (0.5 m^3/h), the generation of preferential flow paths was expected. The shape of the injection pressure logs (Figure 4) confirmed that injection did not occur in the permeation regime. However, the measured pressure was close to the one measured for the same discharge rate in the guar gum injection test, demonstrating that the presence of the iron particles do not significantly influence the injection pressure, and that the particles are not significantly clogging the porous medium while transported through it.

The magnetic susceptibility measurements performed on core samples confirmed the non uniform iron particles distribution but highlighted the presence of a quite extended reactive zone around the injection well; indeed iron particles reached radial distances of the order of 1 m around the injection well (the presence of ZVI particles was measured up to 1.7 m from the injection point).

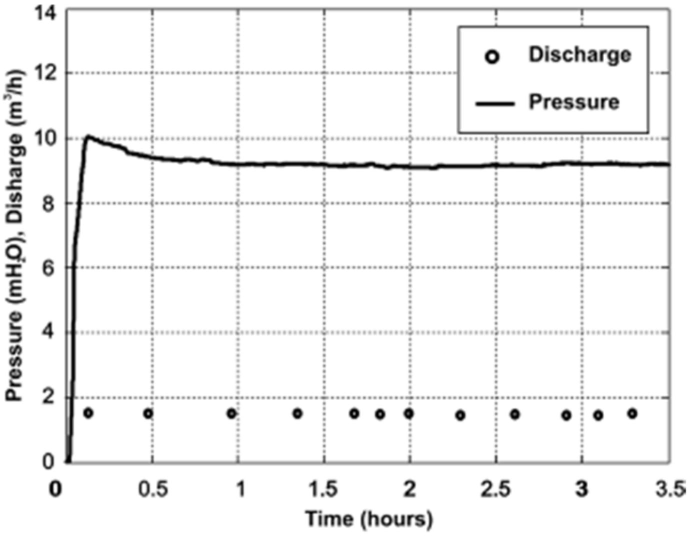


Figure 4: mZVI pilot injection: pressure and discharge rate in P704

The results obtained before and after iron injection show that ORP decreased significantly from 102 mV to – 225 mV (2 weeks after injection) and remained constant (- 247 mV) afterwards. A pH increase from 5.6 to 7.6 was also observed. Results on contaminant reduction obtained during the groundwater monitoring are presented in Figure 5. Two weeks after injection it is evident that the PCE concentration decreased significantly indicating an abiotic reduction initiated by injected mZVI. The increase in cDCE and VC concentrations observed after 8 weeks were higher than expected when considering only dechlorination by the mZVI and suggest that also biological processes may have been induced by the guar gum stabilized mZVI via pH increase, ORP lowering and hydrogen production (Truex 2011). Finally, ethene and ethane were observed as final degradation products. Slightly increased concentration of chloroethane after injection is explicable by abiotic reduction by mZVI.

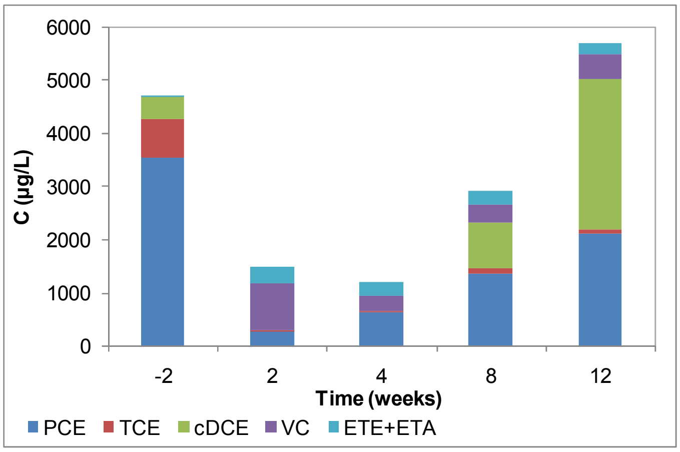


Figure 5: Changes in PCE, TCE, cDCE, VC, CA and ETE+ETA concentrations over time in P704.

CONCLUSIONS

The pilot scale field study demonstrated a successful application of commercially available guar gum-stabilized mZVI particles for the remediation of groundwater polluted by chlorinated hydrocarbons.

On the basis of the results obtained in this study, it is possible to summarize the following major findings:

- The specifically designed injection well allowed to sustain average discharge rate avoiding the product daylighting and the injection set-up was able to deliver particles in the subsurface within a ROI equal to 1m or higher.
- The monitoring set-up proved effective in monitoring the injection process, fluid properties and, thanks to magnetic susceptibility measurements, allowed to determine the iron distribution in the subsurface, which are comparable with results obtained via chemical analysis.

- The injection was performed in a regime on the threshold between fracturing and permeation and the particles migration in the pore space occurred mainly via preferential flow, even if the particles gave rise to a quite extended reactive zone around the well.
- A clear decline in PCE concentration was observed after injection, which is due to a combination of reductive dechlorination by the mZVI and mZVI-induced biological dechlorination.

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Nanosized iron oxides in bioremediation

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Microbial reduction of ferric iron is an important biogeochemical process in groundwater systems. It is associated with the microbial degradation of organic contaminants. However, the low bioavailability of natural iron oxides limits microbial reduction rates. Compared to their bulk and highly crystalline parent materials, nanosized iron oxides in contrast have an enhanced reactivity potential. Therefore, we examined the reactivity of nanosized synthetic and environmental colloidal iron oxides in microbial iron reduction. Colloidal nanoparticles showed a strong enhancement of microbial reaction rates in microbiological experiments. Toluene and benzoate oxidation was increased. Soil column experiments revealed the high sustainability of nanosized iron oxides under simulated environmental conditions. This opens the perspective for their technological application as electron acceptors in the remediation of BTEX and putatively PAH contaminated sites. Furthermore, we developed a unique approach for custom-tailoring the subsurface mobility of these particles after injection into a contaminant plume, and applied it to a field site. Results from batch, column, and from a pilot test site application experiments confirmed this remediation concept. The injection of ferric iron nanoparticles as electron acceptors for microbial contaminant degradation into contaminated aquifers might develop into a novel bioremediation strategy by creating *in situ* reactive biobarriers.

Poster Presentations

Rheology and optimized preparation of guar gum solutions for the suspension of zerovalent iron particles

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ABSTRACT: The use of Micro- and Nano-scale Zerovalent Iron (MZVI and NZVI, respectively) particles represents a promising technology for the remediation of aquifer systems contaminated by a wide variety of pollutants. ZVI particles can be injected in the aquifer systems even at high depths below ground surface.

The application of this technology is limited by reduced suspensions stability and filtration in the porous media due to the fast sedimentation (MZVI) of the iron and to the particles aggregation (NZVI). To enhance stability and mobility of the suspensions it is fundamental to use stabilizing agents which increase the solution viscosity, thus reducing sedimentation and aggregation rates. Some biological hydrocolloids have been demonstrated very effective due to their non Newtonian, shear thinning, behaviour.

In this work, performed in the framework of the AQUAREHAB project (FP7 - G. A. Nr. 226565), the use of guar gum (GG) is presented. GG is an hydrocolloid with shear-thinning behaviour that can be easily biodegraded using enzymes in order to recover the reactivity of the iron after injection.

For the correct dimensioning of a field application a full rheological characterization of the guar gum solution at variable concentration has to be carried out. For this purpose several colloidal suspensions preparations at different polymer concentrations, with and without iron particles, have been tested and functional relationships have been derived.

The evaluation of the apparent viscosity in the porous medium is of pivotal importance for the prediction of the injection pressure. Filtration tests performed in a 1D sand packed column demonstrated that this parameter can be deduced from rheological tests, measuring shear viscosity. Moreover to reduce pressure injection and increase iron particles mobility, stability tests were performed, which allowed to define an enhanced protocol for the preparation of the suspensions.

INTRODUCTION

The injection of water-based slurries of NZVI and MZVI iron particles show a positive potential for the remediation of contaminated aquifers, in both laboratory and field-scale tests. Micro and nanoscale iron particles proved effective in degrading a broad range of organic pollutants in groundwater systems, in particular chlorinated hydrocarbons and recalcitrant compounds (Chang et al. 2005, He and Zhao 2005, Joo et al. 2004, Lowry and Johnson 2004, Zhang 2003). However, NZVI lifetime is shorter, compared to MZVI, with high consumption due to undesired side reactions in groundwater (Almeelbi and Bezbaruah 2012, Velimirovic et al. 2012a). Handling of MZVI is easier and safer in field applications, being dry microscale particles chemically stable in air, while most of NZVI commercial products are available in aqueous suspensions or in modified atmosphere, to prevent combustion and explosion. Moreover, MZVI has a lower commercial cost and lower potential toxicity for the ecosystems (Lee et al. 2008). Laboratory and field studies on MZVI reactivity and mobility have been recently addressed (Dalla Vecchia et al. 2009b, Velimirovic et al. 2012a, Velimirovic et al. 2012b, Xue and Sethi 2012), demonstrating that MZVI is unstable when dispersed in pure water (Dalla Vecchia et al. 2009a, Phenrat et al. 2009, Tiraferri et al. 2008).

The colloidal instability of the suspensions have a severe impact on preparation and storage of the iron slurries before injection, on the mobility of the particles in the porous medium, and consequently on the final radius of influence of field injections (Kocur et al. 2013). The instability of MZVI is related to its larger size, which results in fast sedimentation (Dalla Vecchia et al. 2009b, Velimirovic et al. 2012a). A modification of the dispersant fluid, rather than of the surface properties of the particles, is needed. To meet this requirement, the use of biological hydrocolloids demonstrated to be successful in laboratories studies (Dalla Vecchia et al. 2009b, Truex et al. 2011, Xue and Sethi 2012). Viscous polymeric solutions at concentrations in the order of few g/l, exhibit peculiar non-

Newtonian, shear thinning properties, which guarantee high viscosity in static conditions (thus hindering sedimentation during preparation and storage of the slurries), and low viscosity in dynamic conditions (thus limiting the pressure build up during injection).

Guar gum is selected in the present study as a stabilizing agent due to its easy degradation in the presence of specific enzymes and microorganisms. Guar gum is a polysaccharide extracted from seeds of a leguminous plant widely used as a thickening and stabilizing agent in a vast range of industrial applications (medicine, food, cosmetic). It is commercially provided as a dry powder, which hydrates when dissolved in water forming a shear thinning solution. The hydration kinetics depends on a number of factors, including molecular weight, final polymer concentration, temperature, and dry particle size (Wang et al. 2008). Moreover, it was observed that, as for most biopolymers, the complete hydration is never reached, and residual undissolved particles remain in suspension. The presence of residual undissolved polymeric particles results in a progressive decrease in permeability during injection (clogging) and consequent pressure increase in the subsoil. When studying the permeation of guar gum in porous media, it is important to be able to predict and to limit the pressure build up during injection.

The present paper addresses the issues associated to the colloidal stability of MZVI. In particular, using an experimental approach, a method for the design of microiron dispersions (with the aim of maximizing dissolution and therefore viscosity) and for the identification of the guar gum concentration suitable for stabilizing the selected MZVI particles for the target time was suggested. Moreover the processes associated to the injection of guar gum solutions in porous media via permeation, as well as approaches and methods for the quantitative analysis and prediction of such processes, are investigated.

MATERIALS AND METHODS

Food-grade guar gum (RANTEC, Ranchester, United States) with nominal maximum particle size of 75 µm was used in the form of dry powder.

Several guar gum preparation procedures were tested:

- as received (AR);
- thermally dissolved in warm water (T60);
- thermally dissolved in warm water with removal of residual undissolved particles (T60R).

Solutions were prepared 24 h prior to use, to maximize hydration of the polymer powder. The effectiveness of the procedures were tested for polymer concentrations of 3 and 4 g/l in sedimentation, rheological and single-step column filtration tests.

Multi-step column filtration tests were performed at guar gum concentrations of 1.5, 3 and 4 g/l for the rheological characterization in the porous medium.

Single step and multi step filtration tests were performed injecting in a 42 cm long sand packed (Dorsilit 8) column with 2.4 cm inner diameter. The experimental protocol includes: pre-flushing of the column with D.I. water (5 PVs), polymer solution injection (number of injected PVs variable and depending on the test), post-flushing with D.I. water (15 PVs). During the tests, the total pressure drop along the column was continuously monitored via pressure sensors at column ends (Delta Ohm, Italy).

The rheological characterization of the suspensions in bulk was performed at 20°C using an Anton Paar rheometer MCR 301 equipped with concentrical cylinders. The shear viscosity was measured as a function of shear rate exploring a shear rate range from 10^{-2} to 10^{4} s^{-1}.

Iron micro-sized particles (HQ from BASF, d_{10}, d_{50}, d_{90} equal to 0.7, 1.2, 1.8 µm, respectively) used in sedimentation tests were dispersed in guar gum solutions using a high speed rotor-stator (UltraTurrax, IKA, Germany). The iron particles concentration was equal to 20 g/l. Guar gum based MZVI slurries were placed in elongated cuvettes and the evolution over time of the iron concentration was continuously monitored at a fixed height, using a susceptibility sensor (Bartington, UK). The data were analyzed in terms of sedimentation half time (t_{50}), namely the time when the detected concentration reaches half the initial value.

RESULTS

Optimization of guar gum preparation

Different procedures were tested for the preparation of guar gum solutions, with the aim of maximizing the dissolution of the guar gum powder, thus reducing the presence of undissolved residual particles and maximizing viscosity. The efficacy of the procedures was assessed basing on three criteria: first, the final solution viscosity was measured and compared; second, the porous medium clogging was evaluated running single step column filtration tests at a constant flow rate; third, the efficacy in stabilizing MZVI suspensions was quantified.

The identification of an effective and easy procedure for the minimization of undissolved guar gum particles is particularly important for the application of guar gum solutions: when guar gum solutions and ZVI iron slurries are injected in porous media, solid residuals are expected to be filtered in the soil, due to their large size. If their amount is high, they may have a negative impact on the porous medium permeability and porosity, giving rise to clogging and thus increasing pressure build up during the injection. This process has a negative impact on both mobility and distribution of the iron particles resulting in MZVI mainly retained close to the injection well, so causing an extra pressure, with possible formation of preferential flow paths in the porous medium which leads to fracturing, and to consequent highly non homogeneous distribution of the iron particles.

The impact of the preparation procedure on the fluid viscosity can be evaluated from the rheograms reported in Figure 1. It can be noticed that the low-shear viscosity for AR samples is the lowest one for the investigated concentration (4 g/l), while at high shear rates the difference is less relevant. Also, for the T60R sample the low shear viscosity is slightly lower compared to T60 samples, suggesting that removing the undissolved particles leads to a (limited) removal of dissolved polymer chains.

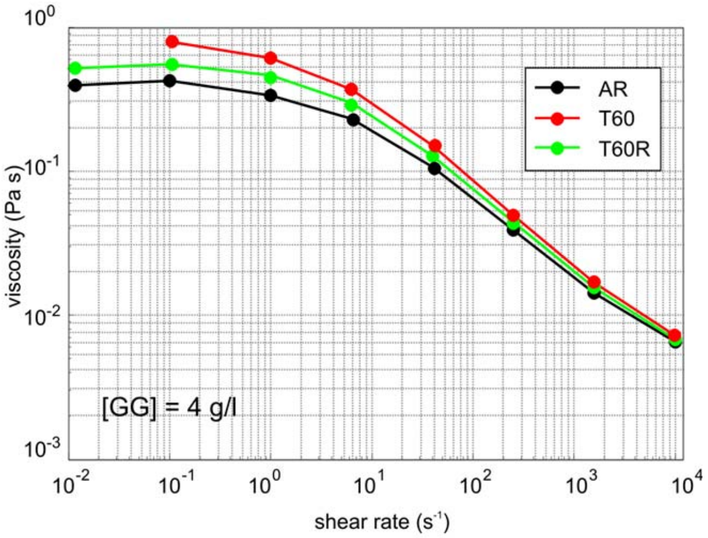

Figure 1: Rheological curves of guar gum solutions at 4 g/l for several preparation procedures.

Retention of undissolved particles in the porous media was tested injecting polymer solutions in a sand packed column and monitoring the pressure drop at the ends of the column. After the first pore volume (PV), the pressure drop is very similar for all tests, since it is directly related to the guar gum viscosity. Conversely, the slope $\Delta P_n/PV$ after the first PV is approximately constant over time, and can provide a qualitative indication of clogging: the higher the slope, the higher the amount of particles retained. Figure 2 reports the slope $\Delta P_n/PV$, where ΔP_n is calculated as pressure gradient referred to Darcy flow rate, $\Delta P/(L \cdot q)$ [M L^{-3} T^{-1}].

For both concentrations, the maximum clogging (i.e. the highest slope) corresponds to dissolution in cold water without any further treatment (AR). The use of warm water improves dissolution (T60), reducing the amount of undissolved particles, and consequently of porous medium clogging. However, the most significant reduction in clogging was obtained when residual undissolved particles were removed mechanically (T60R).

The preparation procedures were then evaluated in sedimentation tests for HQ iron particles. The experimental results (Figure 3) indicate that the use of warm water (T60 and T60R) improves the guar gum dissolution, thus resulting in longer sedimentation half time t_{50}.

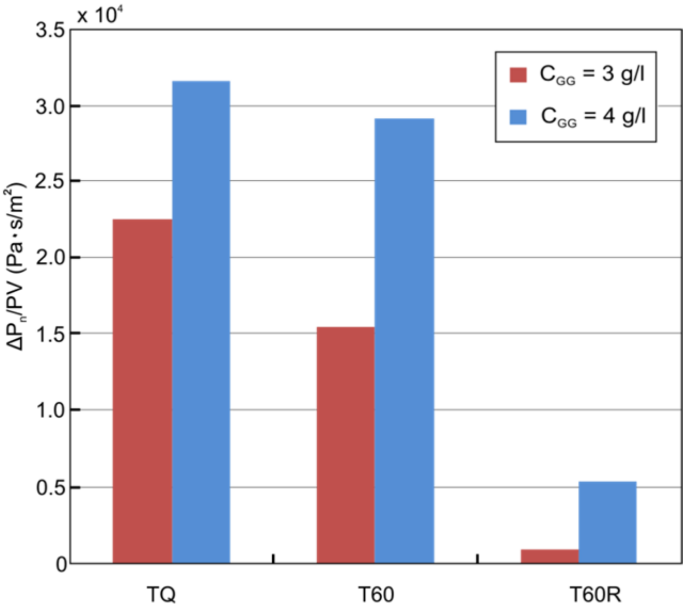

Figure 2: Slope *ΔPn/PV* during injection for filtration tests of guar gum solutions at 3 and 4 g/l prepared using different procedures.

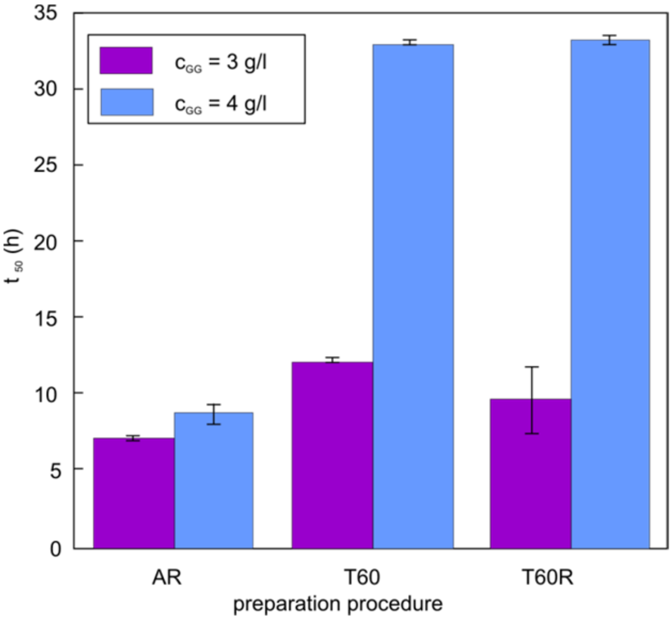

Figure 3: Sedimentation half time of HQ microparticles dispersed in 3 g/l and 4 g/l guar gum solutions, prepared applying different procedures.

Rheology of guar gum solutions in the porous medium

Multi-step filtration tests were aimed at providing a full characterization of the rheology of T60R guar gum solution in porous media. The tests were designed as a step injection of guar gum solution with increasing flow rate from step to step

An increase in flow rate results in a change in shear rate $\dot{\gamma}_m$,and for each step the porous medium viscosity, $\mu_m(\dot{\gamma}_m)$, changes accordingly. Each injection step can be represented by point in the rheogram of the fluid in the porous medium, and the corresponding viscosity and shear rate a can be calculated as:

$$\begin{cases} \mu_m = \dfrac{K}{q}\dfrac{\Delta P}{L} \\ \dot{\gamma}_m = \alpha \dfrac{|q|}{\sqrt{K\varepsilon}} \end{cases}$$

The point data (Figure 4) exhibit a nice agreement with the bulk rheogram, suggesting that the shift factor *α* is close to the unit. A shift factor close to 1 is also in agreement with the literature, that suggests values in the order of few units in the case of well-sorted porous media with regular grain shape, like the sand used for these tests.

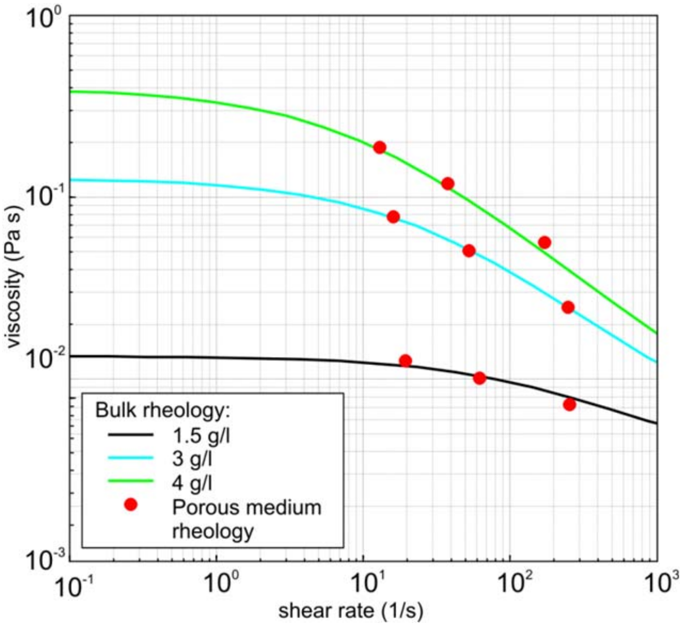

Figure 4: bulk and porous medium rheology; point values represent the apparent viscosity and shear rate calculated at the end of each injection step calculated from experimental pressure drop curves, lines represent the bulk viscosity curves for the corresponding guar gum concentrations.

CONCLUSIONS

The results of rheological, filtration and sedimentation tests indicate that the use of warm water in the preparation of guar gum solutions is required for improving dissolution, with a moderate reduction of clogging. However, if the application envisioned is the injection in porous media, this is not sufficient, because T60 solutions still cause a significant clogging of the column. A post-treatment of the guar gum solution is required for further removal of the residual particles (T60R) with a significant reduction of porous medium clogging compared to the other preparation procedures.

The viscosity of a fluid in the porous medium is similar to that of the same fluid in the bulk, which can be easily measured in the laboratory, but is shifted in shear rate of a constant value α, called shift factor which is a function of the porous media and needs to be evaluated experimentally. The multi-step filtration tests performed in this work on solutions prepared with the best preparation protocol suggest that the shift factor for the considered fluid and porous medium can be assumed equal to 1, implying that in this case the rheological characterization in the bulk is sufficient for a correct simulation of pressure drops (Sorbie et al. 1989, Tosco et al. 2013).

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Sorption and chemical effects of zero-valent iron nanoparticles in removal of waterborne estrogens

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Presence of estrogens in wastewater, surface water, groundwater and even in drinking water is an important environmental problem worldwide, with some synthetic compounds being fairly resistant to biological degradation and hazardous to aquatic life and human health. In the present study, we have investigated the interaction of nanoscale zero-valent iron (nZVI) particles with 17-beta-estradiol (E2) and 17-alpha-ethinylestradiol (EE2) dissolved in water using both high performance liquid chromatography coupled with tandem mass spectrometer (HPLC/MS/MS) and total estrogenic activity (determined by in vitro reporter gene cellular assay). The particulate materials were characterized by X-ray diffraction, 57Fe Mössbauer and X-ray photoelectron spectroscopy, SQUID magnetometry and transmission electron microscopy. Dose-dependent removal of estrogens was observed with higher efficiency for removal of EE2, which is known to be more potent estrogen in vivo compared to E2. The highest efficiency in estrogen removal was observed at the maximal tested dose of 6 g of nZVI / L (up to 93 % removal of EE2). Short contact of estrogens with nZVI (<1 h) was sufficient to reach maximum extent of removal. The observed mechanisms include both chemical transformation and adsorption on the surface of nZVI particles. Decrease in total estrogenity indicated that no potentially more estrogenic intermediate compounds were formed from the parent E2 and EE2 estrogens during their interaction with nZVI.

Modelling field-scale injection of shear thinning slurries of microscale iron particles: coupled flow and transport in radial and 3D geometries

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ABSTRACT: The use of shear thinning solutions of green biopolymers (eg. guar gum, xanthan gum, etc.) have been considered in recent years as an effective approach for the colloidal stabilization and improved delivery of concentrated suspensions of microscale and nanoscale zerovalent iron particles (MZVI and NZVI, respectively) for groundwater remediation. The particles are injected into the subsurface close to the source of contamination, thus creating a reactive zone. Therefore, the design of a field-scale pilot test or remediation intervention requires a reliable estimate of iron distribution after the injection.

The transport in porous media of concentrated MZVI and NZVI slurries is affected by the rheological properties of the dispersing fluid (shear thinning) and by particle deposition and filtration in the porous matrix, which result in porous medium clogging (i.e. reduction of porosity and permeability). Moreover, the kinetics of particle retention is strongly influenced by flow rate and fluid viscosity, as evidenced by experimental results (Gastone et al. 2013). Therefore, the strong coupling of non-Newtonian flow (due to the shear thinning properties of the guar gum solutions) and particles transport requires the development of specific modelling tools. E-MNM1D (Tosco and Sethi, 2010; www.polito.it/groundwater/software) was previously developed by the authors for the simulation of one-dimensional transport of MZVI and NZVI non-Newtonian dispersions at the laboratory scale, while MNM1D was developed to simulate the influence of transients in water salinity on colloid transport in the absence of clogging (Tosco et al., 2009). In this work, the two modelling approaches are extended to more complex geometries. The model equations for the simulation of colloid transport under transients in ionic strength, solved in 1D geometry by MNM1D, are here adopted for more general scenarios of particle transport, and implemented in other commercial and freeware software, namely RT3D (Clement et al., 1998). The flow and transport of MZVI slurries is solved in a radial domain for the simulation of field-scale injection, incorporating the abovementioned relevant mechanisms. The governing equations and model implementation are presented and discussed, along with examples of injection simulations. The work was partly co-funded by the EU projects AQUAREHAB (FP7 - G. A. Nr. 226565) and NANOREM (FP7 - G. A. Nr. 309517).

INTRODUCTION

The efficacy of zero-valent iron (ZVI) for the remediation of polluted groundwater is well known, and has been applied in the last twenty years for the realization of permeable reactive barriers (PRBs). Although the PRB is a successful technology, the granular sizes of iron (0.2-5 mm) can often restrict its applications. Injectable Fe-based materials (nano- and micro-sized zero-valent iron particles, named NZVI and MZVI) can be suspended in a slurry and injected directly into the source of contamination, overcoming most of the limitations of zerovalent iron permeable reactive barriers (Di Molfetta and Sethi, 2006). Furthermore, thanks to the reduced particle size, and thus to the extremely high specific surface area, MZVI and NZVI exhibit an improved reactivity compared to granular iron.

Critical points for successfully full-scale applications are stability against aggregation and sedimentation, mobility in subsurface environments, and longevity in the subsurface. Iron particles should remain in suspension for a time sufficient for slurry preparation, handling and injection in the subsurface. Also, they should have a sufficient mobility in the subsurface to be transported for some extent around the injection point. However, several studies have shown MZVI and NZVI to be scarcely mobile and stable in both laboratory studies and field-scale tests, due to fast sedimentation (MZVI) or aggregation and subsequent sedimentation (NZVI). Coating of the iron nanoparticles with hydrophilic polymers and increasing the viscosity of the MZVI and NZVI slurry were found successful approaches for improving both colloidal stability and mobility in lab-scale experiments (Dalla Vecchia et al., 2009; Tiraferri et al., 2008; Tiraferri and Sethi, 2009). In particular, polymeric solutions of xanthan gum and guar gum proved to be able to prevent sedimentation of both micro- and nanoscale iron particles for several hours (Comba and Sethi, 2009; Dalla Vecchia et al., 2009). Moreover, they exhibit a non-Newtonian shear-thinning behaviour, that facilitates injection and delivery of the colloidal suspension in the subsurface. Shear thinning fluids are characterized by a high viscosity at zero shear rate, that decreases with increasing shear rate till to the value of pure water. Consequently, they can enhance stability of the iron dispersion when the product is stored (as high viscosity prevent gravitational settling and aggregation of the particles) without hindering the injection.

In this work, a study on guar gum-based slurries of MZVI particles is presented. Up to date, modelling of colloid transport in the presence of complex interaction phenomena (eg. transients in pore water chemistry, non-Newtonian carrier fluids, clogging processes) has been mainly faced in one-dimensional Cartesian coordinates. In this work, more complex geometries are considered. Colloid transport in the presence of transient chemical conditions and in the absence of clogging processes was previously studied by the authors is column tests and modelled in 1D geometry suing the software MNM1D, developed on purpose (Tosco et al., 2009). In this work, the colloid transport kinetics are implemented in a well-known model, namely RT3D (Clement et al., 1998), which can be used for multi-dimensional simulations, and the approach is validated comparing the simulation results of MNM1D and RT3D run on a one-dimensional domain. Second, the simulation of MZVI injection at a large (field) scale is faced. In this case, the development of a transport model in multi-dimensional domains requires a detailed knowledge of how the flow rate influences the kinetics of the particles interactions with the porous medium (deposition and release processes), the eventual clogging, and the viscosity of the shear thinning carrier fluid (Ciriello and Di Federico, 2012; Longo et al., 2013). One-dimensional transport tests performed at different flow rates and guar gum concentration were analyzed using a modified formulation of the transport software E-MNM1D (Tosco and Sethi, 2010), the processes governing MZVI transport were identified, and the dependence of the transport parameters on the flow rate and on the fluid viscosity were derived. The identified relationships were then implemented in a radial model.

MATERIALS AND METHODS

COLLOID TRANSPORT UNDER TRANSIENT PORE WATER CHEMISTRY IN MULTI-DIMENSIONAL DOMAINS: MODIFIED RT3D

The flow and transport of colloidal particles under transient in water chemistry were previously modelled by the authors (Tosco et al., 2009) through a simplified transport equations system, which takes into account the dependence of the deposition phenomena on the water salinity. The model was implemented in MNM1D (Tosco and Sethi, 2009) for the simulation of transport in one-dimensional domains, mainly laboratory column tests. The same model is now implemented in RT3D in order to provide a numerical solution for simulation of any generic scenario, in terms of geometries and flow and transport properties, on a well-known software environment.

The user-defined reaction module of RT3D has been adapted, after appropriate manipulation of the model equations according to the operator splitting strategy, to simulate the interactions between colloids and a heterogeneous porous medium. Considering a two-sites model, respectively with linear and non-linear colloid deposition processes, the system of equations, considering only the reactive contribution to the concentration variation, becomes:

$$\begin{cases} n\dfrac{\partial c_t}{\partial t}=0 \\ n\dfrac{\partial c}{\partial t}=-\left(\rho_b\dfrac{\partial s_1}{\partial t}+\rho_b\dfrac{\partial s_2}{\partial t}\right) \\ \rho_b\dfrac{\partial s_2}{\partial t}=nk_{a,2}\left(c_t\right)c-\rho_b k_{d,2}\left(c_t\right)s_2 \\ \rho_b\dfrac{\partial s_1}{\partial t}=nk_{a,1}\left(c_t\right)\left(1-\dfrac{s_1}{s_{\max,1}\left(c_t\right)}\right)c-\rho_b k_{d,1}\left(c_t\right)s_1 \end{cases} \tag{1}$$

where the attachment and detachment coefficients ($k_{a,i}$ and $k_{d,i}$, respectively, with i=1,2, [T^{-1}]) and the maximum concentration for blocking $s_{max,1}$ [-] are a function of ionic strength, here represented by the salt concentration c_t [M L^{-3}], as reported by the authors in previous works (Tiraferri et al., 2011; Tosco and Sethi, 2009; Tosco et al., 2009).

Four different species are considered in the RT3D simulation: two mobile, i.e. the conservative salt (c_t) and the colloid (c) in the liquid phase, and two immobile, i.e. the sorbed colloids on the different active site (s_1 and s_2).

The modified RT3D has been provided of an open source interface, mfLab (http://code.google.com/p/mflab/), and coupled with different parameters estimation routines, namely PEST and Matlab built-in functions, for the inverse problems solution.

MZVI INJECTION IN RADIAL DOMAINS: EXPERIMENTS AND MODEL DEVELOPMENT

Column tests

Iron particles (HQ from BASF, d_{50} = 1.2 μm) were dispersed in a guar gum solution (RANTEC HV7000 from Ranchester, United States) and used for column transport tests. In all tests, the iron concentration was 20 g/l. Column tests were performed in 42 cm long sand packed (Dorsilit 8) columns. Three values of flow rate ($2.8\cdot10^{-4}$ m/s, $1.2\cdot10^{-3}$ m/s, $5.3\cdot10^{-3}$ m/s) and guar gum concentration (1.5 g/l, 3 g/land 4 g/l) were applied. The protocol for the preparation of the iron suspensions and for the transport tests is discussed in details in a previous work (Tosco et al., 2012).

1D transport simulations

The experimental results of column experiments (Tosco et al., 2012) were fitted using an extended formulation of E-MNM1D (Tosco and Sethi, 2010), which couples MZVI transport, porous medium clogging and non-Newtonian flow of the slurries.
The MZVI transport was modeled by a modified advection-dispersion-deposition equation:

$$\frac{\partial}{\partial t}(\varepsilon c_{Fe})+\sum_i\frac{\partial(\rho_b s_{Fe,i})}{\partial t}+\frac{\partial}{\partial x}(q c_{Fe})-\frac{\partial}{\partial x}\left(\varepsilon D_x\frac{\partial c_{Fe}}{\partial x}\right)=0 \tag{2}$$

where ε is the porosity, D_x is the hydrodynamic dispersion coefficient [$L^2\ T^{-1}$], and q is the Darcy velocity [$L\ T^{-1}$].
The source/sink term (second term of the equation) represents the MZVI kinetic deposition onto and release from the solid matrix, and can be expressed by several formulations, depending on the processes involved, and several concurrent interaction sites, each representing a different process. In this work two interaction sites were considered (*i = 1,2*), one (resulting in $s_{Fe,1}$) expressing linear deposition mechanisms formulated following the colloid filtration theory (Yao et al., 1971), and the other one (resulting in $s_{Fe,2}$) taking into account non-linear deposition processes which arise in concentrated and unstable suspensions:

$$\begin{cases}\dfrac{\partial(\rho_b s_{Fe,1})}{\partial t}=\varepsilon k_{a,1}c_{Fe}-\rho_b k_{d,1}s_{Fe,1}\\ \dfrac{\partial(\rho_b s_{Fe,2})}{\partial t}=\varepsilon k_{a,2}\left(1+A_2 s_{Fe,2}{}^{B_2}\right)c_{Fe}\end{cases} \tag{3}$$

The total concentration of deposited particles, s_{Fe}, is the sum of the concentrations in phase 1 and 2, $s_{Fe}= s_{1,Fe} + s_{2,Fe}$. The dependence of attachment and detachments rates, $k_{a,1}$, $k_{a,2}$, and $k_{d,1}$ on flow rate and fluid viscosity was determined from the fitting of the column tests, and implemented in the radial model.
The reduction of permability and porosity due to MZVI deposition was modelled following the approach previously proposed by the authors (Tosco and Sethi, 2010). The pressure build up arising from the injection of the non-Newtonian slurry of MZVI was calculated using a modified formulation of the Darcy law, which takes into account both the reduction in permeability, and the shear thinning nature of the fluid, following the same approach adopted in Part II for the flow of guar gum solutions without particles:

$$-\nabla p=\frac{\mu_m(\dot{\gamma}_m)}{K}q \tag{4}$$

where the fluid viscosity μ_m depends on the shear rate in the porous medium $\dot{\gamma}_m$, and the permeability K is declining with increasing concentration of deposited particles. The whole set of equations is reported in the Appendix.

Radial transport model

The experimental and modeling results of column tests provided the relationships for the dependence of the transport parameters on the flow rate. The transport of MZVI was then simulated in a radial symmetric field, which is representative of a field application using an injection well. In this case, the Darcy flow rate q is not constant any more with increasing radial distance r, but declines hyperbolically with r:

$$q=\frac{Q}{2\pi rb} \tag{5}$$

where Q is the discharge rate [$L^3\ T^{-1}$], and b is the well screen thickness [L].

Consequently, in full-scale applications the flow rate and all flow rate-dependent parameters are not constant over the entire domain any more.
The transport equation becomes

$$\frac{\partial}{\partial t}(\varepsilon c_{Fe})+\frac{\partial}{\partial t}(\rho_b s_{Fe})+\frac{1}{r}\frac{\partial}{\partial r}(rqc_{Fe})-\frac{1}{r}\frac{\partial}{\partial r}\left[r\varepsilon D_r\frac{\partial c_{Fe}}{\partial r}\right]=0 \tag{6}$$

In a radial flow field, deposition and release mechanisms as well as porous medium clogging can be modeled using the same equations presented for the 1D Cartesian domain.
The simulations were performed assuming a discharge rate of 1 m^3/h for 5 h, for a total injected volume of 5 m^3 in a homogeneous porous medium of porosity 0.37 and hydraulic conductivity

RESULTS

COLLOID TRANSPORT IN RT3D: MODEL VALIDATION

The modified version of RT3D, here proposed, has been validated through comparison with MNM1D outputs produced under a very large range of parameters and ionic strength values. Figure 1 shows a simulation performed both with RT3D and MNM1D, in transient ionic strength conditions.

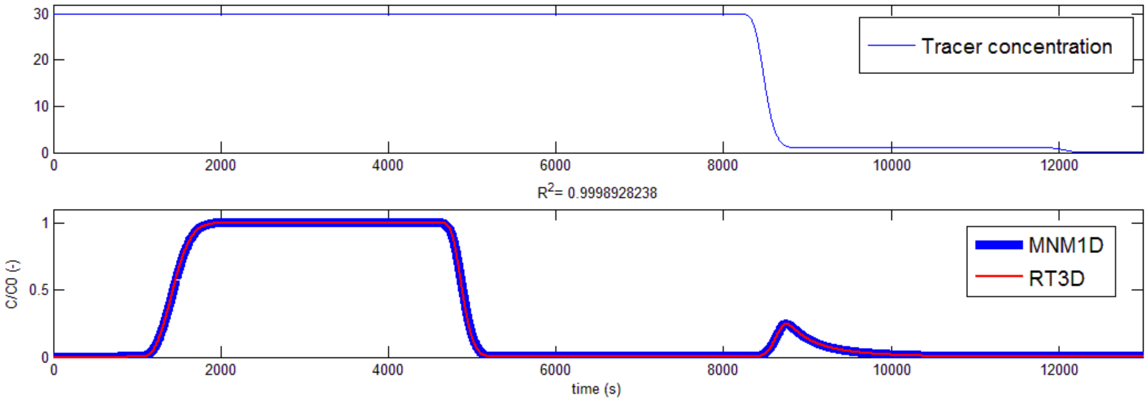


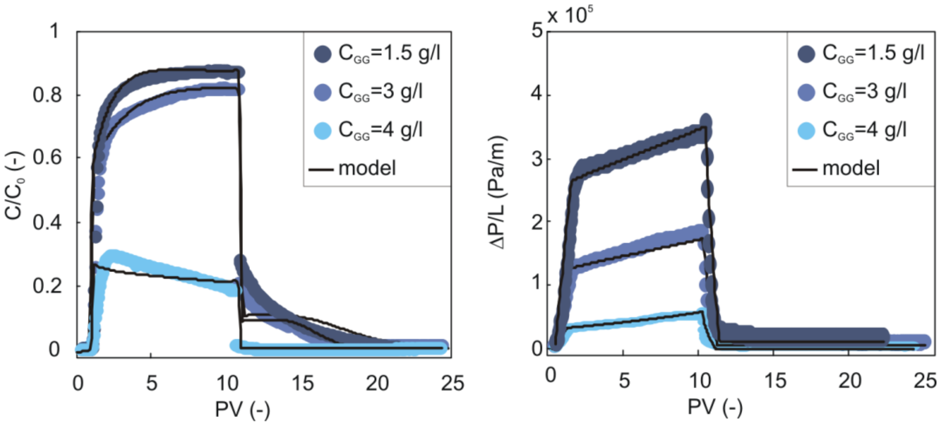
Figure 1: Simulation of colloidal particles transport in one-dimensional domain under transient ionic strength conditions. Tracer (above) and colloids (below) breakthrough curves with MNM1D and RT3D

The good overlap of the breakthrough curves has been obtained selecting an higher order solver for the advection term of the transport differential equation that, more accurate than the finite difference method employed in MNM1D, compensate for the loss of accuracy due to the use of the operator splitting strategy.

MZVI INJECTION IN RADIAL DOMAINS: EXPERIMENTS AND MODEL DEVELOPMENT

1D transport simulations

The experimental data of breakthrough concentration c_{Fe}, pressure drop evolution *Δp/L*, and profiles of total iron retained in the column s_{Fe} were fitted to the model equations, in order to determine the parameters controlling the MZVI transport and the associated clogging of the porous medium. An example of fitted curves is reported in Figure 2.



(a) (b)

Figure 2: Breakthrough curves (a) and pressure drop (b) as a function of the number of pore volumes for three tests of MZVI injection with a guar gum concentration of 1.5, 3 and 4 g/l.

Radial transport model

Three examples of forward model runs in radial symmetry are reported in Figure 3. The viscosity of the guar gum solution significantly varies with increasing radial distance, due to its dependence on the flow rate, and the attachment and detachment coefficients vary with radial distance as well. Figure 3 shows that the guar gum concentration has a major influence on the mobility of the iron particles and on the final distribution of the iron as a function of radial distance from the injection point. Less stable suspensions (1.5 g/l of guar gum) result in a limited radius of influence, and the particles are mainly retained close to the injection well, with a highly inhomogeneous distribution of the iron concentration along the radial distance. Conversely, more stable suspensions (4 g/l) result in a more homogeneous distribution of the iron and in a more homogeneous concentration. Figure 3 also reports the viscosity of the pore fluid along the radial distance: viscosity is higher for higher concentrations of guar gum, and for intermediate distances: the viscosity is lower close to the injection well since the flow rate (and consequently the shear rate) is lower, while at high distance the guar gum has not displaced water yet.

CONCLUSIONS

Concerning colloid transport under transient pore water chemistry, the model equations previously developed by the authors and implemented in one-dimensional domains were here extended for more general scenarios of colloid transport and implemented in well-known software, namely RT3D, suitable for multi-dimensional problems simulation. The validation of the modified RT3D was carried out using one-dimensional transport simulations. Concerning MZVI slurry injection, column transport tests were performed to identify the key mechanisms controlling the transport of shear thinning slurries of MZVI in porous media. The dependence of the removal mechanisms on the flow rate and viscosity was quantified, deriving semi-empirical relationships obtained from the fitting of the column transport tests data, using a modified version of E-MNM1D, previously developed by the authors. The constitutive equations were included in a new transport model implemented in a radial symmetry domain. The radial transport model was run forward for the simulation of a real-like field injection of MZVI slurry.

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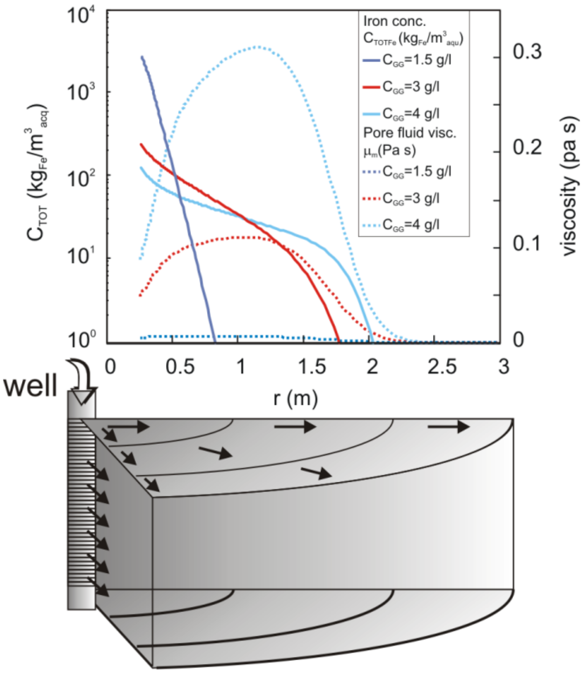

Figure 3: Simulation of radial injection of 5 m3 of MZVI slurry (20 g/l of iron, 1.5, 3 and 4 g/l of guar gum) at a discharge rate of 1 m3/h: final concentration of total iron (suspended + retained) per aquifer volume (left axis) and pore fluid viscosity (right axis) as a function of radial distance.

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Use of a CAH-degrading mixed bacterial culture as test-organisms for evaluating the impact of different ZVI types on the subsurface environment

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ABSTRACT: The release of fine zerovalent iron (ZVI) particles in the environment is a concern, especially when associated with nano-materials. Therefore, careful evaluation of the potential impacts is needed. However, the current methods for evaluating the ecotoxicological effect focus on micro-organisms that are relevant for the surface water or soil, but not on subsurface microflora. Here we present an approach where a CAH-degrading bacterial culture was used as 'test organism' relevant for the anaerobic subsurface.

A CAH batch degradation experiment was performed in liquid medium in the presence of different doses of microscale ZVI (0.05 – 30 g/L) and nanoscale ZVI (0.05 – 30 g/L). Because of the absence of buffer capacity and protecting niches of aquifer material the test results are considered as a worst case scenario. Both mZVI and the used bacteria degrade CAHs. Therefore, the impact of mZVI on the test organisms was evaluated mainly via ATP measurements, giving a general indication of the microbial activity. Further also consumption of lactate (added as electron donor) was followed as a second bio-indicator. Finally, TCE concentrations and degradation products were measured over time to give more details on degradation activity of present CAH-degrading microbial culture.

Laboratory testing demonstrated that the activity of the bacterial community was negatively influenced by nZVI at doses as low as 0.05 g/L. On the other hand, in the presence of lower concentrations of several mZVI particles stimulation of bacterial activities was observed, which was less pronounced with higher doses. Doses of 15-30 g/L of mZVI showed a large negative effect on the present microbial population. The negative effect is confirmed with no lactate consumption in reactors and explicable by the pH increase above 7.5 originating from ZVI corrosion. Finally, when comparing TCE degradation rates in the batches with (positive control) and without ZVI, it is evident that the bacteria are at the short term stressed by the presence of mZVI particles, but at a long term they are adapted to the new conditions. This indicates that mZVI particles can be suitable material for in-situ application. Moreover, aquifer material might provide protecting niches for microorganisms after injection of ZVI particles into the subsurface.

INTRODUCTION

Chlorinated aliphatic hydrocarbons (CAHs) are among the most frequently detected groundwater contaminants representing a significant environmental concern. Microbially mediated degradation is one remedial option which may be used to clean up soil and groundwater contaminated with lower CAHs concentrations. However, the required micro-organisms and/or environmental conditions to allow complete CAH-biodegradation is not present at all sites. Reductive remediation of CAHs by microorganisms might result in production of more toxic compounds such as vinyl chloride (VC). An alternative may be the use of zerovalent iron (ZVI) particles for CAHs remediation. ZVI is known for its capacity to degrade CAHs like chlorinated ethenes abiotically via reductive dehalogenation, whereby the toxic intermediates like VC are formed in much lower quantities (Gillham and O'Hannesin, 1992). ZVI particles have been mostly emplaced into the subsurface in granular form to create permeable reactive barriers comprising for instance funnel and gate systems (Gillham, 1996). More extensive use of microscale zerovalent iron (mZVI) particles and nanoscale zerovalent iron particles (nZVI) for remediation of CAHs via direct injection as a slurry into the subsurface, has raised concerns about their impact on microbial communities. After emplacement in the subsurface, it is important to study the impact of mZVIs and nZVIs on the originally present soil microbial communities and communities capable for CAHs biodegradation. In such a case, knowledge of the bacterial activity before and after the emplacement is essential.

Most available methods for evaluating ecotoxicological effects focus on micro-organisms that are relevant for surface water or soil, but not on the subsurface (often anaerobic) microflora. A limited number of studies show possible negative effects of nZVIs on naturally present soil microbial communities (Barnes et al., 2010, Kirschling et al., 2010) inhibiting biodegradation potential. Finally, it is interesting to expand knowledge on this phenomenon not only in the presence of nZVIs, but also in the presence of mZVIs. The general aim of this study was to evaluate the impact of different ZVI types on the subsurface environment when they are applied for CAHs remediation. In our study, a CAH-degrading mixed bacterial culture was used as test-organisms relevant for the anaerobic subsurface. Because of teh absence of protecting aquifer material, the test is considered a worst case scenario. The impact of different ZVIs on the test-organisms was evaluated mainly via adenosine tri-phosphate (ATP) measurements, and following the (bio)degradation pathway of trichloroethene (TCE) as most relevant pollutant in the subsurface.

MATERIALS AND METHODS

Materials

The reactive mZVI particles used in this study were obtained from Höganäs (Sweden) and BASF (Germany). While nZVI particles were supplied by NANOIRON (Czech Republic). Characteristics of the particles are given in Table 1.

Table 1: Characteristics of studied ZVIs.

Sample	**PSD[a]** D_{10}, D_{50}, D_{90} (µm)	**BET[b]** (m^2 g^{-1})
mZVI-1	22, 41, 62	0.09
mZVI-2	1, 5, 12	1.10
mZVI-3	2, 30, 59	0.51
mZVI-4	24, 56, 99	0.06
mZVI-5	1, 3, 9	nm
BASF HQ	0.6, 1.2, 2.4	0.82
NF25s	D_{50} < 0.05[c]	25.0[c]

[a] Particle Size Distribution.
[b] BET : Specific Surface Area according to Brunauer-Emmett-Teller (Single point measurement) - analysis was conducted by Höganäs.
[c] Producers data.
nm – not measured.

The CAH-degrading inoculums consisted of an enrichment culture containing *Dehalococcoides* spp. and vcrA gene involved in CAHs degradation.

Batch dechlorination experiments

The test is set up in 37 ml glass vials with Teflon lined crimp-caps. Each vial contained different concentration of the iron (0.05; 0.5; 1; 2; 15; 30 g L^{-1}), 18 ml anaerobic simulated groundwater + 2 ml of inoculums and final concentration of 10 ppm TCE. Everything is set up under anaerobic conditions and in duplicates. The vials were incubated at 12°C and shaking. TCE, degradation products and H_2 were measured at start (only blank), and after 2, 4, 10 and 16 weeks. Additionally, 0.5 ml of sample was taken for biomass measurements. After 10 weeks of incubation 1 mL of sample was taken for lactate measurements.

Chemical analyses

Concentrations of CAHs, ethane, ethane and acetylene were determined via headspace measurements using a Varian GC-FID (CP-3800) equipped with a Rt-U plot column for the detection of ethene, ethane and acethylene or a split-splitless injector followed by a Rt-X column (Restek) and a DB-1 column (J&W Scientific) for analysis of CAHs. Hydrogen production at each sampling point was analyzed using a GC-TCD (Interscience). At last sampling point the pH was measured using a pH meter (Radiometer). Lactate was measured by GC-FID (TRACE) – column Alltech ATTM-1 (Length 30 m ID 0.53 Film thickness 5 µm).

Adenosine tri-phosphate (ATP) analyses

Bioluminescent biomass was analysed using commercial ATP bioluminescence assay (Eydal & Pedersen, 2007). Total ATP as an indicator for viable biomass was determined using the BacTiter-Glo™ reagent (G8231; Promega Corporation, Dübendorf, CH) and Luminoskan Ascent Microplate Luminometer (Thermo Labsystems). The BacTiter-Glo™ reagent was prepared according to the manufacturers procedures and stored as previously described by Hammes et al. (2010).

RESULTS

Impact of different ZVIs on CAHs biodegradation potential

A CAH batch degradation experiment was performed in liquid medium supplied by CAH-degrading mixed bacterial culture in the presence of different doses of mZVI and nZVI (0.05 – 30 g L^{-1}). Because of the absence of aquifer material, and as such of buffer capacity and protecting niches, the test results are to be considered as a worst case scenario. Both ZVI and the used bacteria degrade CAHs. TCE concentrations and degradation products were measured over time to give more details on degradation activity of present CAH-degrading mixed microbial culture (Figure 1), which follows predominantly a different degradation pathway (hydrogenolysis) in comparison with different ZVI (predominant β elimination). It is evident that after 16 weeks TCE was completely removed to ethane by the present CAH-degrading bacteria in the used enrichment culture. High concentrations of methane (results not shown) were also observed as an activity of methanogens present in the culture.

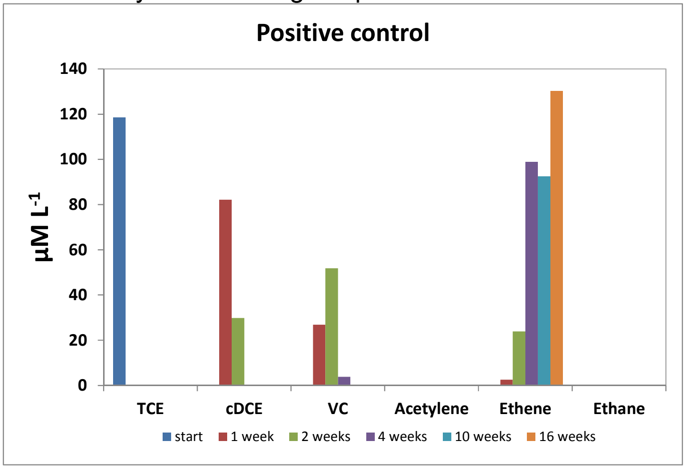

Figure 1: TCE biodegradation in the presence of CAH-degrading mixed bacterial culture.

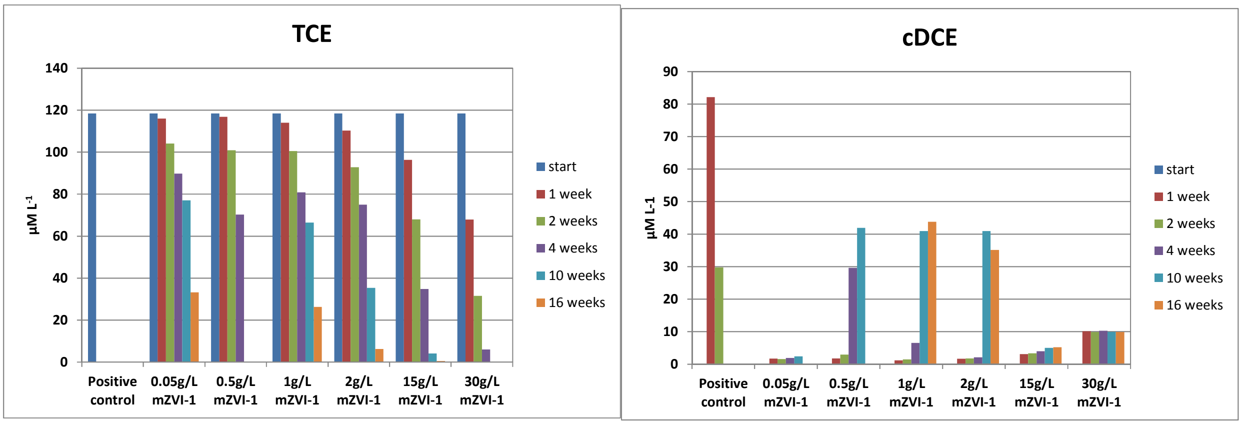

Figure 2: TCE degradation by different concentrations of mZVI-1 with formation of cDCE as degradation product.

TCE degradation in the presence of the bacterial inoculums together with different doses of mZVI-1 are presented in Figure 2. Introduction of mZVI-1 into the system clearly impacts negatively the TCE biodegradation. However, cDCE concentrations measured for the mZVI-1 concentration range of 0.5-2 g L^{-1} indicate that bio processes are still active and microorganisms were adapted to the new conditions after the initial stress. Moreover, based on earlier tests, the main degradation pathway for mZVI-1 was β-elimination where cDCE as degradation product does not appear. Similar effects were observed for other mZVIs (data not shown).

Impact of different ZVIs on bacterial activity

The impact of different ZVIs on the test organisms was evaluated mainly via ATP measurements, giving a general indication of the microbial activity. Results of the ATP measurements during the test with different mZVI-1 and NF25s are shown in Figure 3. Based on ATP measurements, in the batch reactor with microscale irons stimulation of bacterial activities was observed immediately after the start and lasted for several weeks. The addition of lactate after 3 weeks clearly stimulated the bacterial activity. The stimulation was less pronounced and shorter in time with higher ZVI doses. For the highest doses of mZVI-3 (15-30 g L^{-1}) an inhibition of the bacterial activity was found (results not shown). In the presence of these higher concentrations, after 2 weeks, also decreased activity was observed for mZVI-2 (30 g L^{-1}), mZVI-4 (30 g L^{-1}), mZVI-5 (15-30 g L^{-1}) and BASF HQ (15-30 g L^{-1}), without reactivation after the lactate spike. In contrast, in the reactors amended with NF25s, an immediate inhibition of the bacterial activity was observed already with the lowest tested dose (0.05 g L^{-1}). This is even lower than previously reported study stating that a nZVI concentration above 0.3 g L^{-1} is completely inhibitory on biodegradation (Barnes et al., 2010).

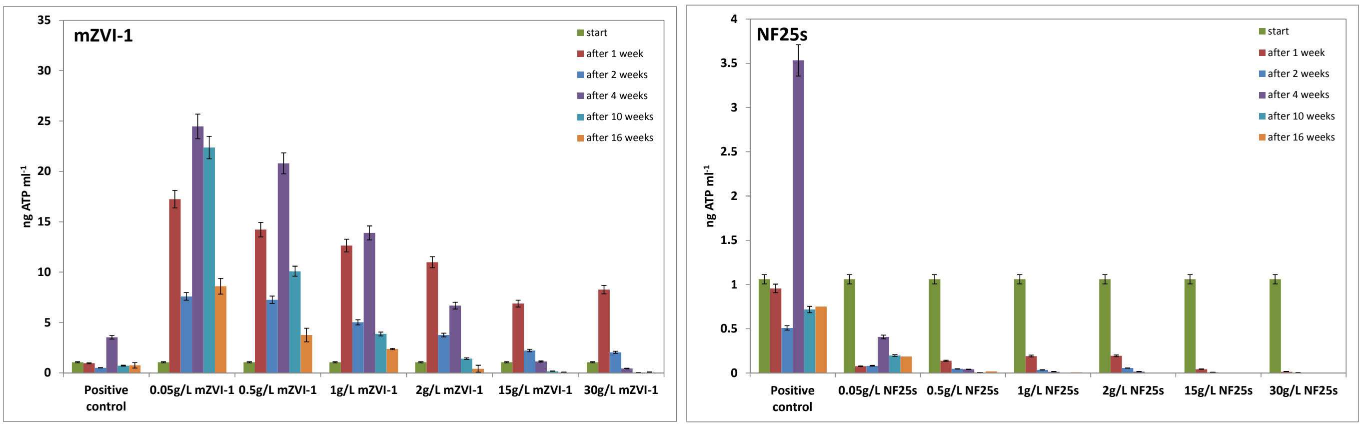

Figure 3: The average ATP amounts as an indication of mZVI-1 and NF25s impact on CAH-degrading mixed culture.

Consumption of lactate (added as electron donor) was followed as a second bio-indicator. Remaining lactate concentrations in the batch reactors (after 10 weeks of experiment) are shown in Figure 4. According to the data, in the presence of NF25s, a complete inhibition of lactate consumption (bacterial activity) was observed from doses as low as 0.5 g L^{-1}. For mZVIs, a clear dose effect was observed with a complete consumption of the lactate till a concentration of 2 g L^{-1} (mZVI-1, mZVI-2, mZVI-4), 1 g L^{-1} (mZVI-3), 0.5 g L^{-1} (BASF HQ) or 0.05 g L^{-1} (mZVI-5). Finally, these inhibitions could be correlated well with the measured pH values (Figure 5). When the pH increased above the cut-off value of pH 7.5, lactate was not consumed. Optimal pH ranges for several Dehalococcoides species capable of reductive dechlorination of chlorinated ethenes and ethanes are near neutral (Gerritse et al. 1999). Overall, the observed inhibiting effects on TCE biodegradation could be related to pH increases above pH 7.5, which are induced by the chemistry of ZVI itself. This is also confirmed by inhibiting effects more pronounced in the batch systems supplied by higher ZVI doses.

CONCLUSIONS

ATP bioluminescence assay was used to examine worst case scenarios for impact of ZVIs on CAH-degrading enrichment cultures. High doses of mZVI (> 15 g L^{-1}) had negative effects on ATP production and lactate consumption of the enrichment culture. These experiments were, however, performed without aquifer material, which is likely to provide buffering capacity and protecting niches for microorganisms. To finally quantify potential negative effects on CAH-degrading bacteria under realistic "in situ" conditions, additional experiments (simulating natural conditions and including the actual aquifer material) would be helpful. However, as the aquifer matrix interferes with the measurement, a worst case scenario was tested in the current test.

According to the presented data, decrease in bacterial activity is less pronounced for mZVI than for nZVI particles. Based on ATP measurements, mZVIs can even stimulate the bacterial activity. The impact of individual mZVIs differs between the mZVI types testes. The impacts of all ZVIs could be correlated well with the pH increase caused by the ZVI, which is more pronounced with higher ZVI doses. Changes of pH values in the subsurface during in-situ remediation are inherently connected to other remediation technologies (for instance alkaline induced chemical oxidation). Therefore the impact of mZVI injections into the subsurface (saturated zone) is not more impacting than some other technologies. Overall, when looking at the data and the concentrations aimed at in the subsurface, the harmful impact of mZVI on the subsurface is estimated to be rather limited.

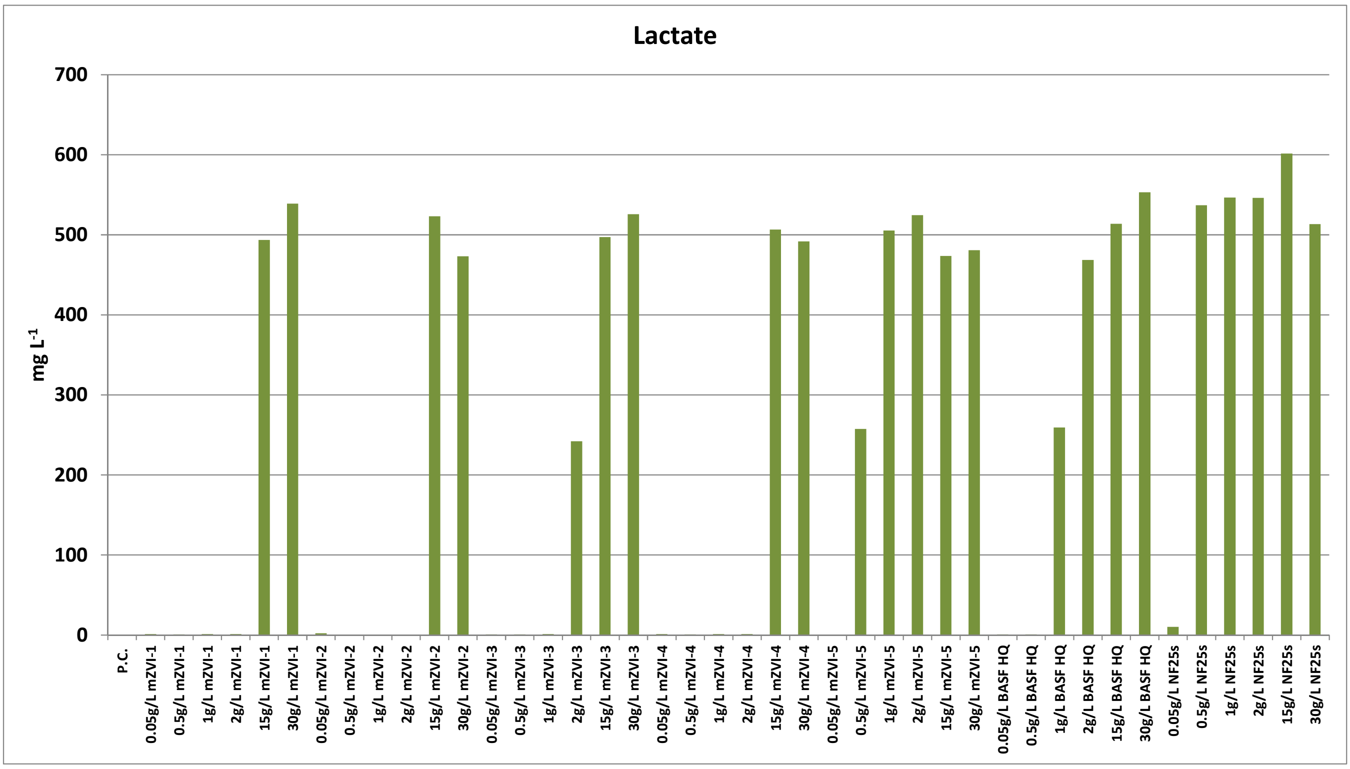

Figure 4: The lactate consumption in batch reactors (after 10 weeks of experiment).

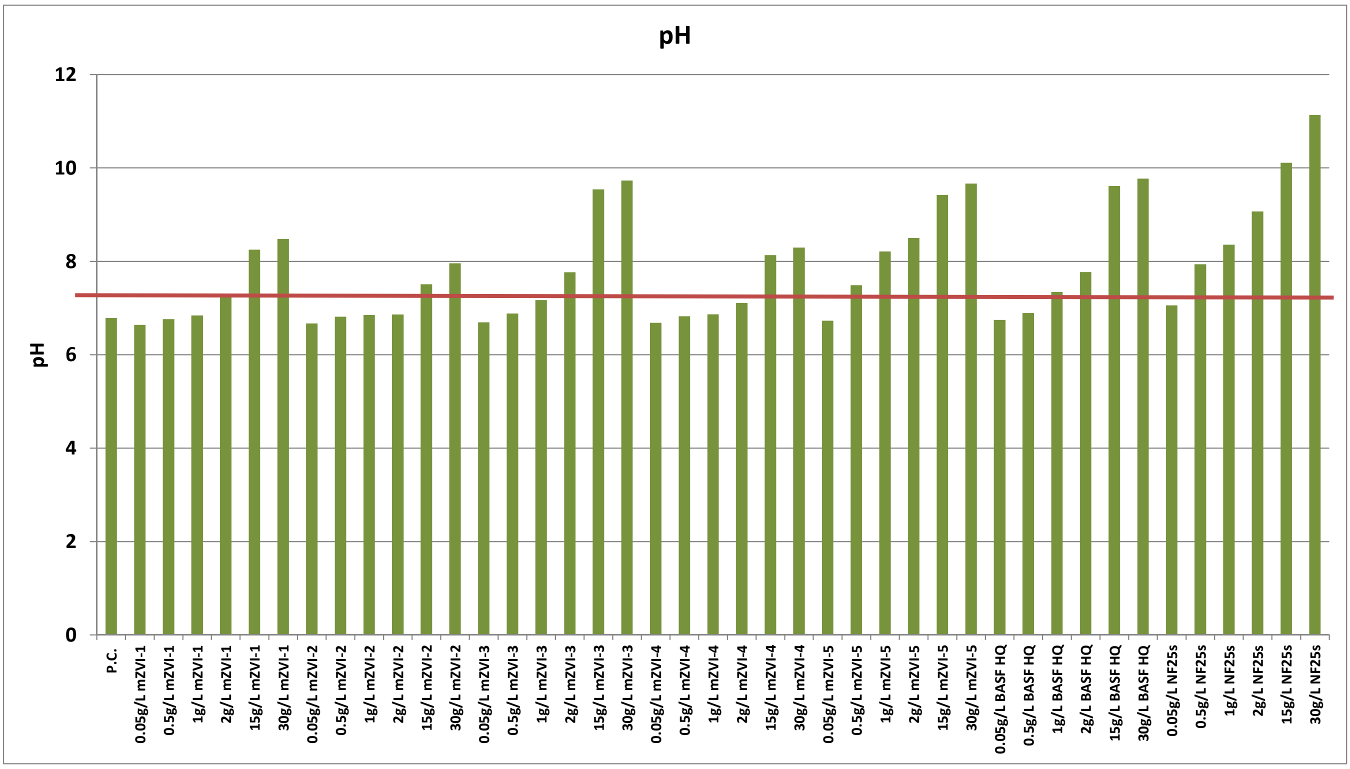

Figure 5: pH values measured at the end of experiment.

ACKNOWLEDGEMENTS

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Ecotoxicity assessment of small-sized reactive iron particles

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Within the AQUAREHAB project, different types of injectable reactive particles have been studied for groundwater remediation purposes. Along with the field application of particles, evaluation of their environmental risks is of concern. The objective of the present study was to assess ecotoxic impacts of small-sized reactive iron particles on both aquatic species (bioluminescent bacteria, algae) and soil biota (plants - two species, annelid worms). Six out of seven tested iron particle samples (differing in size, composition and manufacturer) showed no significant effects in any of the bioassay up to the highest tested doses (2 g/L in water suspension or 5 g/kg in the soil). Tests with one particle sample (coded H16) showed slight inhibitory effects on the growth of aquatic green alga Pseudokirchneriella subcapitata and strong toxicity in soil bioassays, i.e. inhibitions of root growth of two plant species (dicotyledon lettuce Lactuca sativa, monocotyledon oat Avena sativa), and reproduction of annelid worm Enchytraeus crypticus. The effects were concentration-dependent and occurred at relatively high doses of particulate matter (0,5 g/kg soil or higher). Interestingly, leachates prepared from the same particles had no toxic effects in any of the assay, and the composition of the toxic sample H16 was not qualitatively different from all the other tested particles. These observations suggest that the effects were not related to the chemical composition but rather to some other properties of the particulate material such size, surface area, charge, etc. The ageing experiments (i.e. 20 and 40 day prolonged incubation of the particles in the soil) resulted in significant decline in the particle toxicity below the toxicity threshold level. Despite of the effects observed, overall benefit-to-risk ratio is positive considering rather minor and local scale of the potential ecotoxicological impacts (few square meters affected for the worst case situations of accidental spills during the particle application). However, several questions remain open such as non existing environmental quality standards or limited methods for particle toxicity testing. Further research is therefore needed to fully understand environmental risks of particle materials, which appear to be selective to certain but yet undisclosed physico-chemical properties.

Life-time of Zerovalent Iron Particles Determined via Direct Hydrogen Measurements in Batch Reactors

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In the framework of the FP7 AQUAREHAB project (GA 226565) a standardized batch test procedure was developed and used to evaluate the reactivity of different microscale zerovalent iron (mZVI) particles (newly developed by Höganäs - Sweden and commercially available) towards different chlorinated aliphatic hydrocarbons (CAHs) in liquid medium. Granular iron and commercially available nanoscale zerovalent iron (nZVI) particles were included in the study as controls (Velimirovic et al., 2013).

As a consequence of anaerobic corrosion, hydrogen gas is formed in the batch reactors during the degradation of CAHs which can be used as an indicator of iron corrosion. Therefore, zero-order fits of H_2 formed in batch reactors (with and without aquifer material) over time were used to calculate the corrosion rate and derive corresponding life-times for the different zerovalent iron (ZVI) particles. This approach was found to be more reliable than the estimation of the life-time via pressure measurements.

The aim of this study was: (1) to assesses the life-time of different ZVI particles and correlate it to the previously reported particles reactivity (Velimirovic et al., 2013) in aquifer free conditions; (2) to evaluate the impact of aquifer material and real groundwater polluted by different CAHs on the ZVI particles corrosion rate and consequently life-time; and (3) to estimate ZVI particles life-time using a customized PHREEQC model including inhibitory effect of the iron corrosion reaction products.

The obtained results from the batch tests in aquifer free conditions showed that particles with fastest degradation kinetics (nZVI) have the highest corrosion rate and consequently will be consumed faster after the injection in the field. The main outcome of this study was that the corrosion rate of ZVIs increases: (1) with decreasing particle size, (2) with increasing the specific surface area of the particle and (3) with the presence of aquifer (due to pH and buffer capacity). In the presence of aquifer the life-time of mZVIs using zero-order fitting was 0.9-4.7 years for mZVIs and approximately 5 days for nZVI. According to the proposed model estimated life-time of mZVIs (0.4-1.7 years) under field conditions would be higher than for the nZVIs (10 days).

Impact of the composition of microscale zerovalent iron (mZVI) on its reactivity towards chlorinated ethenes

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The use of zerovalent iron (ZVI) for in-situ reductive dechlorination of chlorinated aliphatic hydrocarbons (CAHs) has been shown over the last decades as a proven technology. Moreover, kinetic data for dechlorination of different CAHs has been published extensively. Important factors influencing the degradation kinetics of mZVI comprise its surface characteristics like specific surface area, chemical composition, crystallinity and morphology. In the current study, we focussed on the effect of the carbon, oxygen and sulphur content of the mZVI particles on the rate of perchlorethylene (PCE), trichloroethylene (TCE), cis-dichloroethylene (cDCE) and 1,1,1 trichloroethane (1,1,1-TCA) reduction.

Previously, kinetic data for degradation of common chlorinated solvents by different microscale zerovalent iron (mZVI) particles under consistent experimental conditions were reported (Velimirovic et al., 2013). Comparison of these reactivity data with the C, O- and S-content of the tested mZVIs proofs clearly that not only the surface area of mZVI particles effects the iron reactivity, but also that its chemical composition has an important role in the reduction of CAHs by mZVI. Correlation analysis revealed that dechlorination of CAHs is generally more rapid by irons containing less oxygen, while a high carbon content induces nonreactive sorption of the contaminants on the particles and reduces the degradation rate significantly. The influence of S-content was less clear. Finally, this study reveals that for efficient remediation of CAHs by mZVI particles, the mZVI carbon and oxygen content should not exceed 0.5 % and 1 % respectively.

This study is being performed as part of the European Union Project AQUAREHAB (FP7 – grant agreement Nr. 226565).

Session 4
Water Management

Oral presentations

A scenario analysis of measures tackling nitrogen discharge in the Scheldt river basin

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ABSTRACT: The diffuse pollution from agriculture or other sources is difficult to apprehend, especially in large transnational river basins. Therefore, a spatially explicit conceptual model for scenario analysis (SECOMSA) was developed in the AQUAREHAB project (EU FP7) to enable a long-term cost-effectiveness analysis of measures tackling diffuse pollution. SECOMSA was developed for an evaluation of the nitrogen dynamics in the Scheldt basin since this nutrient is of specific concern in the catchment. The hydrological uncertainty was incorporated in a Bayesian belief network to visualize overall model outcomes in a webbased environment: REACHER. Results suggest that it will not be technically feasible to reach the Flemish Total N threshold value in the entire Scheldt catchment by 2015 and difficult to reach in 2021 or 2027. Natural water retention measures and the extension of the sewer network show the largest potential for the remediation. But other measures could prove more efficient if different legal objectives, e.g. ammonium-N, are taken into account.

INTRODUCTION

The European Union (EU) adopted the Water Framework Directive (2000/60/EC) (WFD) which aims to achieve a 'good status' of the aquatic ecosystems by 2015. The ten years of monitoring and simulation that followed highlighted the impact of the diffuse pollution of nutrients in many river basins with important agricultural activities. Unfortunately, the diffuse pollution from agriculture or other sources is difficult to apprehend. Moreover, the WFD requires an international coordination with the aim of producing a single international river basin management plan (RBMP) for transnational river basins. National authorities remain responsible for the implementation of the WFD regulations on their territory but for aspects related to cross-border river basins and aquifers, a forum is necessary to align the various actions, e.g. the international Scheldt Commission (ISC, http://www.isc-cie.org/). However, as mentioned above it is difficult to evaluate the effect of diffuse pollution on the aquatic ecosystem's status. The evaluation by the various actors can vary significantly since they most often employ different target levels, monitoring strategies and water quality simulation tools, complicating the international coordination. The discussion could thus benefit from a generic analysis tool that highlights the most serious challenges and points to potential cost-effect measures for each stakeholder in reaching an overall good status of the aquatic ecosystem. Therefore, a spatially explicit conceptual model for scenario analysis (SECOMSA) was developed in the AQUAREHAB project (EU FP7) to enable a long-term cost-effectiveness analysis of measures tackling diffuse pollution. SECOMSA was developed for an evaluation of the nitrogen dynamics in the Scheldt basin since this nutrient is of specific concern in the catchment. The hydrological uncertainty was incorporated in a Bayesian belief network to visualize overall model outcomes in a web based environment: REACHER.

MATERIAL AND METHODS

The study area

The Scheldt basin covers almost 22000 km^2 and is located in Belgium, France and The Netherlands (Figure 1). It is a typical lowland catchment with a maximum altitude of 205 m a.s.l. The climate is temperate with an average precipitation of 845 mm/y and an average monthly temperature ranging from 2 to 17 °C (ECA&D, 2008). The Scheldt basin is for 22% industrialized and urbanized with over 10 million inhabitants. Only 8% of the basin is classified as forest or nature reserve in the CORINE 2005 dataset (EEA, 2008). Intense agricultural activities account for the remaining 70% of the landuse. The multiple pressures result in an inadequate ecological status in 64% of the surface waters in 2009 (ISC, 2009). The current measures have reduced the nitrogen load in the surface waters by 15% but no marked improvements of the ecological status are expected before 2015, illustrating the importance of dynamic simulations for a longer period of time.

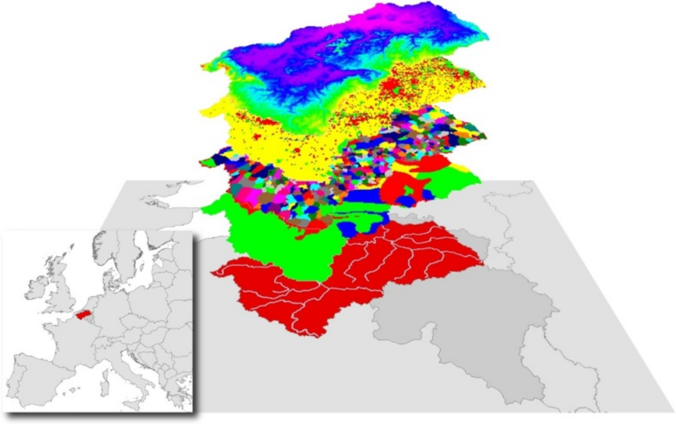

Figure 1: the Scheldt river basin with available GIS data on the location of the main rivers, the aquifer texture, the waste water treatment zones, the land use and the digital elevation model, indicated from bottom to top.

The conceptual model

The conceptual model is a compromise between model complexity, the available data and the applicability to scenario analysis. It consists of 4 modules that describe the hydrology, nitrogen discharge, the reactive transport and the implementation of measures. The four modules were dynamically coupled in a Python environment using the PCRaster and NumPy libraries. A monthly time step was chosen since water quality variables were only available with this time interval and since data on nutrient discharge were available at a higher time resolution as yearly input data per province. A smaller time step (e.g. daily) would thus needlessly complicate the process descriptions. The spatial discretization was set to 1 km^2 due to the large size of the catchment and related processing times.

Nitrogen inputs

Data on industrial and household nitrogen discharges in the river basin were supplied by local government agencies for the year 2006 (VMM, Flanders; DGRNE, Walloon region; Agence de l’eau Artois Picardie, France). The discharge was positioned at the specific location of the industrial discharge or at the location of the waste water treatment plant (WWTP) of the related sewer system. The diffuse discharge of nitrogen is calculated from the difference of atmospheric deposition, agricultural discharge and crop yields. The atmospheric deposition was adapted from data provided by the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP, 2008). The agricultural discharge was calculated from data on fertilizer use and livestock numbers per year and per province obtained from the statistical office of the European Union (Eurostat) and from regional manure import/export data. The crop yield was calculated from crop data per year and per province obtained from Eurostat. The agricultural data were homogeneously distributed over the agricultural area per province.

The hydrological and mass transport modules

The studied domain is described by 4 compartments that can be physically interpreted: the soil, the shallow subsurface, the deep subsurface and the river network (Figure 2). The direction of water movement through the compartments is pivotal in the conceptual model and is determined by the topography. Water moves in the direction of the steepest slope in all model compartments and is characterized by the local drain direction (LDD) (Wesseling & van Deursen 1997). This abstraction of flow paths in the subsurface is considered acceptable at a large scale.

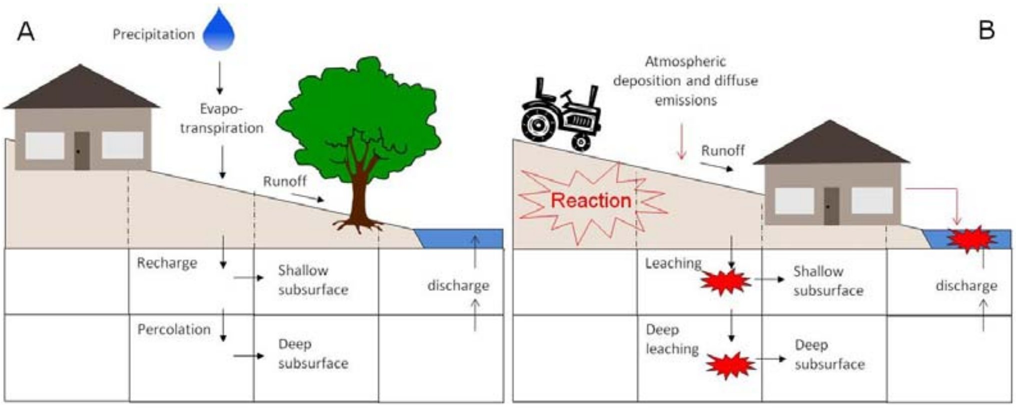

Figure 2: The conceptualisation of the studied domain with the considered processes in water flow (A) and mass transport (B).

The different processes in the hydrological and mass transport modules were calibrated to monitoring data of water flow and nitrogen concentration in the river network. These data were obtained from the VMM, Flanders and the Agence de l'eau Artois Picardie, France. It resulted in a Nash-Sutcliffe efficiency of 0.5 for the hydrological module and an overall root mean square error of less than 50% for the nitrogen concentration in the river network. These values were considered acceptable taking into account the large uncertainty of the input data and the generic description of the agricultural practices.

Measures

Five measures are discerned in the final module of SECOMSA: conventional measures such as cattle reduction, fertilizer reduction or the extension of the sewer network and innovative measures to treat local hotspots of diffuse discharge in surface waters such as wetlands and buffer strips. The impact of a measure is defined by the implementation rate (IR), efficiency (Eff) and the application potential (App):

$$Load\ reduction = IR \times Eff \times App \times Load$$

Conventional measures can be homogeneously distributed over studied area and the effect is directly related to the implementation rate, considering no efficiency changes. The impact of the innovative technologies, i.e. wetlands and bufferstrips, was further spatially distributed by defining the efficiency (in relation to the aquifer texture) and the application potential (in relation to the type of waterways in the subcatchment). The variables are shown in Table 1.

Table 1: Measures in SECOMSA with their respective implementation rates that were considered acceptable.

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

*u.d. the user can define efficiencies based on additional data or expert knowledge
** d. The application potential is distributed per subcatchment as the percentage of smallest class rivers.

The measures were evaluated for the 19 subcatchments in the Scheldt river basin as required by the REACHER tool. Outputs were generated for the years 2015, 2021 and 2027 as the European Commission allows for the Member States to motivate a time derogation for reaching the objectives for 2015 by the next reporting period in 2021 or finally in 2027. The conceptual model evaluated all combinations of measures for 50 different meteorological inputs (derived from historical records) in order to approximate the hydrological uncertainty in the model predictions. The output is evaluated by comparison to the summer average nitrogen concentration threshold, a legislative norm for Flanders (Table 2). Other regions further upstream (Walloon Region, France) apply other threshold values.

Table 2: Thresholds (summer average values) for large rivers in the Scheldt basin

	Reference	Very good/good	Good/moderate	Moderate/bad	Bad/Very bad
Total N [mg/L]	0.93	2.0	2.5	5.0	7.5

RESULTS AND DISCUSSION

Results suggest that the good status will not be attained in the Scheldt river basin by the final reporting period of 2027 if no additional measures are taken compared to the final calibration year 2007 (Figure 3). These results should be treated with care since the simulation results were not validated after the year 2007 and the hydrological uncertainty yielded a standard deviation of 30% for the output values. Moreover, the status is defined based on the summer average total nitrogen concentration and results could be different for ammonium-N or winter nitrate thresholds.

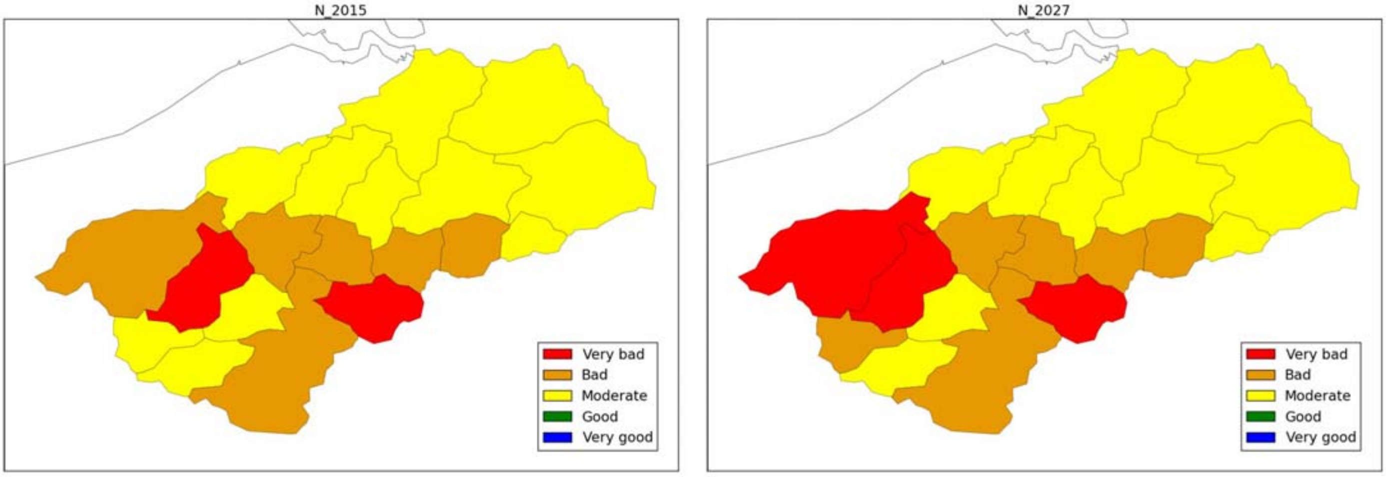

Figure 3: Modelled status of subcatchments in the Scheldt river basin in 2015 and 2027 if no additional measures are implemented compared to the reference year 2006.

The model was subsequently used to assess the required load reduction in each subcatchment relative to the inputs, assuming that the upstream catchments reach the good status. Figure 4 shows that in some catchments the required mass reduction is achievable without large efforts, e.g. the Campine region or the Sensée catchment.

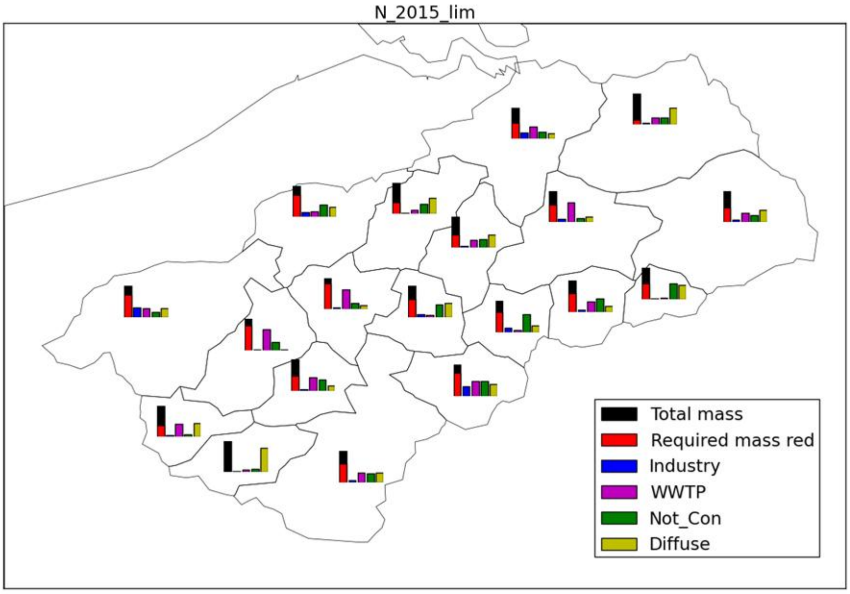

Figure 4: The different inputs of nitrogen in each subcatchment expressed relative to the total mass input (black bar). The required nitrogen load reduction to reach good status, as suggested by SECOMSA is indicated by the red bar. The remaining part of the total mass input (black) is removed by natural attenuation and yields a total N concentration below the threshold at the outflow at the subcatchment. .

In other subcatchments it will be very difficult and additional investments in the treatment of municipal wastewater seem needed in addition to the measures discerned in this research.

Finally, SECOMSA evaluated the best achievable status with the estimated technical feasibility of the evaluated measures. Figure 5 indicates that according to the current conceptual understanding and evaluated threshold, a good status can be reached in almost half of the catchments by the final reporting period of 2027. One catchment seems problematic but this could be related to the uncertain input data of the domestic nitrogen load discharging in the river network. Moreover, the model does not predict an improving status with time. This is not due to long-lasting diffuse inputs out of the groundwater since these are estimated to reach steady-state values within 5 years after measures are implemented. The lack of dynamics in time is related to the simulated point source nitrogen discharges from households and industry that remain at the levels of the reference year 2006 or the last processed data in 2007. As such, the dynamic behaviour of the model should be re-examined to improve the conceptual understanding of the nitrogen dynamics.

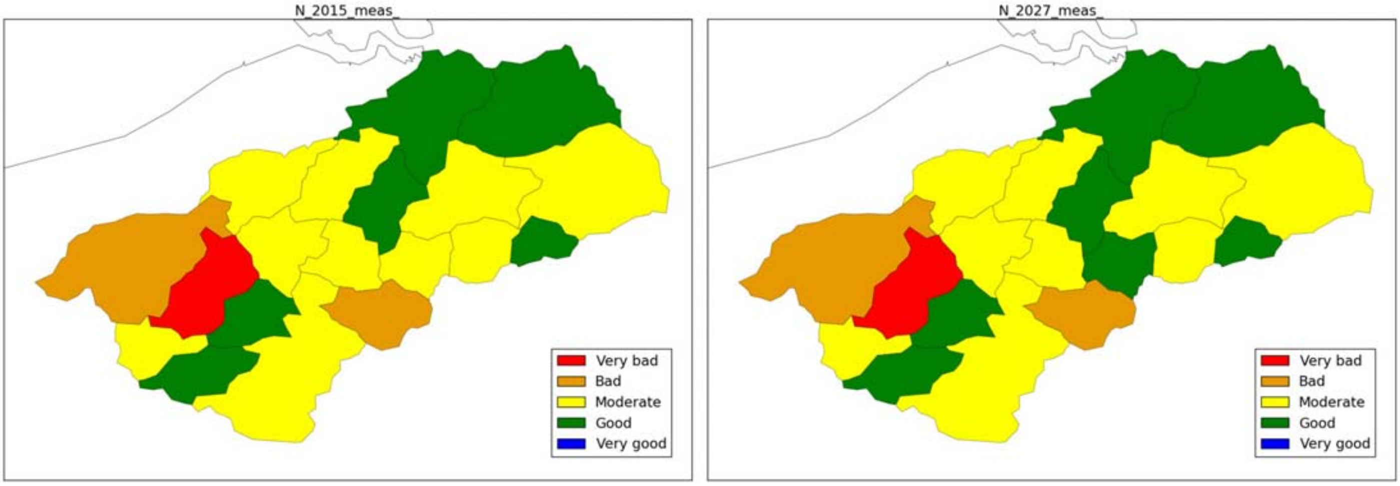

Figure 5: the maximum achievable status in the Scheldt river basin for the Flemish 'Total N' threshold with the estimated technical feasibility of the implemented measures.

A general cost-effectiveness ranking showed that the construction of buffer strips and wetlands outranks conventional technologies such as fertilizer and cattle reduction. But the latter technologies can achieve a larger nitrogen load reduction. An extension of the sewer network seems the most preferable measure with intermediate cost-effectiveness but a high potential for nitrogen load reductions. It should be acknowledged that these results were obtained for the summer total N objective. The ranking could change for other objectives as mentioned above.

CONCLUSIONS

The Python/PCRaster environment provided a good platform for the development of a conceptual model that can further the interaction between stakeholders in river basin management. The development of the SECOMSA model indicated the need for uniform detailed spatial data at the large scale. In addition, the lack of dynamic behaviour in future model predictions should be examined in more detail. Results suggest that domestic waste loads should not be underestimated in order to reach the WFD goals. SECOMSA indicated that it will not be technically feasible to reach the Flemish Total N threshold value in the entire Scheldt catchment by 2015 and difficult to reach in 2021 or 2027. Water retention measures and the extension of the sewer network show the largest potential for the remediation. But other measures could prove more efficient if different legal objectives, e.g. ammonium N, are taken into account.

ACKNOWLEDGEMENTS

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The Water Framework Directive Explorer: An interactive tool for the selection of measures

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The WFD explorer is an analysis tool to calculate the effect of restoration and mitigation measures on the ecological and chemical quality of surface waters. Users will gain insight in the effectiveness of programmes of measures in relation to WFD objectives. Measures can be defined both related to point sources such as wastewater treatment plants, and diffuse sources such as agriculture and traffic. Likewise, it is possible to calculate the effectiveness of restoration measures such as stream re-meandering or the construction of near-natural riparian zones.

The WFD explorer is a flexible tool. Users can easily import or adjust e.g. their own schematisation of a river basin, emission data and area specific characteristics. The user-friendly user interface makes it easy to set up a model structure, perform an analysis and produce reports in an organized and systematic way.

The WFD explorer can be used to:

- assess the current status of WFD water bodies;
- compare the effectiveness of measures in relation to WFD objectives;
- gain insight in the effectiveness of programmes of measures;
- gain insight in the differences between various water bodies within the river basin both regionally and internationally as well as between freshwater and marine water bodies;
- stimulate and structure the development of ecological knowledge;
- produce clear reports (maps and tables) to be used in policy briefings, for the communication with stake

COMFRACS: A conceptual model for a regional assessment of contaminated sites

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ABSTRACT: The European Groundwater Directive (2006/118/EC) states that, where necessary, Member States should assess possible threats for human health and the environment of plumes resulting from point sources. The contaminated sites are typically managed on a case by case approach. But an additional management tool at a larger scale could be worthwhile taking into account that on average 35% of the remediation costs is derived from public budgets (EEA, 2007). A conceptual model for a regional assessment of contaminated sites (COMFRACS) was developed as a prototype for groundwater contaminated with mineral oil and chlorinated hydrocarbons. The GIS capabilities of the Pyhton/PCRaster framework facilitate a spatially resolved evaluation of remediation technologies at a larger management scale. However, improvements regarding the representation of groundwater flow, aquifer characterisation and natural attenuation rates are necessary for an eventual application of COMFRACS. The output of COMFRACS can be used to compare the impact of different remediation measures (flux reductions) with potential economic benefits to comply with sustainable management practices, as is illustrated in the derived REACHER-LOCAL tool.

INTRODUCTION

Member States are establishing national inventories of contaminated sites in accordance with the proposal for the Soil Framework Directive (COM (2006) 232). And the European Groundwater Directive (2006/118/EC) states that, where necessary, Member States should assess possible threats for human health and the environment of plumes resulting from point sources. However, data indicate a challenging and long-lasting effort for preserving groundwater reserves with an estimated total of 250000 contaminated sites in the member countries in 2006 and with only 80000 remediated sites in the past three decades (EEA, 2007). The contaminated sites are typically managed on a case by case approach. But an additional management tool at a larger scale could be worthwhile for regional managers or decision makers, taking into account that on average 35% of the remediation costs is derived from public budgets (EEA, 2007). Therefore, this research examined how data from national inventories can be coupled to readily available data in Geographical Information Systems (GIS) to provide valuable information for risk assessment and trend analysis at a larger management scale.

A conceptual model for a regional assessment of contaminated sites (COMFRACS) was developed for groundwater contaminated with mineral oil and chlorinated hydrocarbons in Flanders, Belgium. It makes use of the extensive database of the Public Waste Agency of Flanders (OVAM) that is coupled to the Python/PCRaster numerical framework via a PostgreSQL/PostGIS database. Four different management options were simulated in the year 2013: no action, source zone remediation or a homogeneous mass removal of 30% or 80% of the contaminants in the groundwater. The latter two options specifically evaluate measures that would tackle contaminant plumes. The resulting effects of the different actions are simulated up to the year 2035. This work was further complemented with a technological evaluation of potential measures and a cost-benefit analysis of reducing groundwater contamination for the society in the REACHER-LOCAL tool.

INPUT DATA AND PREPROCESSING STEPS

The available monitoring data for benzene, toluene, ethylbenzene, xylenes (m-, o- and p-), 1,1,1-trichloroethane, 1,1-dichloroethane, perchloroethene, trichloroethene, dichloroethenes (cis- and trans-), and vinylchloride were obtained from the Public Waste Agency of Flanders (OVAM) for the years 1993 to 2013, yielding 2.3 million data points. Each point contains data for attributes that point to the parcel ID, the contaminant, the measured value and its unit, the sampling date, the top and bottom of the screen, the geographic coordinates in the Lambert 72 projection (EPSG: 31370) and the elevation of the ground surface in mTAW. The raw data were inserted in a PostgreSQL/PostGIS database to enable a fast geographic querying in a later stage.

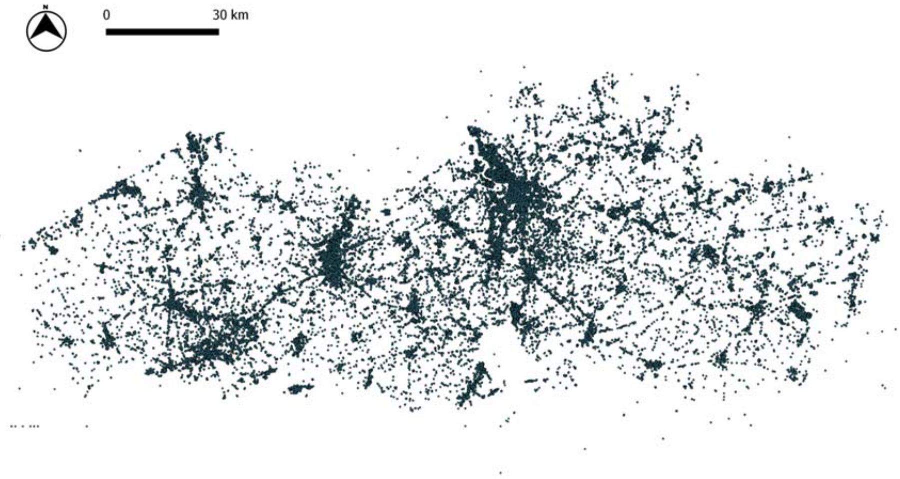


Figure 1: the data points that were obtained from OVAM with the monitoring data of the selected contaminants.

A digital elevation map (DEM) of Flanders at a resolution of 25 m, and a vector dataset that defines the location of the waterways in Flanders (‘Vlaamse Hydrografische Atlas’, VHA) were obtained from The Flemish Geographical Information Agency (FGIA). The geographic extents and discretization of the DEM were selected as the standard in this research, further referred to as the clone. The vectorized VHA data were rasterized to the geographic extents of the clone using GDAL (www.gdal.org).

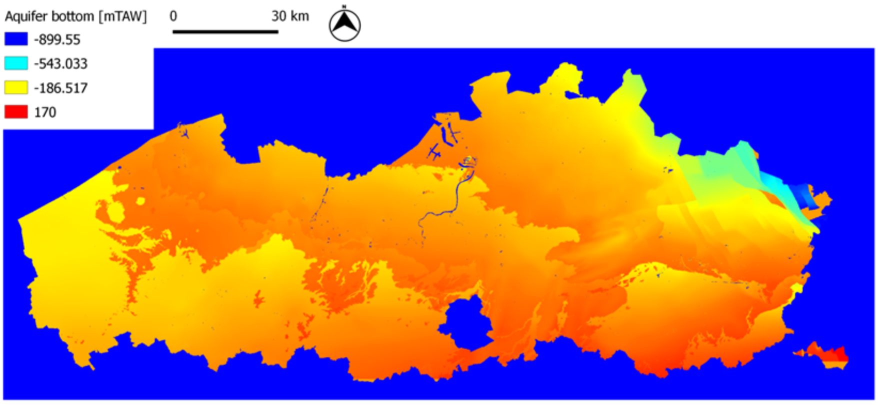


Figure 2: the depth of the conceptual phreatic aquifer in Flanders, as determined from the VGM.

The subsoil is characterized by the main hydrogeologic units as defined in the ‘Concept Vlaams Grondwatermodel (VGM)’ (Meyus et al., 2000). The selected units represent the quaternary layers, the Campine aquifer system, the Brusseliaan, Ieperiaan, groups of Landen, Chalk deposits and the Sokkel. The GIS data were obtained from the Flemish Environment Agency (VMM) as raster maps at a 100 m resolution. The data were resampled to the geographic extents of the clone using GDAL. In order to proceed with the conceptual framework, it was currently assumed that the top layer of the selected hydrogeologic units beneath the quaternary layers represents the bottom part of the phreatic aquifer. The depth of the aquifer was arbitrarily set to 50 m below the groundwater table (see further) if no other data were available within the Flemish territory, and to -999 otherwise (see Figure 2).

A steady state groundwater table elevation in Flanders was previously calculated by VITO (van der Kwast et al., 2009). It was derived by interpolating the monitoring data of the groundwater table elevation of the VMM using a statistical method taking into account the recharge, the soil characteristics and the distance to surface waters. These data were reported at a resolution of 50 meter and were resampled to the clone using GDAL. The direction of the groundwater flow was subsequently determined following of the steepest gradient for each grid cell using the PCRaster operator ‘*ldd*’. Groundwater was assumed to discharge in waterways of class 3 or higher as described by the VHA (see above). The resulting map with the local drain direction (LDD) of each cell can be used to calculate the groundwater velocity as:

$$v = K_c \frac{\partial H}{\partial x}$$

With v the groundwater velocity [m d^{-1}], K_c the hydraulic conductivity [m d^{-1}] and dH/dx [-] the head gradient between two adjacent cells following the LDD.

Table 1: the selected physical properties of the different hydrogeologic units according to literature data and expert opinion (Meyus et al., 2000; Wiedemeier et al., 1999; Patyn J. (VITO) personal communication)

	Porosity [-]	Conductivity [m d^{-1}]	f_{oc} [‰]
Quaternary deposits:			
Sand	0.2	15	3.0
Loam/sand	0.2	5	3.0
Loam	0.15	1	3.0
Loam/clay	0.2	0.1	3.0
Clay	0.2	0.1	3.0
Deeper deposits:			
Campine aquifers	0.2	10	1.0
Brusseliaan	0.2	15	1.0
Ieperiaan	0.15	5	1.0
Groups of Landen	0.2	5	1.0
Chalk	0.2	120	1.0
Sokkel	0.2	10	1.0

Table 2: substance specific parameters for the shallow and deep conceptual layers. The worst-case values of the different isomers were chosen for the xylenes and DCEs. (EPA, 2004; AQUAREHAB WP4, DL4.2)

	K_s [mg L^{-1}]	k_{oc} [L kg^{-1}]	$k_{d,shallow}$ [d^{-1}]	$k_{d,deep}$ [d^{-1}]
Benzene	1780	83	0.9×10^{-3}	0.9×10^{-3}
Toluene	535	300	3.4×10^{-3}	1.3×10^{-3}
Et-benzene	152	1100	0.5×10^{-3}	0.3×10^{-3}
Xylene	170	894	0.6×10^{-3}	0.3×10^{-3}
1,1,1-TCA	4400	183	1.5×10^{-3}	1.5×10^{-3}
1,1-DCA	8700	18	0.6×10^{-3}	0.6×10^{-3}
PCE	150	130	0.3×10^{-3}	0.3×10^{-3}
TCE	1000	130	0.1×10^{-3}	0.1×10^{-3}
DCE	6300	130	0.1×10^{-3}	0.1×10^{-3}
VC	2700	56	0.1×10^{-3}	0.1×10^{-3}

The subsoil is characterized by two layers: the quaternary deposits and the layer beneath with its bottom sealing the phreatic aquifer. However, this assumption resulted in thick aquifers in large parts of the study domain while the contamination is generally situated at a small depth from the ground surface. Therefore, the aquifer bottom was restricted to the maximal depth of the monitoring wells for that region in the database. And the aquifer thickness was calculated from the difference of the former value with the calculated groundwater table. The conceptual model distinguishes two layers that comprise 30%, respectively 70% of the resulting conceptual aquifer thickness. The water velocity in each conceptual layer is calculated from the relative contribution of the hydrogeologic units in the respective layer (f_q and f_d), i.e. the quaternary deposits and/or one of the deeper hydrogeologic units, assuming an equal head gradient between layers.

$$v = \left(f_q K_{c,q} + f_d K_{c,d}\right) \frac{\partial H}{\partial x}$$

Literature data and expert opinions were used to define the properties of the hydrogeologic units, and the sorption and degradation rates of the selected contaminants. The selected values are given in Table 1 and Table 2.

THE COMFRACS MODEL

The COMFRACS model simulates the status of the two conceptual groundwater layers based on the available monitoring data and a simplified mass transport model. The status is sequentially calculated for each contaminant. The degradation from the chlorinated ethenes is assumed to be stoichiometric from PCE to TCE to DCE to VC and finally to ethene. As such, the degradation product of the parent compound is added to the observations of the daughter product for its subsequent calculation. As described above the model makes use of a 25 m grid for which the observed data are averaged in each model timestep of 1 month. The mass in each grid cell is transported to the downstream cell by advective mass transport complemented with retardation and first order degradation as described by:

$$\frac{\partial M}{\partial t} = \frac{1}{R}\left[\frac{-\partial}{\partial x}(vM) - k_d M\right]$$

With M the mass of the contaminant in the grid cell, R the retardation factor [-], v the groundwater velocity [m d^{-1}] and k_d the degradation rate [d^{-1}]. The model calculates from the year 2000 to 2035 with eventual measures in the year 2013. Outputs are generated for the years 2013, 2015, 2025 and 2035.

Model structure

The model runs in the Python environment where necessary parameters are declared. The raw data are stored in the PostgreSQL/PostGIS database and geographic input data are stored as PCRaster maps. Flanders has an area of 13522 km^2 and the overlying grid of 25 m^2 cells counts a total of 40 million cells, of which 22 million are within the Flemish territory. As such, only 'active' grid cells were processed in the Python environment in order to prevent computational problems due to excessive memory requirements. The model runs sequentially for the different contaminants and calculates the four scenarios in parallel. Each model run consists of a preprocessing step to load the steady-state groundwater velocity in the entire domain and calculate the retardation factor for the specific contaminant as:

$$R = 1 + \frac{\rho_b f_{oc} k_{oc}}{\theta}$$

With ρ_b the soil density of 2.65 kg/L, f_{oc} the carbon content of the groundwater layer [%], k_{oc} the organic carbon partitioning coefficient of the contaminant [L kg^{-1}] and θ the porosity (see tables above). The data of the specific contaminant are finally extracted from the raw OVAM data in the PostgreSQL/PostGIS environment using the PostgreSQL database adapter for Python. These data are stored as a temporary table that can be more efficiently queried in the subsequent time loops. The model calculates with a monthly time step from the year 2000 to the year 2035. Each loop generally consists of 3 parts: load monitoring data, simulate mass transport, save output data when necessary.

Monitoring data

Monitoring data are loaded in Python from the PostgreSQL/PostGIS database. The list contains data for the coordinates, the position in the matrix, the value, the conceptual layer it belongs to and the parcel ID of each data point. The data are averaged and converted to total mass for each layer in the grid cells of 25 m^2. In addition, the matrix position of the downstream cell following the LDD is determined. The monitoring data are distributed to active grid cells and simulated data from previous time steps are replaced when new observations are available. An additional step is discerned for the chlorinated ethenes where the degraded parent product is loaded from the database for each specific time step, and distributed to the active grid cells similar to the monitoring data.

Mass transport simulation

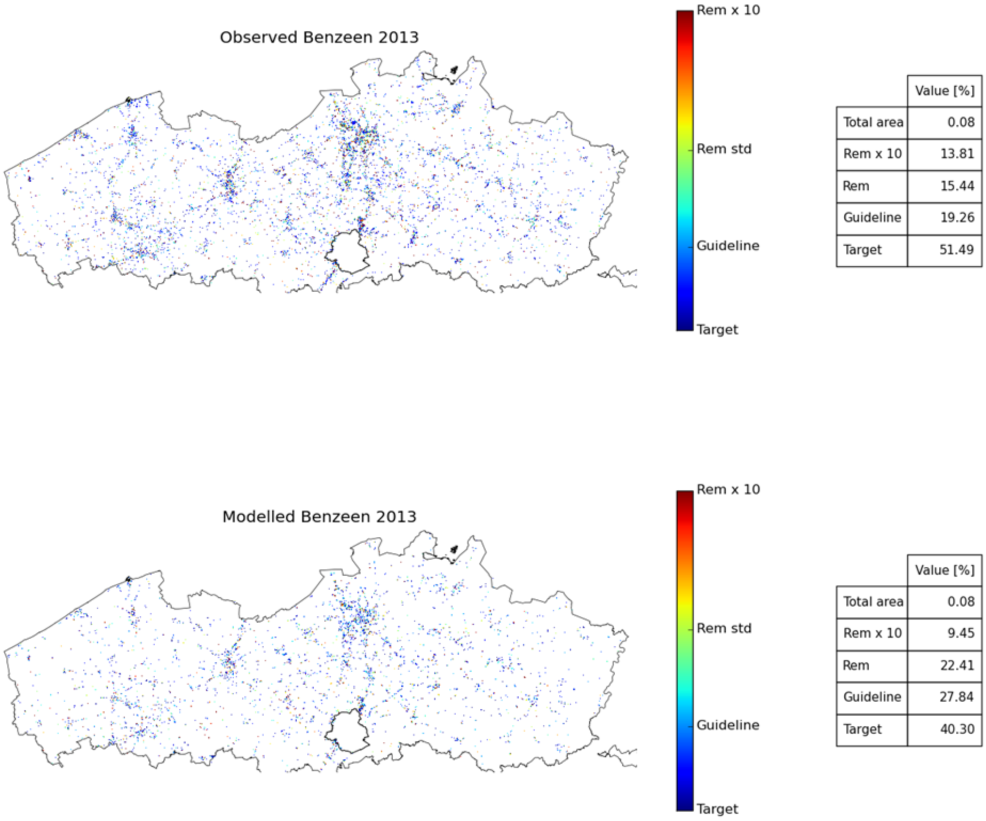
The mass in the active grid cells is first transported downstream and then degraded as described by the equations above. The parcel IDs of the monitoring data are also transferred downstream in order to keep track of the plumes for module 3. If a new grid cell becomes active, the matrix position of the downstream cell following the LDD is determined. In January 2013 the different measures are executed a the start of the mass transport simulation. The maximum mass in each grid cell is limited to the mass equivalent of the water solubility in the porous medium for source zone remediation, and 30% or 80% of the mass in each grid cell is removed to evaluate measures tackling the plumes.

RESULTS AND DISCUSSION

Big data

The combination of the various open-source software tools: Python PostgreSQL/PostGIS, GDAL and PCRaster enabled an efficient workflow in the different processing steps of database development, relating spatial to tabular data, the simulation and the adaptability of the output for the REACHER-LOCAL. The preprocessing steps showed the complementarities of the various databases. But also indicated shortcomings in order to exploit this potential for regional management of contaminated groundwater. The OVAM database is indispensable and could benefit from a validity check of the uploaded data by third parties, especially for the geographic coordinates (x,y,z) of the monitoring data. Importantly, project-specific attributes such as the estimated NAPL content, type and time of remediation, estimated removal rate, and groundwater flow directions and velocities would prove very useful in an eventual application of COMFRACS.

The simulation of the groundwater flow determines to a large extent the spreading of the contaminants and the behaviour in time. The steady-state groundwater table yielded an average head gradient of almost 0.05 at the sites, which is much higher than the 0.001 that is usually assumed for phreatic aquifers in Flanders. Therefore, the head gradient was limited to 0.01 in this conceptual prototype, i.e. maximally 10 times the assumed average for prheatic aquifers in Flanders. It would be worthwhile to integrate available groundwater flow models from the VGM in this framework to achieve a better approximation of groundwater transport. In addition, the characterisation of the aquifers should be further refined to include specific properties, or to include shallow impermeable layers that would significantly influence groundwater transport. More data are available in the HCOV database or in the geological 3D model that is being developed for Flanders at a grid scale of 100 meters (Matthijs, 2001)



	Value [%]
Total area	0.08
Rem x 10	13.81
Rem	15.44
Guideline	19.26
Target	51.49

	Value [%]
Total area	0.08
Rem x 10	9.45
Rem	22.41
Guideline	27.84
Target	40.30

Figure 3: Output of the COMFRACS model for Benzene in the year 2013. The color legend represents the concentration at 10 times the remediation standard down to the target value of 0.5 µg/L

In a previous version, COMFRACS could use the monitoring data to calculate a removal rate for a contaminant from a specific parcel and use this rate for predictions in time. This approach could not be withheld in the current version where simplified mass transport is taken into account along a 1D flow line which is obtained from an estimated groundwater table elevation. These assumptions impede an inverse optimization of the degradation parameters. Therefore, the degradation rates of the selected contaminants were obtained from a literature review but appear to be at the high end of expected values, especially for toluene and the chlorinated ethanes. The degradation rate parameters should be refined for an eventual application of COMFRACS in Flanders.

COMFRACS

Preliminary results of the COMFRACS model show that it adequately simulates the contaminant dynamics in time, taking into account the significant simplifying assumptions in this prototype. Figure 3 shows the results for Benzene in the year 2013 where monitoring data indicate that a pollution was observed at 0.08% of the Flemish territory by this time. The modelled data indicate a total polluted area of 0.08% by 2013, taking into account transport and degradation but excluding eventual remediation actions. As such, results illustrate a limited spreading of benzene in the subsurface. It suggests that the known groundwater pollution is adequately delineated with limited risk for downstream users that are not yet identified. However, the simplifying assumptions in this prototype require more research before definite conclusions can be drawn. Results of the other contaminants and the management actions are currently being processed.

CONCLUSIONS

A conceptual model for a regional assessment of contaminated sites (COMFRACS) was developed as a prototype for groundwater contaminated with mineral oil and chlorinated hydrocarbons. The GIS capabilities of the Pyhton/PCRaster framework facilitate a spatially resolved evaluation of remediation technologies at a larger management scale. However, improvements regarding the representation of groundwater flow, aquifer characterisation and natural attenuation rates are necessary for an eventual application of COMFRACS in Flanders. The output of COMFRACS can be used to compare the impact of different remediation measures (flux reductions) with potential economic benefits to comply with sustainable management practices, as is illustrated in the derived REACHER-LOCAL tool.

ACKNOWLEDGEMENTS

This work was co-funded by the EU-project AQUAREHAB (FP7 – Grant Agreement Nr. 226565). The authors gratefully acknowledge the use of the various datasets in this work and the help of Stijn Van Looy (VITO, Belgium) with the cluster computing.

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Poster Presentations

Optimizating Hydrus 1D for irrigation management purposes in sandy grassland

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ABSTRACT***:*** To improve irrigation strategies in terms of higher efficiency and sustainability, computer simulation models can play a key role. In this study, the Hydrus 1D model was optimized for an irrigated grassland on sandy soil. Manual and inverse stepwise calibration was applied in which both heterogeneous and homogeneous conceptualizations of the soil profile were considered. Local sensitivity analysis showed that the model was most sensitive for saturated hydraulic conductivity K_s and the van Genuchten parameters n and $α$. Results show that Hydrus 1D closely simulated soil water content at five depths as compared to water content measurements from soil moisture probes taken in 2011. The optimized model performed well when validating against water content data taken in the 2012 growing season. The model errors, expressed by deviations between observed and modeled soil water content were, however, different for each individual depth. The smallest differences between the observed value and soil-water content were attained when using an automated inverse optimization method, in which the initial parameter values were optimized using a stepwise approach. Correlation between estimated parameters suggested that the solution was nonunique, indicating an overparameterization of the model. Using inappropriate initial estimates of soil hydraulic parameters in combination with multiple local minima and uncertainties in the data, inhibits the identification of the global minimum. Our results show that optimization is highly influenced by the number of parameters to be estimated and the initial values of soil hydraulic parameters.
Keywords: soil hydraulic properties, Hydrus 1D, water flow, sensitivity analysis, model optimization and validation

INTRODUCTION

Water scarcity due to extreme droughts related to climate change drive water use technologies such as irrigation to become more efficient and sustainable. To improve irrigation strategies, water flow needs to be accurately described using advanced monitoring and modeling. Optimizing the water use needs the accurate prediction of soil-water content and soil-water potential in the root zone in order to simulate infiltration, redistribution and evaporation processes. This in turn requires the determination of hydraulic properties and conditions related to climatology at the upper boundary (Brutsaert, 2005; Li *et al.*, 2012; Nosetto *et al.*, 2012) and groundwater dynamics at the lower boundary of the soil profile(Gandolfi *et al.*, 2006) . Real-time monitoring of surface and subsurface water flow flux, soil moisture, and water potential can be used in inverse modelling to determine soil hydraulic properties, and their tempo-spatial variability for dynamic modelling and irrigation process optimization(Vrugt *et al.*, 2008).

In this study, the numerical Hydrus 1D model (Simunek and van Genuchten, 2008), is used for water flow prediction. We applied a stepwise approach conducting first a sensitivity analysis of the sensitivity of the model to hydraulic properties and then an inverse optimization to the field monitoring data to estimate hydraulic properties and predict soil water content in sandy soil for irrigation management purposes. The parameters affecting the performance of Hydrus 1D in inverse solutions were evaluated.

MATERIALS AND METHODS

The study site is a sandy agricultural area at the border between Belgium and the Netherlands. During the study period 2011-2012, the farmer cultivated grass. The site was equipped with a weather station located on the field (hourly recorded). At the location, one soil water content profile probe (EasyAG50) was placed vertically allowing to measure hourly soil-water content at 10, 20, 30, 40 and 50 cm depths. Soil samples were taken at eight locations and two depths (25 and 75 cm) to determine K_s, soil water retention curve data and some other basic soil properties. Parameters describing the soil hydraulic properties were fitted to the observed data set using RETC program for windows, version 6.02.

Simulation of water flow and grass root water uptake was carried out by using HYDRUS 1D version 4.16 for 122 days in 2011. The profile depth was 100 cm and the profile was subdivided into two materials with different properties (Table 1). The van Genuchten-Mualem (MVG) soil hydraulic model without air entry value and hysteresis was used. The atmospheric boundary condition with surface runoff for the upper and free drainage for the lower boundary condition were chosen. The Feddes model (Feddes *et al.*, 1977) without solute stress was used for root water uptake. The contribution of each input parameter and factor to the uncertainty of the model outputs is determined by manual calibration and sensitivity analysis. A stepwise calibration approach was used to evaluate the effect of soil hydraulic parameters (i.e. using varying values for Ks, n and α), soil layering (i.e. choosing either a homogeneous or a heterogeneous profile and changing the depth of each material), and root water uptake (i.e. root distribution patterns). Results of stepwise manual calibration indicated that a linear decreasing root density distribution and a 45-cm-deep first layer offered the best simulation results and this was used for the initial simulations in this study. In the stepwise calibration approach the model was just sensitive to changes in K_s. The most relevant K_s for first and second layers based on manual stepwise calibration, which was used for the next step, were the average values of given K_s data (0.45 and 1.814 cm h^{-1} respectively).

In a next step of the modelling approach, an inverse modelling technique was applied. To reduce the number of parameters of optimization and finalize the calibration process, local sensitivity analyses (Saltelli, 2008) were conducted by calculating the central total relative sensitivity "CTRS". In the inverse modelling process, first the thickness of soil layers was optimized. Then, we optimized sensitive parameters of the two layers, while keeping the other hydraulic parameters fixed to the measured values. The root-mean-square deviation (RMSE), the coefficient of determination (R^2), and the Nash–Sutcliffe coefficient of model efficiency (Ce), were used to evaluate the difference between the observed and modelled data. Finally, the 2012 data set was used for validation of the calibrated model.

Table 1: Measured physical and chemical soil properties

Soil depth	OC	Sand	Silt	Clay	Bulk density	Ks	ε	Ɵr	Ɵs	α	n
Cm	(%)	(%)	(%)	(%)	(mg m^{-3})	(cm h^{-1})		(m^3 m^{-3})		(cm^{-1})	----
0-50	2.26	91.1	6.68	2.18	1.595	2.187	0.397	0.077	0.378	0.015	2.408
50-100	0.71	93.5	4.78	1.67	1.782	2.271	0.388	0.055	0.365	0.019	2.549

Ɵr, Ɵs are residual and saturated water content, respectively; α and n are shape parameters for the van Genuchten-Mualem equation, which was obtained by RETC software. Ks and ε denote the saturated hydraulic conductivity and porosity.

RESULTS

Figure 1 illustrates the results of the local SA as a function of time for α, n and K_s. A perturbation factor of 0.1 was chosen (a smaller perturbation factor could be better but are not possible given the output accuracy of Hydrus 1D). During SA analysis of each parameter in each layer, the value of other parameters was fixed to the average of the measured values. According to the results α, n and Ks are most sensitive (in decreasing order) and the sensitivity changed over time with the seasonal changes in water status in both soil layers.

Hydrus 1D is run inversely using simulations of soil water content to optimize the values for α ,n and Ks of the two layers (based on SA). Furthermore the layer depth was also optimized. The best result was obtained for a thickness of 30 cm for the first and 70 cm for the second soil layer. The results of the parameter optimization and the performance criteria calculated for the fit between measured and simulated soil water content (water flow) for the case of the two layered profile are presented in Table 2. The best simulated time series of soil water content with the inverse modeling are depicted in Figure 2. Results show that the inverse model overestimates the simulated moisture data at 30 and 40 cm depth during the first half of the simulation period. During the optimization the α and n values increased and decreased respectively. The optimized K_s value for the first and the second layer was 1.899 and 99.082 cm h^{-1} respectively. The optimized value of Ks for the second layer is well above that in the first layer and the value determined by lab analysis. The model is validated to the measurements of 2012 (Figure 2 right part) and performance is satisfactory. However, correlation analysis showed highly significant correlations between the three optimized parameters and this correlation leads to nonuniqueness of parameters which suggests the number of parameters to be optimized should be reduced or the model should be revised.

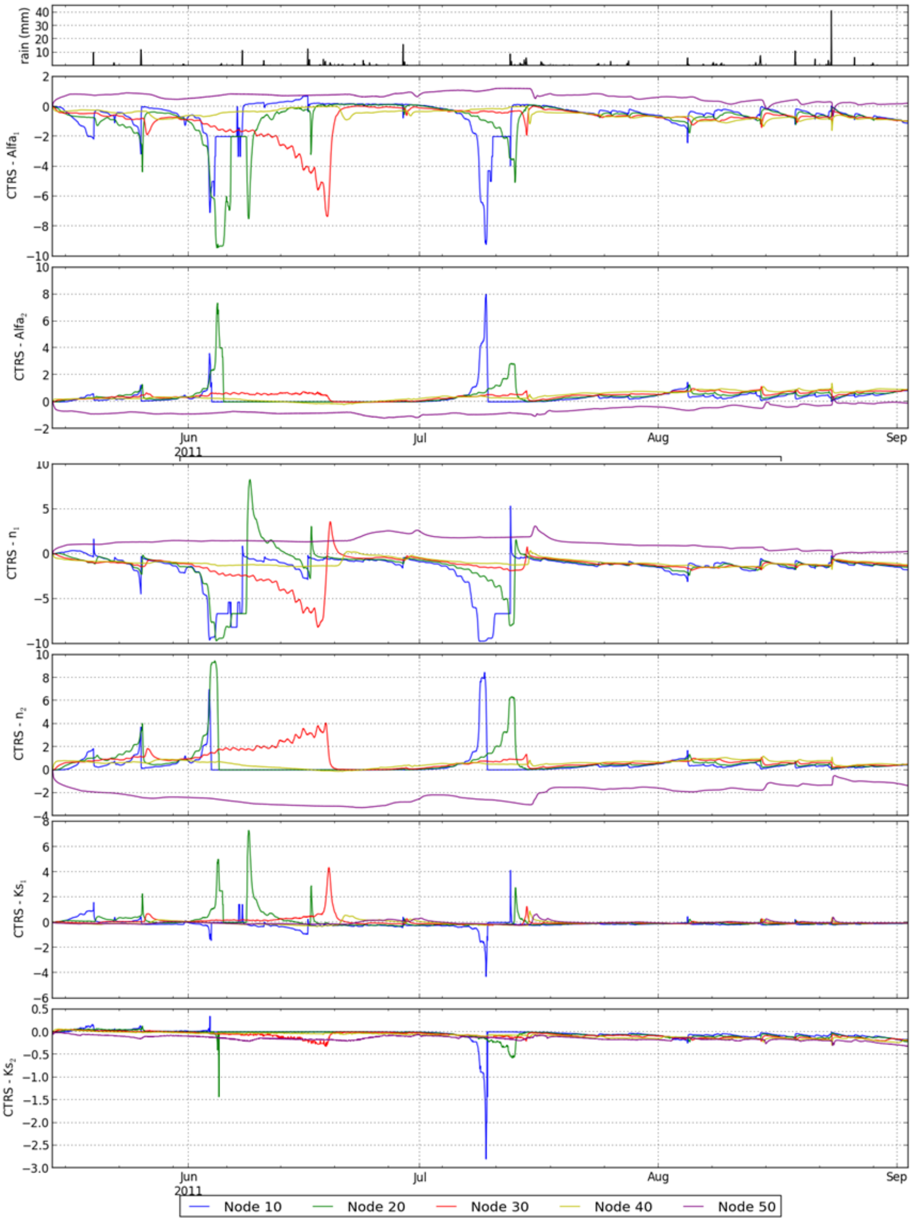

Figure 1: The sensitivity analysis "SA" results for parameters as a function of time. The number 1 and 2 correspond to first and second layer.

Table 1: Optimized hydraulic parameters for the two layers and calculated performance criteria for the fit between measured and simulated soil water content at 5 depths.

	Parameter	Optimized value	95% Confidence limits		RSQ	Mass balance error
			Lower	Upper		
	α (cm^{-1})	0.036	0.034	0.037	0.841	0.243%
First layer	N	1.245	1.239	1.252		
	Ks (cm h^{-1})	1.899	1.722	2.075		
	α (cm^{-1})	0.025	0.021	0.029		
Second layer	N	1.301	1.290	1.3129		
	Ks (cm h^{-1})	99.082	70.001	128.16		
	Depth (cm)	10	20	30	40	50
	R^2	0.834	0.922	0.775	0.769	0.780
Performance criteria	RMSE	4.107	2.743	5.365	2.420	1.087
	Ce	0.803	0.903	0.245	0.568	0.687

R^2, RMSE and Ce are the coefficient of determination, the root-mean-square deviation, and the Nash–Sutcliffe coefficient of efficiency (cm^{3}cm^{-3}).

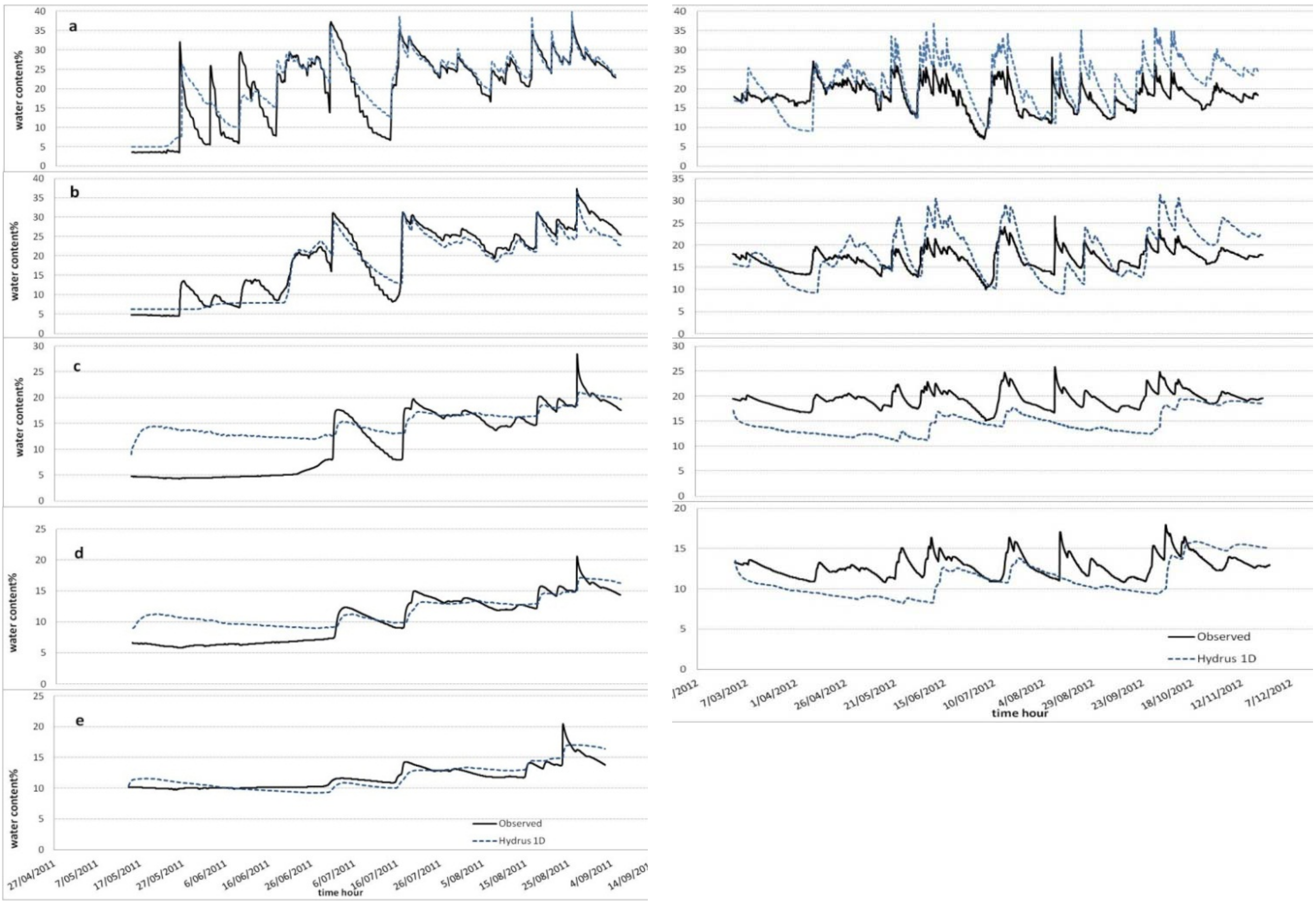

Figure 2: Observed and simulated time series of soil water content with inverse modeling for 30 and 70 cm depth of layers at a) 10, b) 20, c) 30, d) 40 and e) 50 cm depth for 2011 optimization and 2012 validation (the fifth depth data missed).

CONCLUSIONS

A systematic sensitivity analysis can be considered crucial to determine sensitive parameters and set up an inverse model. In this study we set up an inverse modeling based on the results of the sensitivity analysis. Results of the optimization by applying inverse modelling show a good fit between calculated and measured values both in the calibration and validation period but the correlation among optimized parameters and unrealistic parameters value are important aspects to consider. In addition, using improper initial estimates of soil hydraulic parameters can increase the uncertainty of results. Based on these results the next steps, in light of reducing uncertainty and increasing uniqueness of solution, areto check and improve the conceptual model based on additional in situ and laboratory measurements and possibly repeat the modeling exercise.

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Comparison of the Species Sensitivity Distribution (SSD) with ecologically relevant SPEAR index in the retrospective risk assessment of pesticides

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Prospective risk assessment of individual pesticides often uses Species Sensitivity Distribution (SSD) models to estimate HC5, i.e. hazardous concentration to 5% of species (protecting thus 95% of remaining biota). However, pesticides (along with other toxicants) occur in the environment in complex mixtures, and proper characterization of their effects in ecosystems still remains a matter of research. An important approach to investigate influence of stressors on organisms in the field is determination of the effects on local biota using biological indices such as SPEcies at Risk (SPEAR). SPEARpesticides is well validated stressor-specific index, which based on biological traits responsive to the effects of pesticides and also post-contamination recovery. The present work compared SPEARpesticides bioindication results from several catchments in Germany, France and Finland with predictions of pesticide mixture impacts calculated using SSD (25 analyzed pesticides at the same localities, the effects predicted as multisubstance Potentially Affected Fraction - msPAF). The significant correlation ($p < 0.001$) between SPEARpesticides and msPAF values was observed but the 5% threshold used in prospective SSD (corresponding to msPAF=0.05) seemed to be insufficiently protective because SPEARpesticides indicated negative impacts at much lower concentrations of pesticide mixtures than those corresponding to individual HC5. In addition, the results depended on the proper selection of ecotoxicity values for SSD highlighting the importance of chronic effects, toxic modes of actions of individual pesticides, and selection of appropriate target taxa. Taken together, the validation study shows good potential of SSD models in predicting the impacts of micropollutant mixtures on natural communities. However, it should be combined with ecological monitoring since estimation of environmental risks/impacts solely on the basis of the commonly used 5% threshold may lead to incorrect conclusions

Good practice in the clean-up of contaminated land and groundwater

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Contaminated Land: Applications in Real Environments (CL:AIRE) is an environmental charity focused on developing good practice in the clean-up of contaminated land and groundwater. CL:AIRE is involved in several current projects in the field of groundwater remediation, three of these are described below – ADVOCATE, TDP31 and HEISTT.

Firstly, the ADVOCATE Project (**Adv**ancing sustainable *in situ* remediati**o**n for **c**ont**a**mina**t**ed land and groundwat**e**r) is a Marie-Curie **I**nitial Training Network which encompasses both socio-economic and sustainability aspects and different remediation processes with the goal of developing innovative *in situ* remediation concepts for the sustainable management of contaminated land and groundwater, as required by the Water Framework Directive. The ADVOCATE Project comprises different research sub-themes which address the fundamental understanding of *in situ* processes (contaminant transport, biochemical processes and degradation at field scale); evaluation of technological innovations (*in situ* bioprecipitation using a permeable reactive multibarrier (PRmB) system) and methods used to treat contamination (bioremediation processes); socio-economic aspects and knowledge transfer.

Secondly, Technology Demonstration Project TDP31 which uses the Arvia process as an alternative to granular activated carbon (GAC) to treat pumped groundwater containing a range of complex organic compounds. The Arvia process is based on adsorption coupled with electrochemical regeneration, using a proprietary, non-porous, carbon based, highly conducting adsorbent material, Nyex™. Thirdly, the HEISTT Project (High Efficiency In Situ Treatment Technology), an FP7 project, has a goal to create an innovative system for rapidly and efficiently injecting remedial chemicals into the subsurface for the purpose of treating contaminated groundwater.

REACHER: a Decision Support Tool to Evaluate Scenarios of Measures for the Reduction of Pollution fluxes

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Decision makers need tools for assessing the impacts of their management practices on the water quality. The complicated nature of simulation models and the large computation time they need hamper the use of these tools in the decision making process. Furthermore, decision makers often lack the detailed domain knowledge to judge processes included in the models. They need decision support tools with an intuitive user interface design simplifying the interaction with models and the visualization of the produced results. REACHER is a generic river basin management tool that assesses the ecological and economic impact of rehabilitation technologies at the river basin scale. The graphical user interface, geographic visualisation and database of the web-based tool have been developed using open source software. REACHER has been developed based on scenario runs with watershed fate models in which rehabilitation measures and associated costs are included. It allows visualisation of the actual chemical, ecological and ecotoxicological status of a river basin and the change in groundwater and surface water status due to the application of a rehabilitation measure or a combination of measures. The scenarios are visualised in REACHER using a Bayesian Belief Network that is trained by multiple runs with the watershed models. A prototype of REACHER is developed and evaluated for two pilot cases, the Odense river (Denmark) and the Scheldt river (France-Belgium). The REACHER tool will be demonstrated during the interactive poster session.

This study is being performed as part of the European Union Project AQUAREHAB (FP7 – grant agreement Nr. 226565).

Modelling the dispersion of radionuclides in river systems. Study of the Molse Nete River

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Once pollutant effluents are discharged in waters, part of them is transported in liquid phase and the rest is attached to the suspended sediments and to the bed sediments. The magnitude of each fraction is determined classically by the partition coefficient Kd that is a function of several environmental parameters such as the pH. Radioactive effluents interact with the sediments present in the water column (adsorption/desorption on suspended matter and bed sediment) being carried downstream by the water flow. Depending on the flow conditions, settling of the suspended particles may occur while during storm events, resuspension takes place influencing the pollutant distribution and transport.

In order to represent the complete dispersion process in rivers a Finite Element water quality model focused on the transport of radionuclides in river networks is developed. The model constitutes of 3 components for the modelling of tracers, non-cohesive/cohesive sediment and radionuclides transport. The model is first applied at the Molse Nete-Grote Nete river system; the Molse Nete is a watercourse which receives liquid radioactive discharges from the nuclear installations of the Mol-Dessel site via the liquid waste treatment installations of Belgoprocess.

The model was coupled with the MIKE 11 river model and the hourly version of the SWAT model, both previously calibrated. The model was calibrated in four stages. First, the accuracy of the advection-dispersion component was evaluated by comparing the numerical solution provided by the model with the analytical available solution of the advection-dispersion equation. Secondly the sediment transport component was calibrated by comparing the model prediction with the observations at Geel-Zammel. In a third stage, the mathematical formulation of the sorption-desorption kinetics component was calibrated by comparing the mathematical solution with the results of in vitro experiments. Finally the complete model was calibrated and validated comparing the radionuclide concentration measured in the river bed sediments with the model prediction. In all the stages the model outputs resemble the observed conditions. The validated model now can be used to assess the impact of routine, accidental releases or to aim for remediation strategies.

Identifying and Quantifying transient fluxes of groundwater and contaminants into streams and within complex groundwater reservoir by Mixing Cells Modeling approach

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Perennial streams are occasionally fed by various sources of groundwater bearing unites and pollutants through hidden subsurface flow trajectories. Therefore, the stream-water quality is highly affected by the quality and the relative fluxes of groundwater contributed by the connected neighboring sub-aquifer units and the nearby water baring formations with different water qualities and dissolved mineral contents. The complex nature of the hidden hydraulic connectivity results long term special and temporal variations in stream-water quality. Unless the active sub-surface trajectories of contaminated water are identified and the groundwater fluxes into the rivers are quantified it is difficult to precisely assess and predict the temporal and spatial hydro-chemical evolution of the pollutants along the streams.

The differential fluxes of water and pollutants from neighboring sub-aquifers attracted into the river cause long-term temporal distribution of the stream-water quality. The main issue is how to firmly identify the hydraulic connectivity among the various sub aquifers, and to draw the solid pathways into the stream and among the connected active water bearing units. Beyond that, these processes often prevail under announcing a non-steady aquifers environment as function of massive groundwater abstraction and transient release of pollutants. This results gradual, yet substantial spatial and temporal variations in chemical and dissolved minerals distribution, all which suggest on transient flow and mass transport distribution. Common hydrologic models based on the continuous flow and transport equations are difficult to adopt for a complex non-steady river-aquifers system, where the boundaries and initial conditions cannot be well-defined. For such complex hydrologic system, the transient Mixing Cells Modeling approach MCMusf (unsteady flow) has been developed. It illuminates on the active flow paths and assesses the transient groundwater fluxes along streams and rivers from and within the sub-aquifer units.

The model is based on the spatial and temporal distribution of environmental tracers, such as dissolved minerals, and relies on stable isotopes of oxygen and hydrogen. It is assumed that spatial variations of dissolved constituents and isotopic ratios along the stream and within the connected aquifers can be attributed to the mixing and dilution of all sources of stream-water recharge and sources of contaminants.

The flow domain (the river reach and the nearby connected aquifers) is discretized (divided) into homogeneous compartments based on the distribution of the dissolved constituents. Environmental tracers are then used to write a set of water and mass balance equations in a compartmental flow system, such that the unknowns are fluxes of groundwater and pollutants. An optimization scheme based on linear programing has then been applied to assess the above-mentioned unknowns.

The presentation elaborates on the concept and the mathematical set up of the newly developed MCMusf code for transient flow system, and on a feasible solution which is based on linear optimization scheme. Results are presented for synthetic test case and for the shallow alluvial aquifer along the Hovav wash in Israel.

REACHER local: Decision support for integrated management of polluted sites in Flanders, Belgium

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ABSTRACT
REACHER Local is a prototype decision support tool for a regional-scale assessment of all known groundwater polluted sites in a region (e.g. Flanders, Belgium). Users are able to explore the status of 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).

INTRODUCTION

The European Groundwater Directive (2006/118/EC) states that, where necessary, Member States should assess possible threats for human health and the environment of plumes resulting from point sources. In addition, Member States are establishing national inventories of contaminated sites in accordance with the proposal for the Soil Framework Directive (COM (2006) 232). Whereas point source pollution is usually considered on a site by site basis, it can be of added value to have an overview on of the problem and potential solutions on a larger, river basin scale. Esp. to reach a good water status for river basins, as required by the European Water Framework Directive (2000/60/EC), it is important to have a clear idea for larger areas of what the pollution status is now and will be in the future, and consequently of which efforts we still need to make for the different river basins.

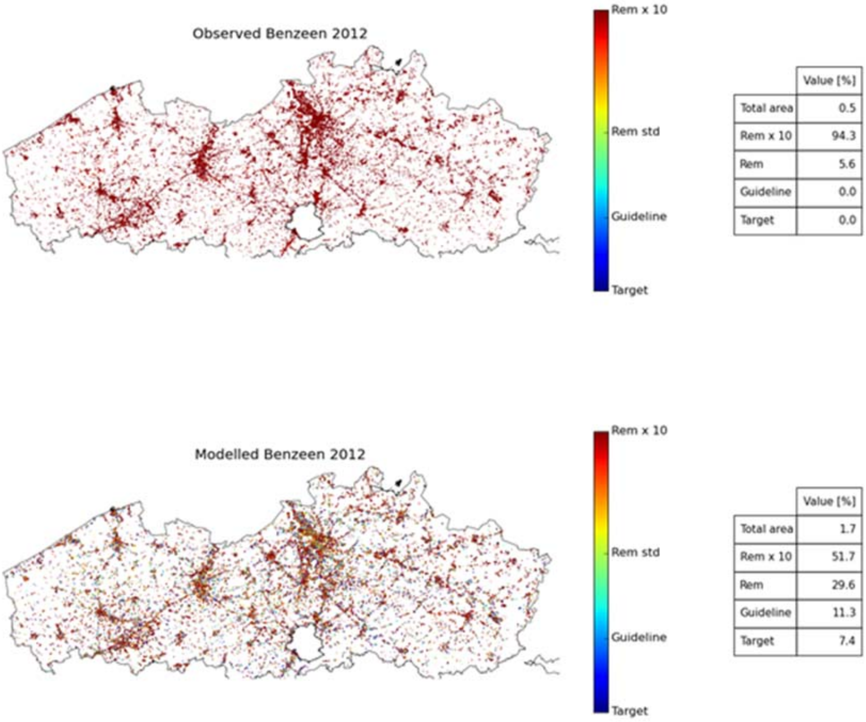
This research examined how data from national inventories can be coupled to readily available data in Geographical Information Systems (GIS) to provide valuable information for risk assessment, trend analysis and potential remediation strategies at a larger management scale.

MATERIAL AND METHODS

Status

The status module presents simulation results of the COMFRACS model for the years 2012, 2015, 2025 and 2035. The results are compared with legal concentration targets. Modeled substances include benzene, toluene, ethyl benzene, xylene, tetrachloroethene, trichloroethene, dichloroethene, vinyl Chloride, trichlorethane, dichloroethane

COMFRACS+ was developed for groundwater contaminated with mineral oil and chlorinated hydrocarbons in Flanders, Belgium. It makes use of the extensive database of the Public Waste Agency of Flanders (OVAM) that is coupled to the Python/PCRaster numerical framework via a PostgreSQL/PostGIS database. The monitoring data of the surveyed sites were averaged in a regional grid with a spatial resolution of 25 m. Plume development was approximated assuming steady state groundwater flow with advective mass transport in the direction of the steepest gradient, including retardation and first order degradation. Four different management options were simulated in the year 2013: no action, source zone remediation or a homogeneous mass removal of 30% or 80% of the contaminants in the groundwater. The latter two options specifically evaluate measures that would tackle contaminant plumes. The resulting effects of the different actions were simulated up to the year 2035.



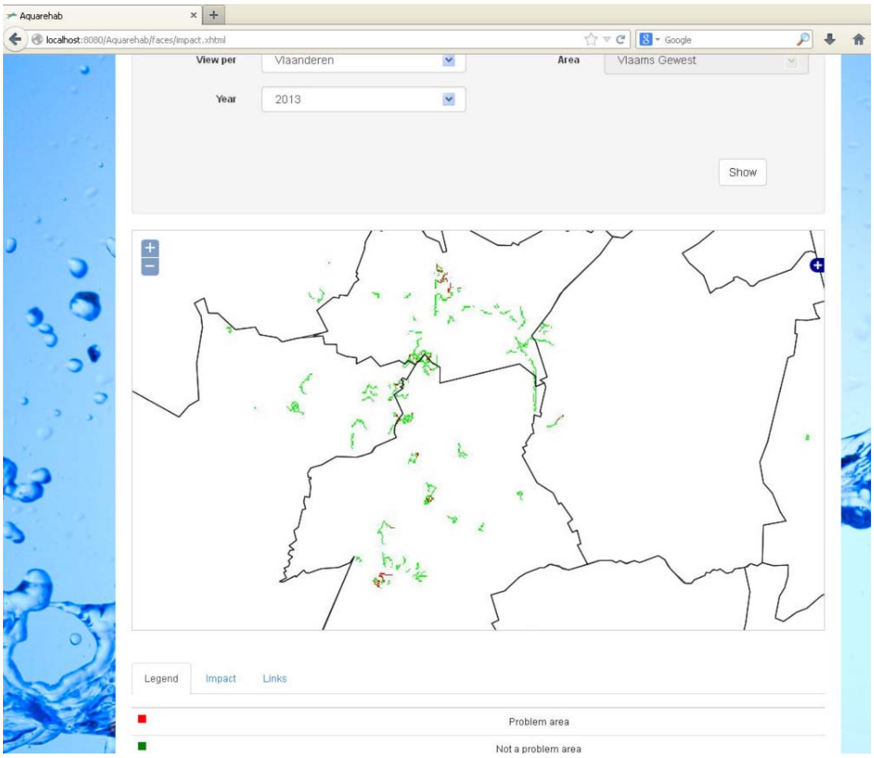
	Value [%]
Total area	0.5
Rem x 10	94.3
Rem	5.6
Guideline	0.0
Target	0.0

	Value [%]
Total area	1.7
Rem x 10	51.7
Rem	29.6
Guideline	11.3
Target	7.4

Figure 1: Status module – Predicted concentrations of benzene vs. observed concentrations

Impact

In the impact module we distinguish the impact on public drinking water supply, on groundwater supply, on indoor air quality and on surface water. The difference with the previous module is that concentrations are compared to specific targets (risk based threshold values) for every impact category. This impact category depends on the location of the pollution.



View per: Vlaanderen
Area: Vlaams Gewest
Year: 2013

🟥 Problem area
🟩 Not a problem area

Figure 2: Impact module - Map for all impacts (Problem area: Red, No Problem Area: Green)

The impact on drinking water supply and on groundwater supply is checked for areas having an overlap with respectively a protection zone of a drinking water or groundwater catchment. The impact on indoor air quality is checked for residential and industrial land use. The impact on surface water is checked when pollution is reaching surface water.

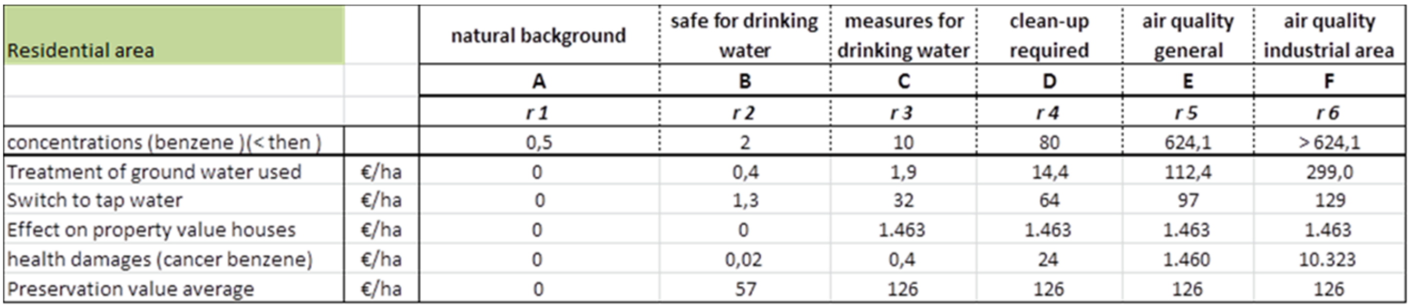
Damage

The damage module estimates the societal cost we experience due to the environmental damage (impact on housing prices, health damages) caused by the pollution and hence the benefits that can be achieved by reducing pollution levels. For all impact categories, the damages are calculated in €/ha per year. We apply a series of valuation methods, data and assumptions. These include:

- Additional costs for groundwater use, assuming that polluted groundwater is treated before use. Costs depend on the degree of pollution, the volumes used and the intended use of the water (required quality) (Derden, 2001 ; Rijkswaterstaat (2013), VMM, 2012)
- Additional costs for water supply, assuming that polluted groundwater is replaced with tap water for uses that require high quality. Costs depend on the difference between market prices of tap water and operational costs of groundwater use and the amount of water which needs to be replaced. (VMM, 2013)
- Loss of property values for houses above the pollution plume, which depends on the amount of residential areas above the plume, housing prices and depreciation (based on hedonic pricing studies on the impacts of leaking underground storage tanks on property values in the US, Boyle, 2010; Guignet, 2013)
- Potential health damages from inhalation of pollutants that evaporate from groundwater into indoor air of buildings (cancer risks from benzeen, health costs for cancers), and that depend on the level of pollution and the type land-use (residential, industrial,…) (Beukers, 2009)
- Loss of preservation value which depends on the value average citizens attach to the protection of groundwater sources for later uses, as estimated with stated preferences studies (Willingness to pay for groundwater protection assessed during the EU project BRIDGE, ; Hasler et al, 2005, Brouwer et al, 2006)

Depending on the valuation method, the land use and the degree of pollution potential benefits of remediating groundwater pollution differ largely. The table below indicates what potential benefits are for remediation of ground water pollution in residential areas for different levels of pollution (going from natural background, to highly polluted areas

Table 1: Potential benefits in € per ha per year for remediation of groundwater pollution (Benzene) in residential areas.



Residential area		natural background	safe for drinking water	measures for drinking water	clean-up required	air quality general	air quality industrial area
		A	B	C	D	E	F
		r 1	*r 2*	*r 3*	*r 4*	*r 5*	*r 6*
concentrations (benzene)(< then)		0,5	2	10	80	624,1	> 624,1
Treatment of ground water used	€/ha	0	0,4	1,9	14,4	112,4	299,0
Switch to tap water	€/ha	0	1,3	32	64	97	129
Effect on property value houses	€/ha	0	0	1.463	1.463	1.463	1.463
health damages (cancer benzene)	€/ha	0	0,02	0,4	24	1.460	10.323
Preservation value average	€/ha	0	57	126	126	126	126

Technologies

The technology selection module lists potential technologies that can be used to remediate the site and gives a first assessment of its relevancy. Based on a multi-criteria analysis, it is estimated for which amount of areas which techniques score best. Based on a series of criteria that determine whether a specific technology can be implemented on a site or not (e.g. depth of the aquifer, plume size...), a short list of applicable technologies that can be suitable for the site is determined. In a second step, a multi-criteria analysis ranks measures according to specific criteria like cost, efficiency, availability, … . Those criteria can be weighted differently according to the decision makers' preferences. Technologies include both conventional technologies such as pump and treat, and innovative technologies examined with the EU FP7 AQUAREHAB project like permeable zero valent iron barriers or sediment capping. Eventually, an overview is proposed, giving for each technology the amount of areas on which it scores best.

CONCLUSION

REACHER local proves to provide an interesting holistic picture on contaminated sites in Flanders, Belgium. To have a better picture of the size of the problem, how this problem evolves in time, what the potential damages are that we can expect for different remediation scenarios and which technologies are potentially interesting to implement is of added value for more integrated water management. This tool provides a screening method on the potential application levels we can expect for innovative technologies.

However, we also need to be aware of the large differences between different sites and how local circumstances can be very influential for technology selection. This is difficult to grasp in integrated decision support systems and requires more in-depth site specific analyses.

ACKNOWLEDGEMENTS

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Session 5 treatment technologies for micropollutants in wastewater

Oral presentations

Removal of micro-pollutants with Laccase-conjugated nanoparticles in advanced wastewater treatment

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INTRODUCTION

Wastewater treatment by conventional activate sludge processes cannot completely eliminate micro-pollutants from the wastewater [1-4]. In order to achieve further removal of micro-pollutants from wastewater various types of technologies such as advanced oxidation process and activated carbon have been tested as advanced wastewater treatment methods in recent years. In the EU funded Minotaurus project (grant agreement no. 265946), a series of environmental biotechnologies which are all based on the concept of immobilized biocatalysts is being developed in order to provide novel treatment methods for micro-pollutants in wastewater.

LACCASE-CONJUGATED NANOPARTICLES

As a part of the Minotaurus project, the current study mainly focuses on the pilot-scale application of *Laccase*-conjugated nanoparticles (LcNP) as advanced wastewater treatment [5]. In the current study, laccase is immobilized on the surface of silica nanoparticles at multi-kilo scale in order to maintain its enzymatic activity following a recently published protocol [6].

EXPERIMENTAL SET-UP FOR LCNPS

The laccase (*Genus Thielavia*) conjugated nanoparticles are applied in a pilot-scale fixed-bed tandem ultra-filtration membrane reactor (FB-UF). The fixed bed is used for the purpose of effluent polishing before contacting with LcNPs. The FB contains eight sequential compartments including a primary settling followed by six fixed bed compartment with 450 L volume each and a secondary settling compartment at the end. Treated wastewater effluent from the local wastewater treatment plant ARA Birs in Birsfelden, Switzerland is pumped into the fixed bed at 168 L/h as feed to the system. The fixed bed is operated in aerobic mode. Effluent from the fixed bed is directed into the following UF reactor. An UF module BIO-CEL produced by Microdyn-Nadir, Germany is installed in the reactor tank. The surface area of the membrane is 10 m^2 with membrane pore size of 0.04 µmThe reactor is constantly aerated at 4 Nm^3/h to keep aerobic conditions. At the end of October 2012, LcNPs were dosed directly into the membrane tank.

RESULTS

Different types of immobilized laccases have been tested at first regarding their obtainable immobilization yield and their ability to oxidize selected pollutants (Bisphenol A, Carbamazepine, Diclofenac, Sulfamethoxaxole and Ibuprofen) in bench scale experiments. In all cases, the laccase conjugates revealed remarkably increased transformation activities towards standard substrate. Furthermore, long term stability assays were performed in application-relevant wastewater over 40 days and revealed a considerable stabilization of the enzymes compared to free enzymes and demonstrated that the great potential of these catalysts to be applied in WWTP. However, the pilot-scale experiments did not yield similar results. No significant removal of any target compounds was observed during the experimental period. It could be caused by the low background concentrations of target compounds and alkaline pH condition in the treated effluent. Therefore a new generation of LcNPs has been developed. Currently bench degradation experiments are being carried out with these particles.

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Micro-pollutant Oxidation by a Laccase from an Aquatic Ascomycete

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Diverse micro-pollutants are often only insufficiently removed by conventional wastewater treatment and hence may contaminate receiving waters in minute amounts. Such substances have increasingly gained concerns about their further environmental fate and their hazardous potential. We have investigated the removal of the endocrine disrupting chemicals (EDCs) technical nonylphenol (NP, surfactant), bisphenol A (BPA, used in polycarbonate polymer and epoxy resin production), 17α-ethinylestradiol (EE2, contraceptive) and triclosan (TCS, antimicrobial), and the pharmaceuticals carbamazepine (CBZ, antiepileptic), diclofenac (DF, anti-inflammatory) and sulfamethoxazole (SMX, antibiotic) by isolated extracellular laccase from the aquatic ascomycete *Phoma* sp. UHH 5-1-03. Micro-pollutants were either applied as single compounds or as a mixture of all 7 compounds. The compound removal efficiency followed the rank order EE2 ≈ BPA > DF > NP > TCS, with SMX and CBZ persisting when applied as single compounds. Micro-pollutant oxidation was confirmed by the detection of products with molecular masses higher than that of the respective parent compound for EE2, BPA, DF, NP, and TCS. EE2 and BPA were more slowly degraded in mixture than alone, most likely due to competitive inhibition of substrate oxidation in presence of multiple micro-pollutants. In contrast, all other pollutants (except CBZ which was found to resist laccase attack under any conditions) were faster degraded when applied in mixture; with SMX also becoming biodegradable in the micro-pollutant mixture. These results suggest that micro-pollutants efficiently oxidized by laccase such as EE2 and BPA may act as redox mediators, thus facilitating the concomitant removal of those compounds which are more slowly or not at all attacked by laccase.

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Application of sulfamethoxazole-degrading bacteria to improve the removal of antibiotics from wastewater

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Recent studies have shown that the constant exposure of soil and sludge to sublethal concentration of antibiotics can lead to increased number of resistant strains. This could severely hamper the effectiveness of such antibiotics in treating bacterial infections. In order to minimize this risk, the removal of especially recalcitrant antibiotics, such as the sulfonamide sulfamethoxazole (SMX) needs to be enhanced. A promising technology is the bioaugmentation of sludge in a wastewater treatment plant.

We recently isolated several bacterial strains capable of degrading SMX from a membrane bioreactor continuously fed with SMX for over ten months. Of these strains *Microbacterium* sp. strain (designated BR1) was chosen as the fastest degrader for subsequent studies.

For eventual field studies, a better understanding of the metabolism of SMX is necessary; therefore we investigated key metabolites and the reaction mechanism. The degradation appears to proceed via *ipso*-hydroxylation of the carbon atom adjacent to the sulfo group. This induces a concerted cleavage of the molecule, releasing 4-aminophenol, sulfite and 3-amino-5-methylisoxazole. While the latter was identified as a dead-end metabolite, 4-aminophenol presumably serves as a source of carbon and energy. It is not known yet whether the sulfite serves any purpose. Experiments using cell free cell extracts showed that the reaction depends on a flavin monooxygenase.

Currently, attempts are undertaken to identify the enzyme responsible for this hydroxylation both by analysis of genomic data and chromatographic purification of the enzyme activity. With this information at hand, it will be possible to evaluate the dissemination of SMX degrading activity in the environment. This is especially interesting, as other sulfonamide-degrading *Microbacterium*, but also *Pseudomonas* strains have been isolated.

Eventually, knowledge of the genes involved will allow monitoring of SMX-degrading bacteria in bioaugmented membrane bioreactors, which are currently operated at pilot-scale.

The pilot scale setup consists of two membrane bioreactors with a volume of 200 L each. They are independently operated, allowing direct comparison of an augmented system to a non-augmented one. They are equipped with ceramic UF membranes (0.2 µm pore size with 0.8 m^2 membrane area each). Both MBRs contain a denitrification zone without aeration and nitrification zone with vigorous aeration. Raw wastewater after sand trap and pre-settling from a local wastewater treatment plant is used as feed.

Combining biotechnology, chemical analysis and molecular biological analyses will result in a comprehensive understanding of the processes occurring consequential to a bioaugmentation event..

Micropollutants clean-up by bio-inspired entrapped laccases in a continuous reactor with magnetic retention

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ABSTRACT:
Microbial laccases are powerful enzymes capable of degrading lignin and other recalcitrant compounds. For that reason, there is an increasing interest in these enzymes as biocatalysts for the removal of micropollutants in wastewater, with very promising results so far. However, the establishment of efficient industrial processes greatly depends on the availability of robust, stable and cost-effective immobilized biocatalysts.

Recently, a novel immobilization technique based on bio-inspired enzyme entrapment has emerged as a fast and versatile tool for generating robust, cheap and highly stable (nano)biocatalysts, with a very high potential for environmental applications. The enzyme entrapment via bio-inspired mineralization aims to mimic the natural reactions in diatoms, whereby silica precipitation is induced by polypeptides called silaffins. By analogy, different polymers (natural or synthetic) are able to induce the precipitation of different inorganic oxides to form different nanosized structures in which the enzyme is entrapped.

Highly active biocatalysts consisting in laccase-doped particles with a magnetic core have been produced using a fast and easy bio-inspired enzyme entrapment technique with a high potential for the degradation of a variety of micropollutants in wastewater. A continuous reactor with particle retention was set up to test the micropollutant degradation potential of these biocatalysts at laboratory scale. In the proof-of-concept experiment, degradation efficiencies of 60% for ethynylestradiol, 45% of bisphenol A and 8% for diclofenac have been achieved.

INTRODUCTION

The removal of micropollutants from wastewater, especially endocrine disrupting chemicals (EDCs), is one of the major environmental challenges that our society is facing nowadays. EDCs can alter the normal function of the endocrine system of human and wildlife organisms causing adverse health effects in the organism or its progeny even at very low concentrations. Potential EDCs are found as additives or contaminants in common goods, in food, personal care products, cosmetics, plastics, textiles and construction materials. They are usually difficult to degrade due to their complex chemical structure and remain intact after chemical and biological processing in wastewater treatment plants. A recent report of the World Health Organization written in collaboration with the United Nations Environment Program highlights the adverse endocrine-mediated effects that these compounds have already provoked on wildlife species and encourages decision-makers to search for new and effective ways to enable their complete removal from the environment (http://www.who.int/ceh/publications/endocrine/en/).

Laccases are oxidoreductases of great interest in environmental biotechnology because they can degrade a broad range of xenobiotics including EDCs (Demarche et al., 2012a; Cabana et al., 2007; Torres et al., 2003; Durán and Esposito, 2000). Laccases catalyze the one-electron oxidation of substrates with the reduction of molecular oxygen to water. The use of atmospheric oxygen as the final electron aceptor along with low substrate specificity provides a considerable advantage for laccase based catalysis compared to other available oxidoreductases.

Enzyme immobilization on solid carriers (e.g. by ionic adsorption, affinity or covalent binding) or enzyme “insolubilization” (e.g. as cross-linker enzyme aggregates) has contributed to widespread the use of enzymes as catalysts for many industrial applications (Brena and Batista-Viera, 2006). The facilitation of the separation of the enzyme from the reactor media allowing the reuse of the biocatalyst as well as the increase in stability that usually accompanies the immobilization are seen as the major advantages of these techniques that contribute to the reduction of the process costs. However, enzyme immobilization still suffers from different drawbacks, such as activity losses during immobilization and mass-transfer limitations, among others (Betancor and Luckarift, 2009). Novel immobilization techniques aimed to overcome these limitations are arising, being the immobilization on nanoparticles and nanostructures one of the most promising (Kim et al., 2006). The use of nanosized carriers allows achieving high specific loadings while contributing to reduce the mass-transfer limitations. Additionally, an enhancement of the enzyme stability after attachment to the nanoparticle has been reported for many systems (Heiz and Landman, 2006).

An emerging immobilization method is the use of bio-inspired mineralization techniques to encapsulate enzymes resulting in highly stable nanosized biocatalysts (Betancor and Luckarift, 2009). These methods aim to mimic the natural biomineralization reactions that allow diatoms to generate nanosized silica structures by using polypeptides called silaffins (Figure 1). Different polymers, either natural or synthetic analogues, have been shown to be able to induce the precipitation of different inorganic oxides with the formation of nanosized structures with various morphologies. This reaction has been used to entrap different enzymes, in some cases together with magnetic nanoparticles, inside the formed inorganic matrix obtaining a highly robust biocatalyst which preserves most of its initial enzyme activity and also shows very high stabilities in many examples. Additionally, the immobilization technique is fast, uses cheap reagents and proceeds under mild conditions (Betancor and Luckarift, 2009).

In this work, we propose the immobilization of laccase from *Thielavia* sp. using a bio-inspired immobilization technique to produce particles with entrapped enzyme in a titania shell with a magnetic core. The potential of these particles for degradation of a mixture of 6 model endocrine disrupting chemicals was assessed in batch experiments at different pHs. Finally, a laboratory-scale reactor with magnetic retention was developed and tested for the continuous degradation of the mixture of 6 model endocrine disrupting chemicals and the limitations of this technique were discussed.

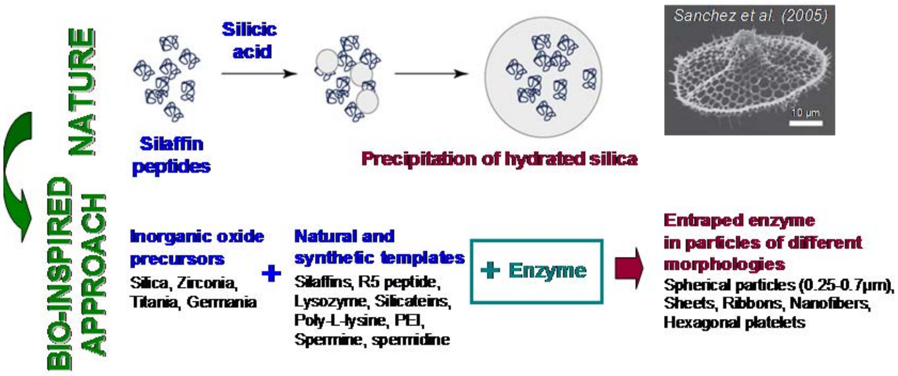

Figure 1: Scheme of the bio-inspired approach proposed and comparison with the natural process

MATERIALS AND METHODS

Laccase immobilization

A suspension of Fe_3O_4 particles in 12 g/L citric acid previously sonicated (2 hours) was mixed with polyethyleneimine (Sigma-Aldrich, St. Louis, USA) in a weight ratio of 2 and incubated for 3 minutes at room temperature. After neutralization and washes with water, 1 mL of laccase from *Thielavia* sp. (AB Enzymes GmbH, Darmstadt, Germany) was added. 25 mL of 0.5 M titanium(IV) bis(ammonium lactato)dihydroxide (Sigma-Aldrich, St. Louis, USA) was added and incubated for 5 minutes. Particles were washed with water and stored at 4ºC.

Laccase activity was determined according to Demarche et al. (2012b). One unit of laccase activity ($U_{ABTS,pH3}$) was defined as the amount of laccases required to oxidize 1 mM of ABTS per minute at pH 3.0.

Degradation of micropollutants with biotitania particles

Batch tests were carried out in 100 mL of a mixture of 6 micropollutants (bisphenol A, triclosan, nonylphenol, diclofenac, sulfamethoxazole and ethinylestradiol, all from Sigma-Aldrich, St. Louis, USA) in a concentration of 5 µM each in tap water at three different pHs: 4, 6 and 8. Degradation was started by addition of biotitania particles of 150 $U_{ABTS,pH3}$/g. A control with soluble enzyme at a comparable final activity was used. Samples of the experiment with soluble enzyme (1mL) were directly withdrawn and the reaction was stopped with addition of sodium azide (final concentration of 0.2%) whereas samples from the experiment with immobilized biocatalysts (1 mL) were taken, the particles separated with a magnet and the supernatant filtered through 0.2 µm PTFE filters. Sodium azide was also added to the filtered samples.

A 100 mL reactor was used for the continuous degradation of the same mixture of micropollutants as in the batch tests in a concentration of 5 µM each in tap water at pH 8. Biotitania particles containing *Thielavia* sp. laccase (TVL) with an enzyme loading of 200 $U_{ABTS,pH3}$/g were added to a final activity of 800 $U_{ABTS,pH3}$/L. A flow rate of 1.2 mL/min (HRT of 1.4 hours) was selected for the first continuous with a valve change every 20 minutes. In a second stage, the reactor was operated at a flow rate of 0.6 mL/min (HRT of 2.8 hours) and a valve change every 40 minutes. Samples of the outlet were collected at regular time intervals and filtered through 0.2 µm PTFE filters in order to determine the enzyme activity and the micropollutant concentration.

Monitoring of micropollutant degradation was done in an Agilent 1290 Infinity UHPLC system equipped with a Zorbax SB-C18 Rapid Resolution HT column (2.1 x 50 mm, 1.8 µm) from Agilent and thermostatized at 40ºC. The mobile phase flow rate was 0.5 mL·min-1 with 15 µL of injection volume. The UV absorption was monitored at a wavelength of 278 nm. The mobile phase system employed was 0.1% (v/v) HPLC-grade formic acid (Fluka, Buchs, Switzerland) in 10% (v/v) MS-grade methanol (Merck, Darmstadt, Germany) as eluent A and 0.1% (v/v) HPLC-grade formic acid in MS-grade methanol as eluent B. The gradient profile was a 4.4 minute linear gradient from 30% to 90% of eluent B, followed by 0.5 minutes at 90% B, a linear gradient back to 30% B in 0.1 minutes and stabilized at 30% B for 1 minute. The quantification was performed using external standards. Degradation efficiency was calculated as $\%D = [(C_0 – C_t)/ C_0] \times 100$, being C_0 the initial micropollutant concentration and C_t the concentration at a defined time.

RESULTS

Laccase immobilization via bio-inspired titanification

A novel procedure was developed to entrap laccase via bio-inspired titanification on the surface of commercial iron oxide particles. This method consists in the adsorption of a NH_2-rich template on the surface of the magnetic iron oxide particles via electrostatic interactions followed by addition of laccase and a titanium precursor. The presence of the NH_2-rich template provokes the bio-inspired precipitation of titanium oxide on the particle surface and the consequent entrapment of the laccase in the titanium oxide layer. In the proof-of-concept experiment, an enzyme loading of *ca.* 30 $U_{ABTS,pH3}$/g was obtained with no enzyme leaching detectable and the biocatalysts were able to catalyze the degradation of BPA, EE2, NP and TCS in batch experiments.

Higher enzyme loadings are necessary for the continuous degradation of micropollutants. Since the enzyme entrapment occurs on the surface of the magnetic particles, one of the main parameters that influence the enzyme loading is the particle size of the magnetic core. Although commercial particles of size <50 nm were employed it was observed by optical microscopy that these particles formed aggregates of much higher size (>100 µm) when resuspended in buffer (data not shown). Different protocols were tested to favour the disaggregation of the observed aggregates prior to laccase immobilization, being 2 hours of sonication under mechanical stirring of the particles at acidic pH the most suitable one. Measurements of the particles by dynamic light scattering (DLS) showed two distributions of particle sizes of *ca.* 1 µm and 250 nm of diameter.

Highly active laccase biocatalysts (up to 200 $U_{ABTS,pH3}$/g) was produced via bio-inspired titanification using the previously sonicated iron oxide particles, which represents a 6-fold increase compared with the preliminary immobilization.

Degradation tests in batch using biotitania particles

Biotitania particles containing *Thielavia* sp. laccase (TVL) were used for the degradation of a model mixture of 6 micropollutants in batch with a concentration of 5 µM each in tap water at room temperature and three different pHs: 4, 6 and 8 (Figure 2). This mixture contains 6 model endocrine disrupting compounds: bisphenol A (BPA, plasticizer), triclosan (TCS, biocide), nonylphenol (NP, detergent by-product), diclofenac (DF, anti-inflammatory), sulfamethoxazole (SMX, antibiotic) and ethinylestradiol (EE2, synthetic estrogen). In previous works in our lab it has been observed that the presence of other micropollutants can enhance the degradation due to a mediator effect (Nair et al., 2013).

The bio-inspired laccase particles were able to degrade the majority of the micropollutants analyzed except SMX, following in many of the cases the same trend than the soluble counterparts(NP was not possible to be monitored due to a low resolution of the HPLC analytical method). BPA and EE2 degradation at pH 4 were slower than at the other pHs as in the case of the soluble enzyme, although the trend was not so marked. Interestingly, very low degradation of DF was observed at any of the studied pHs, contrary to the case of soluble enzyme where degradations of 90%, 73% and 45% were obtained for pH 4, 6 and 8, respectively. In the case of TCS, it got adsorbed on the PTFE membranes used for filtering the samples prior to HPLC measurements (samples until 20 hours). The last two samples (not filtered) presented the same trend as with the soluble enzyme (pH 6 > pH 8 > pH 4). However, lower degradation percentages (36% and 22% at pH 6 and 8, respectively, compared to 61% and 30% with soluble enzyme) were obtained.

The biotitania particles preserved 100% of the activity during the batch experiments in all the essayed pHs, compared to a loss of 23% of activity for pH 6 and 51% for pH 4 in the case of the soluble enzyme (data not shown). The increase in stability together with the possibility of biocatalyst reuse may counteract the lower degradation rate observed with the biotitania particles.

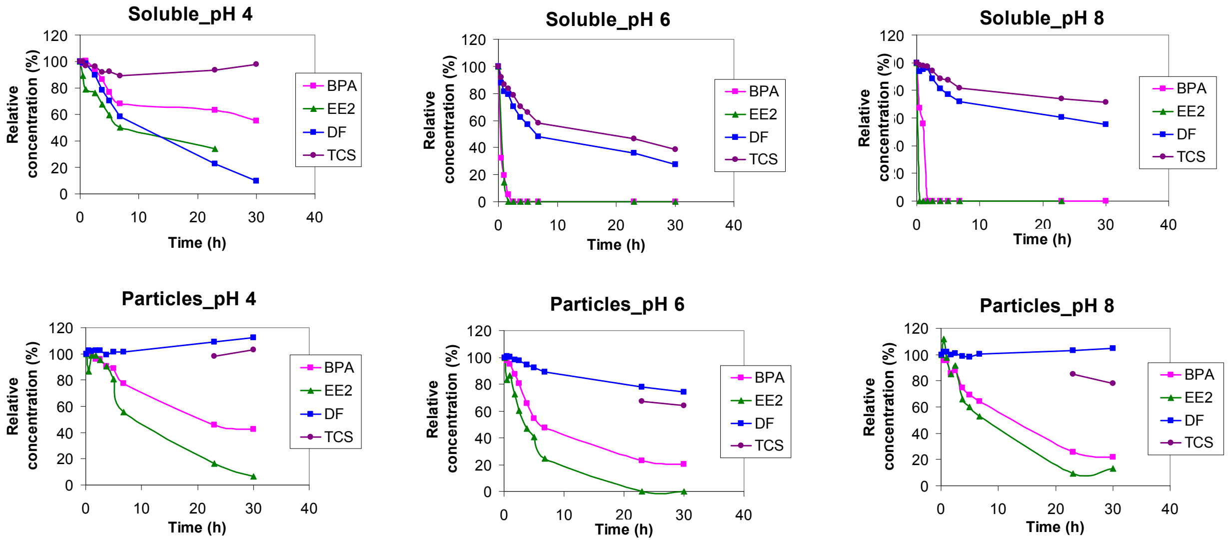

Figure 2: Degradation profiles of a mixture of 6 micropollutants in tap water at different pHs with soluble and immobilized Thielavia sp. laccase

Continuous operation of a reactor with magnetic retention

An operational reactor for the continuous degradation at lab-scale of micropollutants catalyzed by bio-inspired laccase particles were designed and constructed at UCL. The reactor with magnetic retention principle consists in a reactor of 100 mL with mechanical agitation. A magnet is placed at the outlet stream of the reactor to collect the biocatalytic particles and a system of valves allows reversing the flow at regular time intervals to bring back the biocatalyst particles in the reactor (Figure 3).

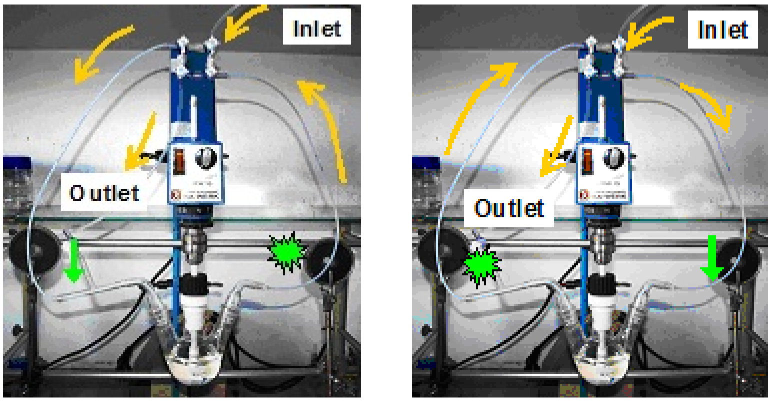

Figure 3: Schematic representation of the operation of the lab-scale reactor for the removal of micropollutants by bio-inspired titania laccase biocatalysts

Biotitania particles containing *Thielavia* sp. laccase (TVL) with an enzyme loading of 200 $U_{ABTS,pH3}$/g were used for the degradation of a mixture of 6 micropollutants (SMX, BPA, EE2, DF, TCS, NP) with a concentration of 5 μM each in tap water at room temperature. The final activity on the reactor was 800 $U_{ABTS,pH3}$/L with a particle concentration of 4 g/L. Prior to the reactor run, the possible adsorption of the micropollutants on the reactor pipes was studied by pumping the inlet solution through the system and analysing the outlet. SMX, BPA and DF did not get adsorbed on the system's components. On the contrary, EE2 seemed to be slightly adsorbed and it was necessary to run the system for 5 hours to achieve the saturation conditions (data not shown).

The reactor was operated in a first stage in batch for 1.4 hours (corresponding to approximately 1 HRT of the first continuous run) in order to decrease the time to achieve the steady state after changing to the continuous mode (Figure 4). No degradation of SMX was observed, as expected from the results of the batch tests, considering that the pH of the reactor inlet was 8. At the end of the first continuous stage, degradation efficiencies of *ca.* 30% for

BPA, 40% for EE2 and 4% DF were observed. In the case of TCS, it was not possible to accurately measure the concentration due to adsorption on the PTFE filters used, as previously observed.

In a second continuous stage, the HRT was doubled by reducing the flow rate to 0.6 mL/min. Maximal degradation efficiencies of 47% for BPA, 65% for EE2 and 8% for DF were obtained. These results suggest that the expected increase in degradation efficiency due to the increase on residence time is counteracted by a decrease on the degradation capacity of the biocatalyst during the second continuous stage. Enzyme leakage is not likely to occur since no activity was detected in the outlet stream all over the run. Therefore, the decrease in degradation efficiency is more likely to be caused by particle aggregation (visible to the naked eye) due to the magnetic retention, reducing the particle surface area exposed to the bulk reaction medium.

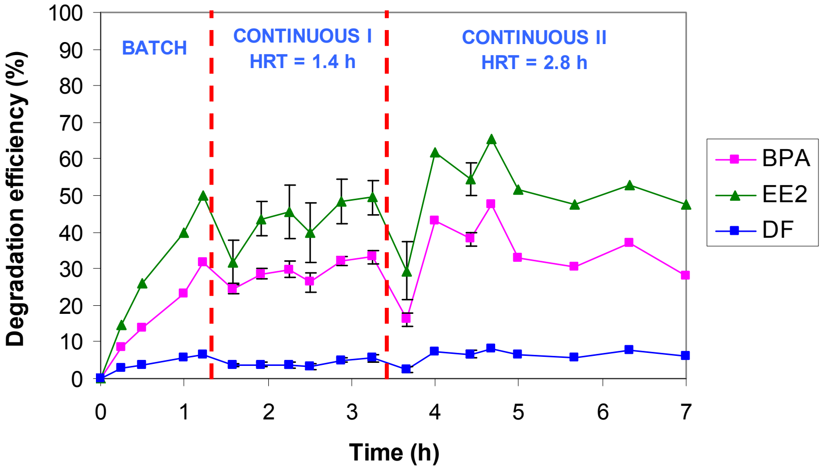

Figure 4: Concentration profiles of 5 micropollutants during the run in the lab-scale reactor with magnetic retention

CONCLUSIONS

In this work, a novel immobilization approach has been developed in order to produce highly active laccase biocatalysts (200 $U_{ABTS,pH3}$/g) consisting in laccase-doped particles with a magnetic core using a fast and easy bio-inspired enzyme entrapment technique.

The potential of these particles for degradation of a mixture of 6 model endocrine disrupting chemicals (bisphenol A, triclosan, nonylphenol, diclofenac, sulfamethoxazole and ethinylestradiol) was assessed in batch experiments and in a continuous laboratory-scale reactor with magnetic retention. The laccase-containing biotitania particles were able to catalyze the degradation of bisphenol A and ethinylestradiol at the three studied pHs (4, 6 and 8), triclosan was degraded at pH 6 and 8 and diclofenac only at pH 6. However, a lower biocatalytic efficiency was observed in most of the cases compared to the soluble enzyme. The different structure, hydrophobicity and physico-chemical properties of the micropollutants involved may cause the different degradation behaviour comparing with the soluble enzyme probably due to a different accessibility for the enzyme caused by mass-transfer limitations.

Degradation efficiencies of 60% for ethynylestradiol, 45% of bisphenol A and 8% for diclofenac have been achieved in a continuous lab-scale reactor with magnetic retention. The major identified challenges for the development and scale-up of the lab-scale reactor are the need to find a compromise between suitable HRT, biocatalyst loading, valve shift frequency and operation time in order to achieve sufficient degradation efficiency. Additionally, particle aggregation due to the magnetic separation should be overcome in order to ensure a long stability of the biocatalyst over long-term operation.

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Poster Presentations

Juncus acutus: A halophyte suitable for remediating contaminated groundwater with organics

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Selection of appropriate plant to stimulate pollutant degradation and to be tolerant to high concentrations of the contaminant is a key element in successful phytoremediation applications. Halophytic vegetation often grows in contaminated soils and various studies have revealed that these plants can also tolerate stress from various sources. In this work, *Juncus acutus* (family Juncaceae), a robust tussock-forming perennial halophyte, was selected for an in depth investigation of its phytoremediation potential to degrade bisphenol A from groundwater. *Juncus acutus* has an extensive deep-root system thus providing large root surface for the growth of microbial populations not only in the interior but also in the rhizosphere. Bisphenol A (BPA, 2,2-bis-(4-hydroxyphenyl)-propane) is a high volume chemical used in a wide variety of products, and may cause reproductive toxicity because of its estrogenic activity. It may still stimulate cellular responses and alter cell functions at very low concentrations.

A Shallow Aquifer Rhizodegradation Pilot was developed to assess this technology for the remediation of BPA-contaminated groundwater. Contaminated groundwater from an external tank was recirculated through the pilot unit. Following the addition of 160 mg BPA to the external feed tank corresponding to an initial concentration of 2,667 μg-BPA/L (ppb), the system was operated for 35 days although after 19 days BPA could not be detected, while the halophytes developed no toxicity symptoms. In order to investigate the hypothesis that this is linked to the effective detoxification provided by endophytic bacteria, the diversity of culturable endophytic community found in association with *Juncus acutus* was assessed. The isolated strains were genotypically and phenotypically characterized regarding their BPA tolerance, heavy metal resistance and plant growth promoting traits. This study demonstrated that several endophytic strains had the potential to enhance not only bioremediation of bisphenol A but also plant growth.

Experiments in small-pots were also conducted in order to understand the mechanisms involved in BPA degradation. During these experiments, several concentrations of BPA were tested for their potential impact on the halophyte and shifts on degradation rate. Also, differences between the pattern of organic acids that *Juncus acutus* excretes with and without the presence of the pollutant were investigated. Lastly, the tolerance of this halophyte to heavy metal contamination was tested.

The results of all the above experiments demonstrate that *Juncus acutus* is an appropriate plant for implementing phytoremediation strategies in areas with contaminated groundwater.

A Novel Ozone Assisted Process for treatment of EDCs in Biological Sludge

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Variations in the chemical properties of endocrine disrupting compounds (EDCs) affect the removal efficiencies in conventional treatment facilities. Although some are biodegradable and removed in the usual biological processes, the ones with hydrophobic nature tend to accumulate in sludge. Ozonation can achieve more than 90% removal of several emerging contaminants, such as pesticides, anti-inflammatories, antiepileptics, antibiotics and natural and synthetic estrogens in waters and wastewaters. It is also a very strong agent for biological sludge minimization owing to its successful full-scale applications and high sludge volume reduction capability.

In this study, a novel aerobic sludge digestion process to stabilize and decrease the amount of excess sludge produced during biological treatment and simultaneous removal of EDCs sorbed onto sludge is discussed. The selected compounds were diltiazem, carbamazepine, butyl benzyl phthalate, acetaminophen and two natural hormones, estrone and progesterone. Waste activated sludge samples from two different wastewater treatment plants were ozonated for different periods in Erlenmeyer flasks once a day on each of four consecutive days. Flasks were continuously aerated between ozone applications by shaking on an orbital shaker. The residual EDC concentrations in sludge samples were analyzed at the end of digestion periods. The analyses were conducted by using LC (ESI) MS/MS after solid phase extraction (SPE). An MLVSS reduction of up to 95% was achieved with an ozone dose of only 1.05 g O_3/kg MLSS in this process on the fourth day with a removal of more than 99% of the EDCs.

The destruction of EDC`s is attributed to the direct mechanism where O_3 is known to be a selective electrophile that reacts quickly with amines, phenols, and double bonds in aliphatic compounds. By this process even non-biodegradable compounds like carbamazepine can be effectively removed.

The results showed that by this process it became possible to save on contact time as well as achieving a bio-solids digestion far exceeding the standard aerobic process and concomitant removal of the micropollutants at the expense of minimum ozone dose compared to previous studies.

Removal of micropollutants from wastewater by suspended and immobilized bacteria in a pilot scale MBR

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Wastewater treatment by conventional activated sludge processes cannot completely eliminate micropollutants from the wastewater. Various types of technologies such as advanced oxidation process and activated carbon have been tested as advanced wastewater treatment methods in the recent years in order to achieve further removal of micropollutants from the wastewater. Biological removal of micropollutants by means of bacteria able to degrade targeted micropollutants is being tested within this research project, which is part of the MINOTAURUS project.

Sphingomonas sp. strain TTNP3 and *Microbacterium sp.* strain BR1 are interesting bacterial strains able to degrade xenobiotics. *Sphingomonas sp.* strain TTNP3 has been shown to degrade endocrine disruptors, such as bisphenol A (BPA). *Microbacterium sp.* BR1 has been recently isolated and shown to partially mineralize sulfamethoxazole (SMX). Within this project the two strains are being tested for the removal of the respective target compound (BPA and SMX) in a pilot scale membrane bioreactor (MBR) for municipal wastewater treatment.

Each of the selected strains is being tested for bioaugmentation in two forms: as freely suspended culture, bioaugmented directly into the activated sludge tank of the pilot MBR, and as immobilized microorganisms in alginate beads. The pilot plant consists of two parallel MBRs, 220 litres each, fed by municipal wastewater and operated under the same operating conditions. One MBR is bioaugmented by the suspended form of the tested microorganism (approx. 1 % of suspended solids), the other serves as reference. The effluent of the reference MBR is further treated in a 3 L continuous mixed reactor containing the tested microorganism immobilized in alginate beads. Flow proportional samples of influent, effluents from both MBRs and effluent from the alginate beads tank are analysed for the concentration of target compound and their general toxicity and estrogenic potential, respectively. Yeast estrogen screen (YES) by expressing rainbow trout estrogen receptor (rtER) is used to detect compounds acting as an estrogen whereas *Daphnia magna* immobilisation test is performed for acute toxicity of samples. Grab samples of biomass are regularly tested for their degradation activity towards the target compound. The two selected microorganisms are being tested in two consecutive pilot experiments (approx. 1 month each). The experiment with *Sphingomonas sp.* strain TTNP3 is currently running; the experiment with *Microbacterium sp.* BR1 is scheduled for the following weeks.

Session 6
permeable reactive barriers/zones for in-situ groundwater treatment

Oral presentations

Biological sulfate reduction for remediation of acid mine drainage and overburden from sulfidic mine

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ABSTRACT: The exposure of the post mining waste, rock or overburden, which valuable minerals are taken out from sulfidic mine activities to water and air undergoes chemical and biological oxidation processes result in a highly acidic leachate. This acidic leachate known as acid mine drainage (AMD), which contains low pH and high concentration of sulfate as well as toxic trace metals such as iron, copper, and lead. Active treatments, such as pump and treat techniques, are widely used in an attempt to control AMD but their operational costs are very high and they produce huge volumes of potentially hazardous unstable sludge. One of the most promising passive treatment technologies for remediation of AMD from groundwater plumes is the Permeable Reactive Barrier (PRB) due to its effectiveness and its low cost compared to other technologies. The purpose of this research is to select the appropriate organic materials used as electron donors for treating AMD, to evaluate the suitable residence time in PRB, and their investigate heavy metal removal efficiency. A number of organic substrates were assessed through batch and continuous column experiments under anaerobic conditions with AMD obtained from an abandoned lignite coal mine. Under anaerobic conditions, sulfate reducing bacteria convert sulfate into sulfide using the organic substrates as electron donors. The sulfide that was generated precipitated heavy metals as metal sulfides. Organic substrates, which yielded the highest sulfate reduction in batch tests, were selected for continuous column experiments which lasted over 200 days. A mixture of pig-farm wastewater treatment sludge, rice husk and coconut husk chips yielded the best heavy metal (Fe, Cu, Zn and Mn) removal efficiencies of over 90%. These organic mixtures can also use for treating the overburden which has a high gypsum content and cannot be used for agriculture. The accumulation of gypsum in soils results in a low water retention capacity, shallow depth to a hardpan and vertical crusting. Overburden from a gypsum mine was treated using the organic mixture in order to reduce its gypsum content. The highest sulfate removal efficiency of 59 % was achieved from the overburden mixed with 40 % of organic mixture. This is corresponding to a reduction of the gypsum content from 25 to 7.5 % of soil.

INTRODUCTION

Acid mine drainage (AMD), which has a pH of 4.0 - 4.5 or lower, solubilizes heavy metals present in the mine tailings (Chang et al., 2000; Christensen et al., 1996). Due to its highly toxic nature, AMD poses a significant environmental threat. Virtually no life can survive in such acidified waters. AMD generated from abandoned mines and mine tailings have created large lagoons worldwide. Heavy metals in soluble form affect the food chain through bio-accumulation and bio-magnification, posing a greater threat to all forms of life (Gray, 1997). AMD from these lagoons percolates through soil, thereby affecting the soil chemistry and contaminating the groundwater (Gibert et al., 2011), which is a valuable source for drinking water and for agriculture. Soils in some mining area, especially the gypsum mine, have a high sulfate content which can induce adverse effects on the environment. Normally these kinds of soils can also generate AMD, results mass mortalities of plants and aquatic life. Such land cannot be used for agriculture, and these soils have a poor fauna and flora.

Pump and treat remediation methods are often difficult to employ when dealing with groundwater contamination from AMD (Keely, 1989; National-Research-Council, 1994). Metal hydroxides can resolubilize the metals depending on the redox potential and pH (Masscheleyn et al., 1991). Passive treatment methods such as the Permeable Reactive Barrier (PRB) technology may be more appropriate (Lapointe et al., 2006; Walton-Day, 2003). PRBs can be both abiotic and biotic treatment systems (Pagnaneli et al., 2009). In the abiotic treatment system, neutralizing agents (lime), adsorbents (silica sand or perlite) or zero-valent iron are used as reactive materials (Pagnaneli et al., 2009). In biological system, PRBs employ natural organic substrates as electron donors to facilitate the growth of SRB. When an AMD plume containing sulfate and heavy metals passes through the reactive barrier, SRB in the reactive barrier convert the sulfate into sulfide while consuming the organic substrates as electron donors (Tsukamoto et al., 2004). Heavy metals present in the contaminated feed water are then removed as metal sulfides (Dvorak et al., 1992; Jong and Parry, 2003). This research describes the results obtained from batch and continuous column experiments testing no or low cost organic substrates as electron donors for the SRB in AMD and sulfate contaminated soils treatments.

MATERIAL AND METHODS

Acid Mine Drainage (AMD)

AMD was collected from an acidified lagoon generated from leachate of an abandoned coal mine in Lamphun Province (Thailand). AMD was stored in a cold room maintained at 4°C. AMD was characterized for its pH, metals content and sulfate concentration (Table 1). This original AMD was supplemented further by metals whenever necessary and then used as feed for the experiments (Table 1).

Table 1: Characteristics of acid mine drainage (AMD) used in batch and column tests

Parameters	AMD (batch tests)	Added	AMD (column tests)
pH	4.16±0.08	-	4.16±0.08
Sulfate, mg L^{-1}	731±55.2	-	838±65.0
Iron, mg L^{-1}	0.08±0.05	30	26.9±0.78
Manganese, mg L^{-1}	16.7±0.91	-	16.7±0.56
Copper, mg L^{-1}	0.04±0.01	20	17.5±0.53
Zinc, mg L^{-1}	0.92±0.11	5	6.35±0.03

Mine soils (overburdens)

Gypsum mine overburden (GMOB) was collected from a gypsum mine in Nakhon Si Thammarat (Thailand). The samples were air-dried and sieved at 2 mm. GMOB had a very low OM (1%) and total nitrogen (0.05%) content, and contained 25% of gypsum.

Inocula

Sludge from a full scale mesophilic anaerobic baffled reactor treating tapioca starch wastewater, and from a pilot scale mesophilic anaerobic channel digester and upflow anaerobic sludge blanket (UASB) reactor treating pig farm wastewater were used as source for SRB in AMD and sulfate contaminated soils, respectively. The seed sludge had a total suspended solids (TSS) of 9.78 and 33.3 g L^{-1}, and volatile suspended solids (VSS) of 8.12 and 21.3 g L^{-1}, respectively, corresponding to a VSS/TSS ratio of 0.83 and 0.64.

Organic substrates

Five organic substrates were selected for their possible use as electron donors for SRB. These included bamboo chips (BC), rice husk (RH), pig farm wastewater treatment sludge (PWTS), municipal wastewater treatment sludge (MWTS) and coconut husk chips (CHC), based on their availability, ease of handling and no or low cost. Organic substrates were washed by tap water, air dried, cut to the desired size.

Batch experiments

Five organic substrates were evaluated individually in 1.5 L batch containers at ambient temperature (30 ± 5°C) and anaerobic conditions to assess their ability for promoting biological sulfate reduction. During the acclimatization period, biological sulfate reduction by SRB may progress at a considerably slower pace, leading to a lower alkalinity generation. Therefore, to compensate the lower alkalinity production during this period, it was necessary to adjust the pH of the AMD to the optimum range for SRB (pH 6-7). Each reaction bottle contained 20% by volume (300 mL) of each organic material, deoxygenated AMD from the abandoned lignite coal mine 66% by volume (1000 mL), and SRB inoculum 7% by volume (100 mL). The remaining volume (7%) is the headspace of the batch bottle. Based on the results from the single substrate batch tests, 3 organic substrates were selected for mixed substrate batch tests.

Continuous column experiments

Long term continuous column experiments were conducted at room temperature (30 ± 5°C) with mixtures of 3 organic substrates from the batch experiments. PWTS, RH and CHC were selected and mixed in 4 different proportions, including 33:33:33 (Reactor 1), 60:20:20 (Reactor 2), 20:60:20 (Reactor 3) and 20:20:60 (Reactor 4) *v/v* and then filled in 4 column reactors made of polyvinyl chloride (PVC) each with a volume of 12 L. 1.8 g of lime was mixed with organic material in each reactor prior to filling into the reactor columns (0.15 g of lime L^{-1} of AMD (Huttagosol and Kijjanapanich, 2008)). A HRT of 16 d was maintained in the continuous column experiments. Deoxygenated AMD supplemented with metals (Table 1) was fed at the bottom of the reactor at a flow rate of 30 mL h^{-1} (37.18 L m^{-2} d^{-1}) using a peristaltic pump. AMD travelled through the fixed bed of the organic substrate mixture which also acted as support for immobilization of SRB, while the effluent was withdrawn from the top of reactor.

Bioreactor experiments

GMOB with a high sulfate content (around 150 g kg^{-1}), classified as gypsiferous soils, was selected for the bioreactor experiment. The reactors (working volume of 5 L) were made of polyethylene (PE) and operated at room temperature (25 ± 5°C). Each reactor had a biogas releasing tube at the top. This hydrogen sulfide (H_2S) rich biogas was lead through a zinc acetate solution (1 M) in order to trap H_2S. Nitrogen gas was used to purge the reactor prior to sampling in order to make sure that most of the H_2S was trapped in the zinc acetate solution. GMOB (2500 g) was mixed with the best organic mixture selected from the continuous column experiments treating AMD in different amounts: 10, 20, 30 and 40% of the GMOB, respectively. A SRB inoculum of 250 g (10% of the GMOB) was added to each bioreactor. During the acclimatization period, biological sulfate reduction may progress at a considerably slow pace, leading to a lower alkalinity generation. It was therefore necessary to adjust the pH of the soils to the optimum range for SRB (pH 6-7) at the beginning of the experiment. This was done by adding lime (0.02% of the GMOB) to the GMOB. Water was added to the reactors in order to maintain the desired moisture content (20-25%). Samples were collected once a week for analyzes.

Analytical methods

pH was measured using a Mettler Toledo pH meter, while ORP was measured using a Hach ORP meter. Alkalinity in the column experiments was measured using the titration method. DOC which was monitored as an indicator of dissolved carbon available for bacterial activity was measured using the high temperature combustion method by a Shimadzu TOC analyzer (Eaton et al., 2005). Sulfate removal was used as an indicator of SRB activity. Sulfate was measured using the turbidimetric method by a Shimadzu UV visible spectrophotometer. Sulfide was measured using the gravimetric method by precipitation as zinc sulfide in a zinc acetate solution (1 M). Metals (Fe, Cu, Zn, and Mn) were measured using Perkin Elmer Inductive Coupled Plasma (ICP) optical spectrophotometry. During the sampling process, care was taken to minimize sample aeration and air infiltration into the batch bottles and columns.

RESULTS AND DISCUSSION

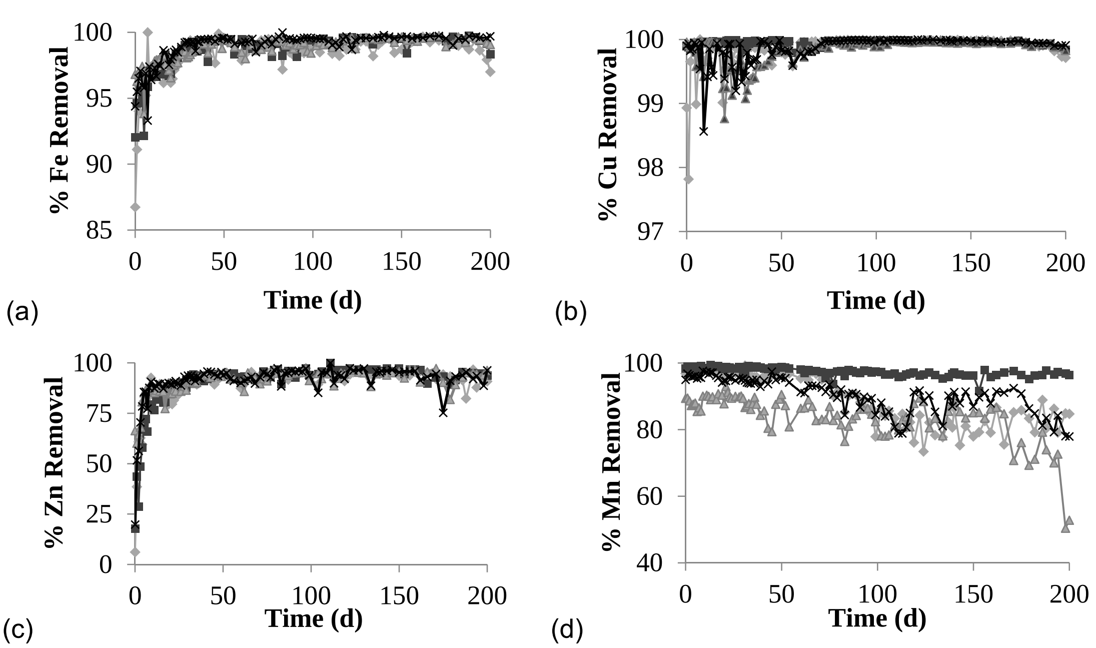
Batch experiment for the treatment of acid mine drainage

Comparing sulfate concentrations on day 2 and day 16, the batch tests with RH as the organic substrate recorded the highest sulfate removal efficiency (77.8%), followed by PWTS (66.7%), MWTS (60%), CHC (36.1%) and BC (30.3%). All the organic substrates except BC were able to maintain the pH in the range 5-8 suitable for growth of SRB (Gibert et al., 2002); could generated alkalinity, which is an indicator of biological sulfate reduction (Brown et al., 2002); and could also maintain the ORP in a negative range indicating the existence of anaerobic conditions necessary for SRB (Gibert et al., 2002). All organic substrates except BC yielded a significant percentage of sulfate reduction although CHC recorded a lower percentage of sulfate reduction than MWTS, PWTS, and RH. Therefore, it can be concluded that all organic substrates except BC are suitable as substrates for SRB. PWTS is a fast degrading organic substrate, RH is moderately degrading and CHC is a slow degrading organic substrate. Thus, PWTS, RH and CHC were selected for multiple substrates batch tests.

For the multiple substrate batch test, the RH + CHC mixture had the lowest sulfate reduction efficiency of 84% on day 32. The sulfate reduction efficiencies (comparing sulfate concentrations on day 2 and day 32) of the PWTS + RH, PWTS + RH + CHC and PWTS + CHC mixtures were slightly different (99%, 98%, and 95%, respectively). The sulfate removal efficiencies of the mixtures of PWTS + RH and PWTS + RH + CHC were not significantly different. Therefore, the mixture of a fast, moderately and slow degrading organic substrate (PWTS + RH + CHC) was used for the continuous column experiment.

Continuous column experiment for the treatment of acid mine drainage

Heavy metal removal from the column experiments is presented in Figure 1. The results reveal that the four reactors achieved over 80% removal of Fe, Cu and Zn within the first 10 d of operation. These heavy metal removal efficiencies remained consistently high with Zn removal, which remained over 80% throughout the period of 200 d. However, the Mn removal efficiency was satisfactory (over 90%) only in reactor 2 while the other reactors showed a lower Mn removal efficiency. Reactor 2 yielded the best Fe, Cu, Zn and Mn removal efficiency. More than 90% of all these heavy metals were removed in Reactor 2. Although Fe, Cu and Zn removal has been satisfactory in Reactor 1, Reactor 3 and Reactor 4, Mn removal in these reactors was not satisfactory. Out of these 3 reactors, Reactor 3 gave the lowest Mn removal efficiency.



(a) (b) (c) (d)

Figure 1 Heavy metal removal efficiency (%) of column test.
(♦) Reactor 1, (■) Reactor 2, (▲) Reactor 3 and (×) Reactor 4.

The metal removal can be attributed to the precipitation of insoluble metal sulfides as a result of sulfide production from SRB activity in the continuous reactors. Cu removal was the most stable and efficient (Figure 1b), followed by Zn and Fe (Figure 1c and a, respectively). Metal removal from AMD in an experimental constructed wetland was found to follow closely the trend in solubility product (K_{sp}) values (Machemer and Wildeman, 1992). Log K_{sp} values of CuS, ZnS, FeS and MnS are -35.06, -20.96, -18.10 and -14.29, respectively (Chang, 2009). The metal removal trend in the continuous column experiment indeed followed this trend as Cu removal was the highest (Figure 1b), while the Mn (Figure 1d) removal was the lowest. Mn removal was least in Reactors 1, 3 and 4; Reactors 2 and 3 yielded the best and the worst Mn removal, respectively (Figure 1d). As the log K_{sp} of MnS was the highest of all the metal sulfides investigated in this research, not all Mn in the reactor precipitate as MnS and the remaining Mn was discharged in the effluent in its dissolved form.

Batch experiment for the treatment of sulfate contaminated soils (GMOB)

The GMOB had a very low OM (1%) and total nitrogen (0.05%) content, and contained 25% of gypsum prior to the treatment. The OM, total nitrogen, phosphorus and potassium content of the GMOB increased considerable after mixing with the organic mixture and remained at a high level after treatment (data not shown). Mixing of GMOB and the organic mixture created some dilution (up to 28% in case of 40% organic mixture) of the gypsum content of GMOB (Figure 2). However, the biological sulfate reduction process is still the main process of sulfate removal from the system and the dilution value is less when compared to the reduction of the gypsum content of GMOB by SRB (Figure 2). The reactor with a 40% organic mixture yielded the highest amount of sulfide (14 g wk^{-1}). The lowest sulfate concentration (42 g kg^{-1}) was achieved in the 40% organic mixture reactor, corresponding to a sulfate removal efficiency of 59%. The calcium content of all soil mixtures remained constant throughout the experiment.

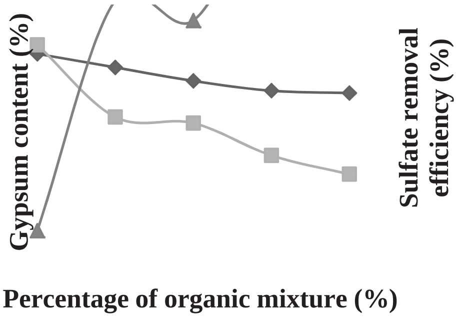


Figure 2 Performance of the gypsum removal from GMOB by biological sulfate reduction using different percentage of organic mixture for 105 d treatment. (♦) GMOB before treated, (■) GMOB after treated and (▲) gypsum removal efficiency (by sulfate reduction).

CONCLUSIONS

- Batch experiments showed that both mixtures of PWTS + RH and PWTS + RH + CHC yielded better conditions for sulfate reduction. Both mixtures developed conditions (generation of alkalinity and a low ORP) that favor the activity and growth of SRB leading to biological sulfate reduction.
- Continuous column experiments showed that a mixture of PWTS, RH and CHC could successfully facilitate growth of SRB and yielded above 95% removal of Cu, Zn and Fe.
- It is recommended that a mixture of fast and slow degrading organic substrates such as PWTS, RH and CHC are utilized in PRBs as electron donor for growth of SRB for removal of heavy metals from AMD.
- Mixtures of no or low cost organic substrates, such as PWTS + RH + CHC, can also be utilized as electron donor for growth of SRB for the removal of sulfate from sulfate contaminated soils when applying soil bioremediation.

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Predicting performance and longevity of permeable reactive iron barriers via labscale tests and modelling

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Permeable reactive zerovalent iron (ZVI) barriers represent a passive in situ approach to prevent further spreading of pollutants such as chlorinated ethenes by degrading them while the groundwater flows through the system. Although the maintenance costs of ZVI-barriers are generally very low during more than 10 years after the installation, the initial investment cost is higher as compared to pump and treat. Therefore, a good design of the barrier system and information on its long-term performance are important for the site owner to predict the return on investment.

Within the FP7 project AQUAREHAB (GA 226565), earlier, an improved labscale feasibility test procedure has been worked out to collect site specific input data required for a numerical model that has been elaborated to predict the performance of ZVI-barriers over time.

In the second phase of this project, these protocols and tools have been evaluated by using them for predicting the performance and longevity of a ZVI-barrier at a new site. For this purpose, > 50 L of representative groundwater (TCE 25 mg/L; cDCE 8 mg/L) was sampled and used as influent for a column test (L=50 cm; 25 cm/day). During the first 50 pore volumes, samples of the liquid phase have been taken for pH, ORP and CAH-concentration profiles, as well as profiles for inorganics. Next, the flow rate was increased 8-fold to accelerate the process and again concentration profiles were made. All collected data was used as input for parameter estimation (CAH-degradation rates, mineral precipitation rates, iron corrosion rates, iron deactivation parameters, ...) and longevity estimation using complex but also simplified numerical models. Further, a PRB-design for the site was elaborated.

Special attention has been given to aspects that are important for end-users, like the required resources, the usefulness of the generated results and the type of output information. Another objective of the study was also to evaluate how easy non-modellers can work with the numerical tools. A comparison of the results obtained with the classical and optimised protocol & processing methods will be presented, as well as the time and budget needed to collect them.

Microbial characterisation of Angled Core Samples of a 6 year old Zerovalent Iron Barrier in Belgium

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ABSTRACT: This study focuses on the characterisation of the present and active microbial population in a 6 year old ZVI-barrier that was installed in 2005 at an industrial site in Belgium. Angled undisturbed core samples were taken across the barrier, comprising (1) aquifer material upstream of the ZVI-barrier, (2) a transect of the ZVI-barrier, as well as (3) aquifer material just downstream of the barrier. The samples were frozen at the site immediately after sampling. The cores were sliced in 2-4 cm thick ZVI/aquifer-sections, which were each subjected to a microbial characterisation via (1) quantification of species specific and catabolic genes, and (2) 16S rRNA tag-pyrosequencing. The analyses were performed on DNA-extract as well RNA-extracts, providing information about the presence and activity, respectively, of the species/genes. Genes encoding for enzymes involved in CAH-degradation and *Dehalococcoides mccartyi* species were found present in the ZVI-barrier. Significant differences in the community structure were revealed in the ZVI-barrier as compared to the adjacent aquifer material.

INTRODUCTION

In 2005, a 200 m long zerovalent iron (ZVI) barrier was implemented at a site (site A) in Belgium to contain a chlorinated aliphatic hydrocarbon (CAH) plume. The ZVI barrier (30 cm thick) consisting of 20% fine ZVI and 80% of coarse sand was installed on a clay layer situated 3.5 and 6 m below ground surface. The contaminated aquifer (2-6 m bgs) has a low permeability resulting in a groundwater flow of a few meters per year.

Six years after the implementation, 40° angled core samples were taken comprising (1) aquifer material upstream of the ZVI-barrier, (2) a transect of the ZVI-barrier, as well as (3) aquifer material just downstream of the barrier. After sampling, the core samples were frozen immediately and transferred to the laboratory where they were divided under nitrogen atmosphere in 2-4 cm slices under which were used for several types of analyses. Earlier we reported that the porosity was at least 33% in the whole ZVI transect, which was either similar or higher than the porosity of the surrounding aquifer material. Batch degradation tests proved that the reactivity of the barrier material did not decrease compared to original material used. (Bastiaens et al., 2012).

The current study focused on characterisation of the microbial community within and near the 6 year old ZVI-barrier. For this purpose, two core samples (one taken in the contamination plume, and one at the edge of the barrier outside the contamination plume) were sacrificed for characterisation of the microbial community in the ZVI-barrier transect and the adjacent aquifer material. DNA as well as RNA was extracted from the ZVI/aquifer-slices and the present and active microbial community was characterised by quantitative PCR (q-PCR) and 16S rRNA tag-pyrosequencing.

MATERIALS AND METHODS

Angled cores

An overview of angled core sampling is shown in Figure 1. Core sample number AC-2 was taken outside contamination plume, near the edge of the ZVI-barrier, which explained the only thin section of the ZVI-barrier observed in this liner. On the other hand, core sample AC-3 was sampled within the contamination plume, and a wider barrier part was observed in the core sample at this spot. Each frozen core was cut into small slices of 2 cm thickness. Out of each section separate samples of 2 g each were taken for DNA and RNA extraction, respectively. 2 ml RNAlater (Ambion Inc.) was added to the RNA samples and all samples were stored at -80°C. A selection of the samples was made for DNA and RNA extraction.

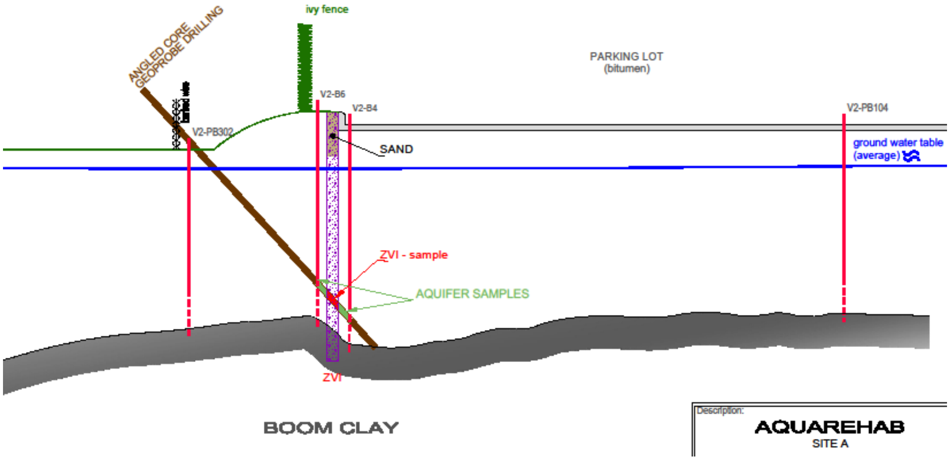

Figure 1: Overview of angled core sampling from the ZVI-Barrier

Molecular analyses

DNA-extraction: was performed according to the protocol described by Hendrickx *et al* (2005). RNA was extracted using the MOBio Powersoil RNA extraction kit. The extracted DNA and RNA samples were subsequently prepared for 16S rRNA -tag Pyrosequencing and quantitative PCR with specific primers.

q-PCR: High-throughput (HTP), ligation-based circularization assay for simultaneous quantitative detection of multiple organohalide respiring bacteria and their key reductive dehalogenases was used in these bioremediation case studies. The ligation probes are long oligonucleotides with target complementary regions at their 5' and 3' ends. Upon perfect target hybridization, the ligation probes are circularized via enzymatic ligation, subsequently serving as a template for individual and standardized amplification via unique probe-specific primers (van Doorn et al., 2007). The assay has now been adapted for use on a 384 wells plate qPCR machine. The ligation probes were designed to target 10 reductive dehalogenases and 16S rRNA genes from 9 phylogenetic groups, involved in reductive dechlorination (Table 1). Multivariate and comparative analyses were done to further understand the organohalide respiring community dynamics associated with the different geochemical parameters.

Table 1: q-PCR primers used.

Q-PCR Primer (16S RNA-gene)	Target	Q-PCR Primer (catabolic gene)	target
Sul	*Sulfurospirillum*	sul_pceA	*Sulfurospirillum* tetrachloroethene reductive dehalogenase
De 195	*D. mccartyi 195*	tceA	*D. mccartyi* 195 trichloroethene reductive dehalogenase
Dcbdb1	*D. mccartyi CBDB1*	cbrA	*D. mccartyi* CBDB1 chlorobenzene reductase
Dsb	*Desulfitobacterium*	Det_pceA	*D. mccartyi pceA*
Dhb	*Dehalobacter*	vcrA	*D. mccartyi* VC vinyl chloride reductive dehalogenase
Dsm	*Desulfuromonas*	bvcA	*D. mccartyi* BAV1 Vinyl chloride reductive dehalogenase
Geo	*Geobacter*	cprA1	Chlorophenol reductive dehalogenase A1 from *Desulfitobacterium*
Ana	*Anaeromyxobacter*	cprA5	Chlorophenol reductive dehalogenase A5 from *Desulfitobacterium*
Sed	*Sedimentibacter*	Dsb_pceA	*Desulfitobacterium pceA*
		dcaA	Dichloroethane reductive dehalogenase *Desulfitobacterium*

16S-tag Pyrosequencing: Tag encoded amplicon pyrosequencing was performed. Pyrosequencing data were analysed using the QIIME 1.3.0 pipeline (Caporaso et al 2010). Low quality sequences were removed using default parameters and operational taxonomic units (OTUs) were identified at the 97% identity level. A representative sequence from each OTU was aligned using PyNAST (DeSantis et al 2006). The taxonomic affiliation of each OTU was determined using the RDP Classifier at a confidence threshold of 80% (Wang et al 2007). Possible chimeric OTUs were identified using QIIME's ChimeraSlayer and subtracted from the previously generated OTU list, producing a non-chimeric OTU list.

RESULTS

Quantitative PCR

The qPCR analyses showed the presence (Figure 2A) and activity (Figure 2B) of *Dehalococcoides mccartyi* (*Dhc*) and the reductive dehalogenase (Rdh)-encoding genes *vcrA* and *bvcA*. *vcrA* is the most strongly expressed *rdh* gene found in this site. Except for few samples, the copy number of *vcrA* was generally higher than *D. mccartyi* numbers. In contrast, *bvcA* showed relatively lower counts especially in the barrier samples taken inside the plume. This may point to lower abundance and activity of the *D. mccartyi* strains harbouring the *bvcA* gene or negative impact of ZVI on these bacteria. The presence and activity of *D. mccartyi* and *vcrA* was generally found to be higher in the core samples taken inside the plume (AC-3) than corresponding upstream and downstream samples from the same core, except in the middle part of the ZVI-barrier. This can be due to direct access of these bacteria to chlorinated ethenes as the electron acceptors or electron donor rich and subsequently strong reducing conditions created by the ZVI.

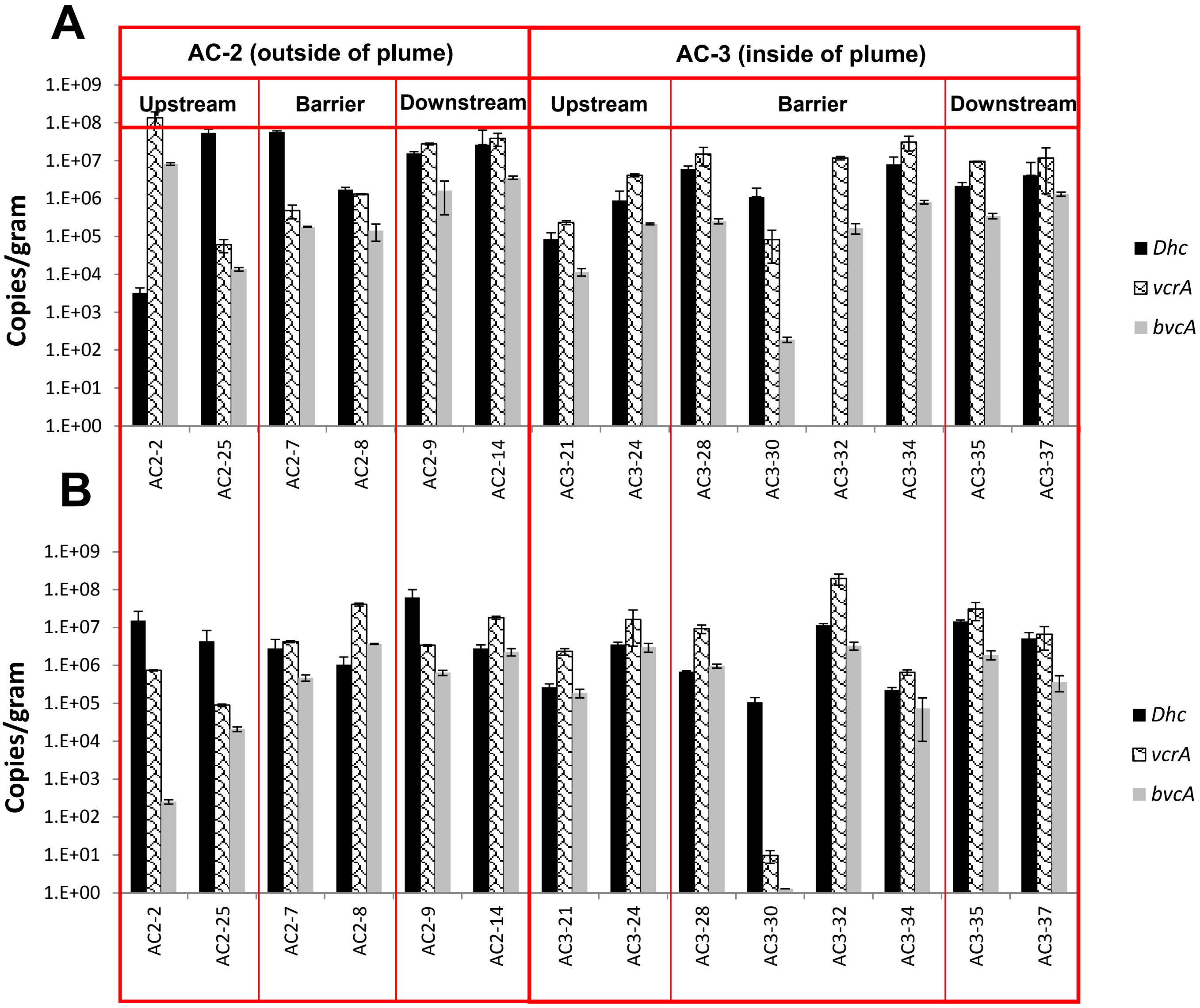

Figure 2: 16S rRNA gene copy numbers of D. mccartyi, vcrA and bvcA as determined by ligation-based qPCR at DNA (A) and RNA (B) level. Each value represents the average value obtained from triplicate qPCRs performed on one sample. Note that the results of selected samples and targets are shown.

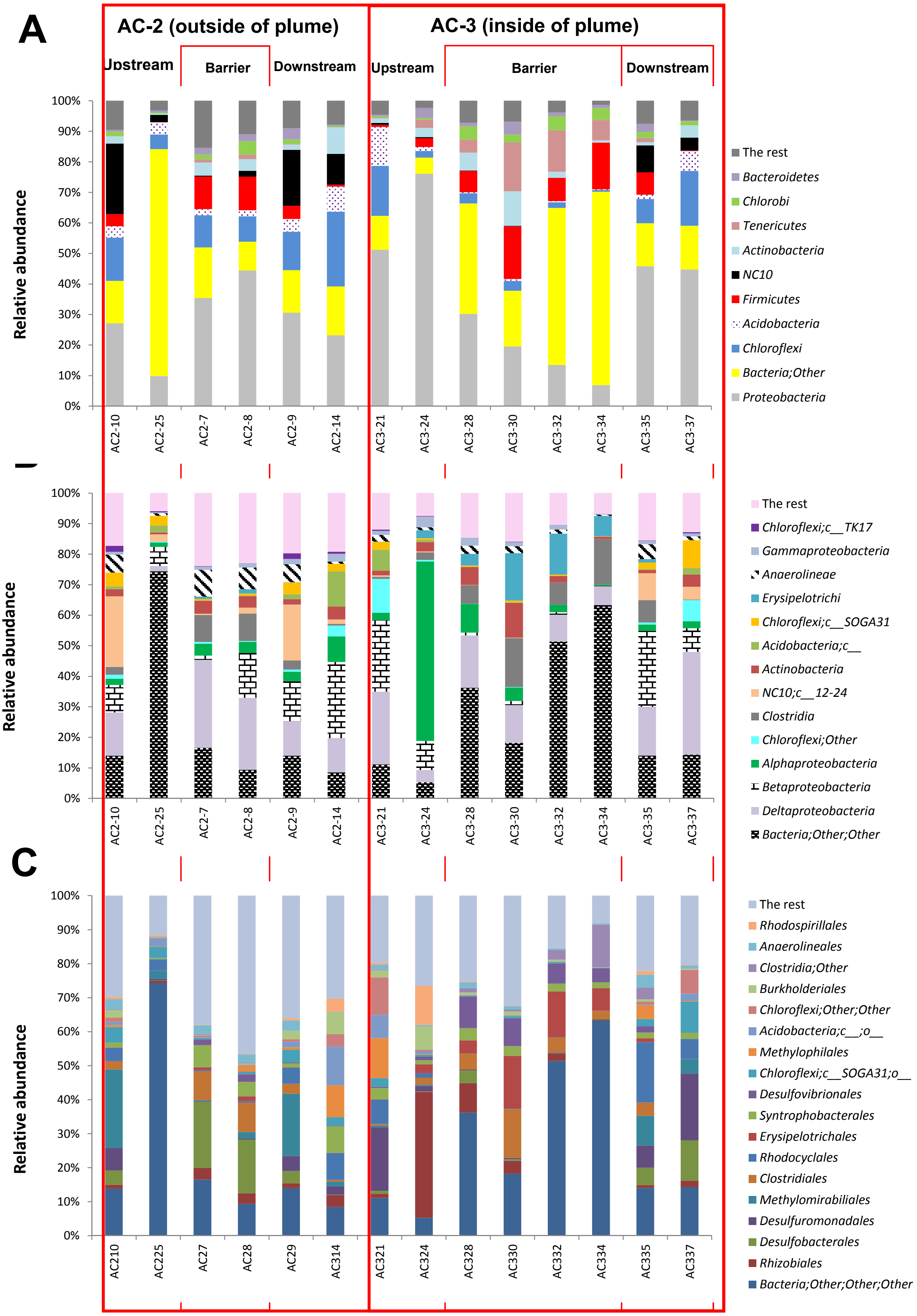
A
AC-2 (outside of plume)
AC-3 (inside of plume)
Upstream
Barrier
Downstream
Upstream
Barrier
Downstream
Relative abundance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
AC2-10
AC2-25
AC2-7
AC2-8
AC2-9
AC2-14
AC3-21
AC3-24
AC3-28
AC3-30
AC3-32
AC3-34
AC3-35
AC3-37
The rest
Bacteroidetes
Chlorobi
Tenericutes
Actinobacteria
NC10
Firmicutes
Acidobacteria
Chloroflexi
Bacteria;Other
Proteobacteria
Relative abundance
The rest
Chloroflexi;c__TK17
Gammaproteobacteria
Anaerolineae
Erysipelotrichi
Chloroflexi;c__SOGA31
Acidobacteria;c__
Actinobacteria
NC10;c__12-24
Clostridia
Chloroflexi;Other
Alphaproteobacteria
Betaproteobacteria
Deltaproteobacteria
Bacteria;Other;Other
C
Relative abundance
AC210
AC225
AC27
AC28
AC29
AC314
AC321
AC324
AC328
AC330
AC332
AC334
AC335
AC337
The rest
Rhodospirillales
Anaerolineales
Clostridia;Other
Burkholderiales
Chloroflexi;Other;Other
Acidobacteria;c__;o__
Methylophilales
Chloroflexi;c__SOGA31;o__
Desulfovibrionales
Syntrophobacterales
Erysipelotrichales
Rhodocyclales
Clostridiales
Methylomirabiliales
Desulfuromonadales
Desulfobacterales
Rhizobiales
Bacteria;Other;Other;Other

Figure 3: Relative abundance of the dominant bacterial phyla (A) class (B) and order (C) levels. Note that the results of selected samples are shown.

16S RNA gene tag-pyrosequencing

Phylum-level taxonomic distribution showed presence of *Proteobacteria, Chloroflexi, Acidobacteria* and *Firmicutes* as the most abundance phyla (Figure 3A). In contrast to reduced relative abundance of *Proteobacteria* within the barrier of AC-3, thier relative abundance was higher in the barrier samples taken outside of the plume (AC-2) (Figure 3A). In both barrier samples from in/outside of the plume, *Chloroflexi* phylum showed reduced relative abundance whereas the relative abundance of *Firmicutes* increased inside the barriers. However, according to qPCR data (Figure 2), the higher counts of *D. mccartyi* and *vcrA* biomarkers especially in barrier samples of AC-3 points to negative impact of ZVI on *Chloroflexi* groups other than the known dechlorinating members as evident from the class level distribution.

Of all *Chloroflexi* members, the application of ZVI seems to favour the *Anaerolineae* class (Figure 3B). Although never associated with dechlorination, members of this taxon have been found in environments with elevated nutrient concentration and highly reducing conditions. A recent study showed pronounce presence of *Anaerolineae* in the riverbed sediments from Zenne river, Belgium (Atashgahi, unpublished data). In line with the trend observed with *Firmicutes* (Figure 3A), the relative abundance of *Clostridia* and Clostridiales (Figure 3B and C respectively), members of which are known as secondary (i.e. non-dehalogenating) drivers of organohalide respiration, increased within the barrier both inside and outside of the plume. Of all proteobacterial classes, *Betaproteobacteria* seemed to be most negatively impacted by ZVI application as their relative abundance dramatically decreased within the barrier in/outside of the plume. Similarly, strongly reduced abundance of *Betaproteobacteria* was previously reported following exposure of soil microcosms to ZVI using fluorescence in situ hybridisation (FISH) (Fajardo et al., 2012).

Within *Deltaproteobacteria*, higher relative abundance of sulphate reducing bacteria (SRB) *Desulfobacterales* was noticed inside the barrier of AC-2 while their relative abundance was higher downstream of the plume (Figure 3C). Using denaturing gradient gel electrophoresis (DGGE), Philips et al. (2010) showed presence of SRB only in material collected more down-gradient of a ZVI barrier applied to remediate trichloroethene contaminated ground water.

Similar to most, if not all, studies using tag-pyrosequencing, pronounced presence of unclassifiable bacterial sequences in the samples taken from the barrier within the plume (AC-3) was noticed at all taxonomic levels (Figure 3A, B, and C), and presents a significant barrier to elucidating the ecological roles of these bacteria.

CONCLUSIONS

ZVI-barriers are installed to realise abiotic degradation of CAHs via reductive dehalogenation. However, the presence and impact of microbiological processes in and near the barrier has been neglected for a long time. During the last years, prove has been delivered that bacteria are present and active in ZVI-barriers (Van Nooten et al.,2007; Phillips et al., 2010). DNA/RNA based quantification of biomarkers indicative of organisms and genes involved in organohalide respiration coupled to the application of next generation sequencing in the current study shed more light on the dynamics of microbial communities within PRB. Such data is vital for a better understanding of the impact of biological processes on the functioning and longevity of ZVI-barriers, which may be valuable for the effective design and implementation of this technology.

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The HP1 program aids in the experimental design of multifunctional permeable reactive barriers

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ABSTRACT: The implementation of an *in situ* groundwater remediation technology requires substantial knowledge on the behaviour of the groundwater system and the interaction with the given technology. The coupled Hydrus-1D and PHREEQC model (HP1) proved effective in different steps of the experimental design from the start of the conceptual model to the definition of boundary conditions and objectives for the actual experiments, as well as for the design of full scale multifunctional permeable reactive barriers. The concurrent simulation of flow, heat and mass transport allowed to evaluate the uncertainties of the hydrological regime, the lab-scale constants and the potential effects of buffering or sorption capacities on the reactive barrier's performance.

INTRODUCTION

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

A multifunctional reactive barrier was previously developed and implemented at two sites in Flanders, Belgium (site H and site O). Extensive lab-scale testing and simplified flow-through calculations were used to dimension the pilot tests. These data proved indispensable for a proper evaluation of the barrier's performance but monitoring data illustrated unexpected behaviour during start-up due to processes that were not specifically considered in the experimental design. It was evaluated if simulations using HP1 could approximate this behaviour and indicate influential parameters or processes to include in step 2 and 3 of the procedure described above. Additionally, HP1 could aid in the experimental design of multifunctional permeable reactive barriers to specifically evaluate rate-limiting processes before the technology is implemented *in situ* (step 4 and 5). And finally, it was evaluated if HP1 could be used to indicate eventual adjustments to the technology when monitoring data show this would be required (6).

MATERIAL AND METHODS

PHREEQC and HP1

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

Site H

Site H is located near Antwerp, Belgium. The aquifer at site H is contaminated with CAHs (70 – 758 µg/L), benzene (75 – 5500 µg/L), mineral oil (100 – 7820 µg/L) and MTBE (101 – 3000 µg/L). A multi-barrier is considered to prevent off-site migration of the polluted groundwater. The contamination at the position of the eventual barrier amounts to 320 µg/L TCE, 774 µg/L DCE, 3603 µg/L benzene, 472 µg/L ethylbenzene, 493 µg/L xylene, 3270 µg/L M.O. and 2500 µg/L MTBE with an average groundwater flow of 5 m/y.

The considered multi-barrier system consists of a zero-valent iron (ZVI) part to remove the chlorinated ethenes and an aerobic bioactive part to remove the MTBE, BTEX and mineral oil. A buffer zone is situated between both reactive parts to avoid oxygen intrusion from the aerobic bioactive zone in the ZVI part. Both active zone were previously characterized in laboratory column experiments with half-lives of the chlorinated ethenes in the ZVI compartment of 0.5 to 1.3 hr. And half-lives in the bioactive zone of 0.1 to 0.3 days for the BTEX compounds and 3.2 to 12.4 days for MTBE.

The well-known numerical model PHREEQC was used in step 5 of the implementation procedure described above. The experimental constants are used to dimension the multi-barrier and evaluate mass transport and oxygen diffusion from the bioactive zone to the ZVI for different boundary conditions. A first order degradation was assumed for all compounds with minimal sorption and equilibrium transport. Oxygen was introduced at the start of the bioactive zone at water saturation.

Site O

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

The multi-barrier system consists of 5 compartments to treat the various contaminants by denitrification, sorption and nitrification (Figure 1). Two compartments contain oxygen diffusers to allow for nitrification and are separated by a clinoptinolite that sorbs peak amounts of ammonium. A compartment with granulated activated carbon (GAC) sorbs the AOX and COD. Butyrate is added to the final compartment to achieve anaerobic conditions and allow for denitrification to remove nitrates from the flow-through.

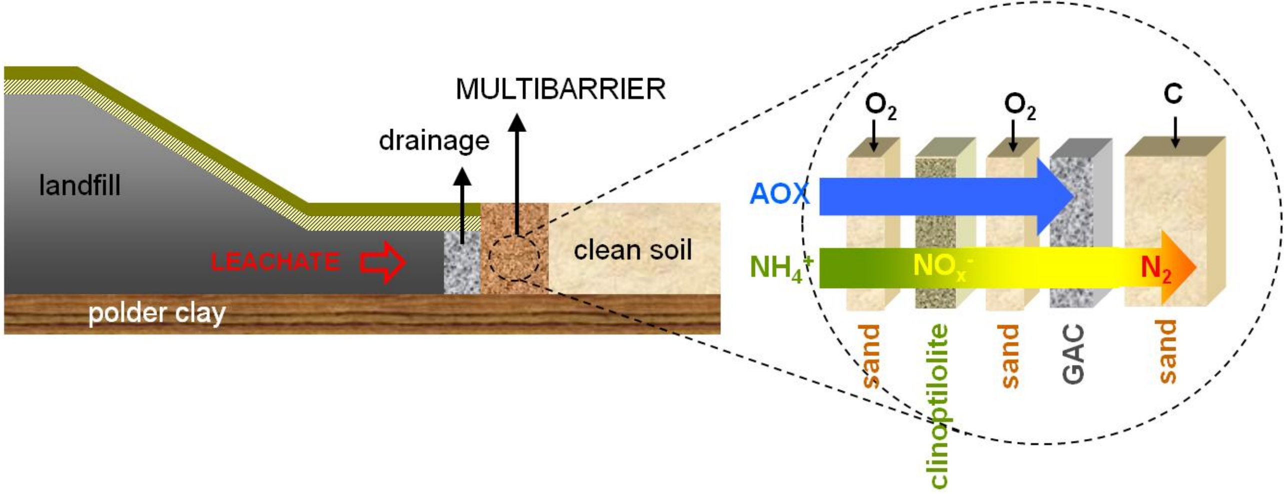

Figure 1: The multi-barrier at site O to treat ammonium, AOX and COD of landfill effluent.

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

The barrier was homogenously discretized at 10 cm and 5 different materials were defined for the different compartments. These were characterized by their measured porosities but were given equal hydraulic conductivities of 7.2 m/day since no additional data were available. This also applied for the solute transport with a homogeneous dispersivity of 0.4 m, and for the heat transport parameters that were derived from the default values for sand in the HP1 program. The monitoring data yielded 47 time-variable boundary conditions in the barrier over a time-span of 719 days. Water flow boundary conditions (BCs) were defined by the variable pressure heads, solute transport by a concentration BC at the inflow and a zero concentration gradient at the outflow, and heat transport by two temperature BCs. The solute transport discerned 20 components (the current maximum of HP1) to describe the redox and pH dependant reactions in the barrier. Microbial reactions were approximated by 1st order kinetics adjusted for temperature dependant degradation as described by the Arrhenius equation assuming that the reaction rate is halved with a temperature decrease of 10°C:

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

With C the modelled compound, k_{t1} the reaction rate at lab temperature T_1, E_a the activation energy, R the gas constant and T_2 the ambient temperature in that modelled period. The nitrification rates were determined at 2.67 to 2.82 day^{-1} and the denitrification rate at 17.7 day^{-1}.

Sorption of COD and AOX on the GAC was described as a first order kinetics with an assumed maximal sorption capacity of 10 g/L:

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

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

RESULTS AND DISCUSSION

Site H

Results show that at the ambient groundwater flow of 5 m/yr a ZVI of 30 cm suffices to degrade the chlorinated ethenes while the aerobic bioactive zone would require a length of 1 m (Figure 2). The buffer zone between both reactive parts requires a length of 30 cm in order to prevent diffusion of O_2 from the aerobic bioactive zone in the ZVI part. These dimensions are conservative since the model predicts that the pollutants entering the reactive zones are degraded in the first half of the zone. But the residence time of the pollutants in the reactive zones is important and results showed that especially for MTBE a higher groundwater velocity could result in a breakthrough of the pollutant. However, if one assumes that the bioactive zone is characterized by a large degradation capacity as was observed at the end of the column experiment, the MTBE is again degraded below the threshold level before exiting the multi-barrier. The proposed dimensions are therefore considered acceptable. The numerical model largely confirmed the back-of-the-envelope calculations that were previously made. Its main contribution is the indication of the oxygen diffusion in the buffer zone between the reductive and oxidative degradation compartments and the evaluation of MTBE degradation uncertainty at different flow rates.

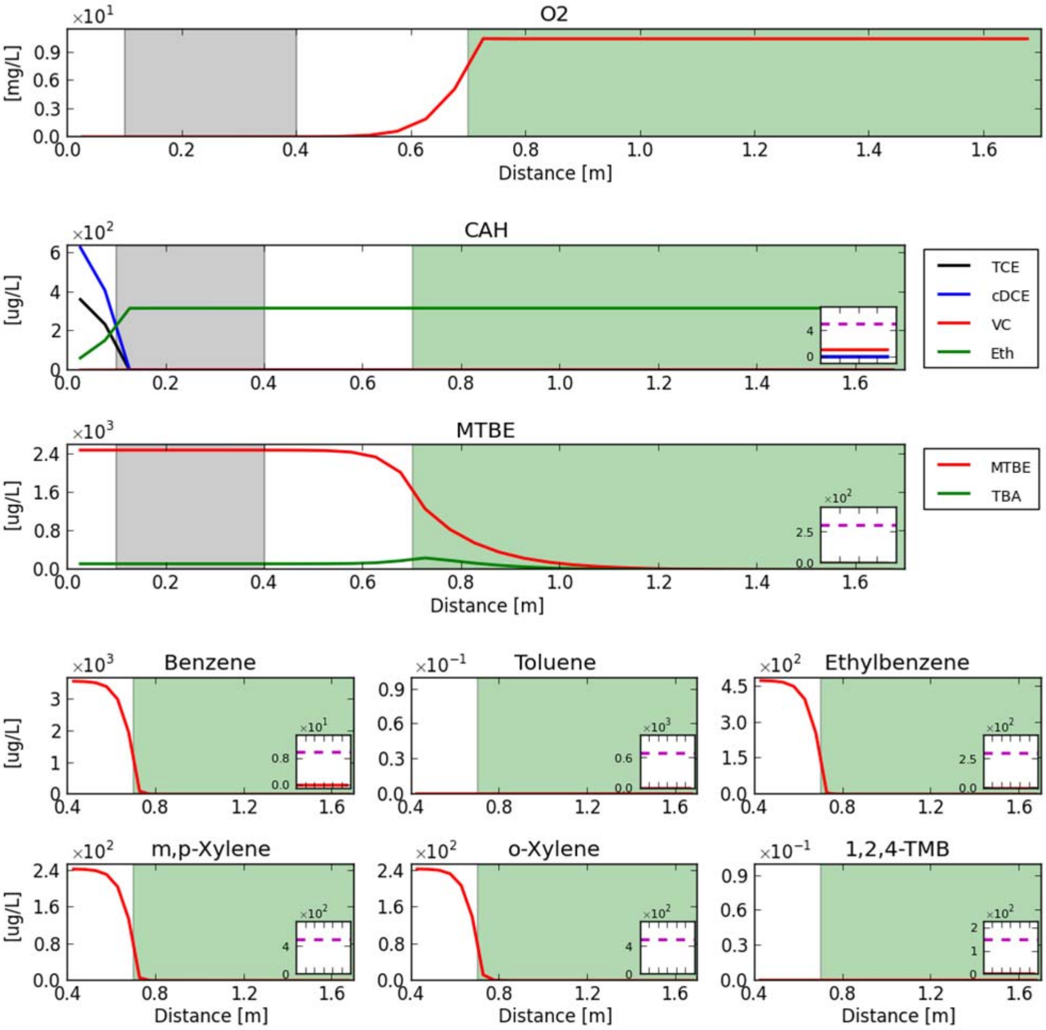

Figure 2: the concentration profiles of the pollutants in the proposed multi-barrier system at site H with a ZVI part (gray) and an aerobic bioactive zone (green) for a groundwater velocity of 5 m/y. The pollutant's thresholds are indicated by the dotted line in the inserts representing the outlet of the multi-barrier system.

Site O

The numerical model proved effective in step 6 and illustrated that its use in steps 2 to 5 could also have added to the good implementation of the technology. Reactions appeared to be limited by temperature or flow-through, aspects that can be approximated by HP1. A tracer test was performed in the pilot-test but the numerical model showed that its monitoring was halted prematurely in order to derive valuable information (bromide data on Figure 3). The temperature could have played part in the inefficient nitrification during the start-up but it was not well described by the Arrhenius equation. It was more likely a combination of microbial adaptation (or growth), temperature and the flow-through. The model indicated high flows during the initial phase of the experiment with nitrification kicking in after a period with low flows and higher temperatures.

The lab-derived nitrification constants were higher than the observed nitrification rate in the pilot test. The model predicts a complete nitrification in the first compartment which was not observed during the entire monitoring period. The temperature could have had a larger effect on the nitrification rate than described by the Arrhenius equation but even at 20°C the nitrification is overrated. As such, other factors influenced the microbial reactions but these are difficult to discern from the monitoring data. The pH could have played part with a small observed decline of maximally 1 unit due to the nitrification reaction. But the model simulates a significant acidification of the flow-through in the first compartment due to the complete nitrification of the ammonium in the inflow. This acidification was not observed during the test indicating an unknown buffering capacity of the medium since the measured alkalinity of the inflow was included in the model calculations. The simulation indicates that it is important to estimate this buffering capacity to be able to adjust the inflow buffering capacity in time and prevent negative effects on the microbial community.

The exchange capacity of the clinoptinolite was quickly reached during the start of the experiment and was adequately described by the numerical model. The sorption of the AOX and COD on the GAC was not well simulated with an overestimation of the sorbed AOX and an underestimation of the COD sorption. Most probably the GAC had a higher sorption capacity than simulated and preferential flow paths resulted in the apparent breakthrough of some AOX and COD. A better estimation of the sorption capacity is required to allow for a timely replacement of the GAC, preventing unnecessary costs or pollutant breakthrough by tardily action.

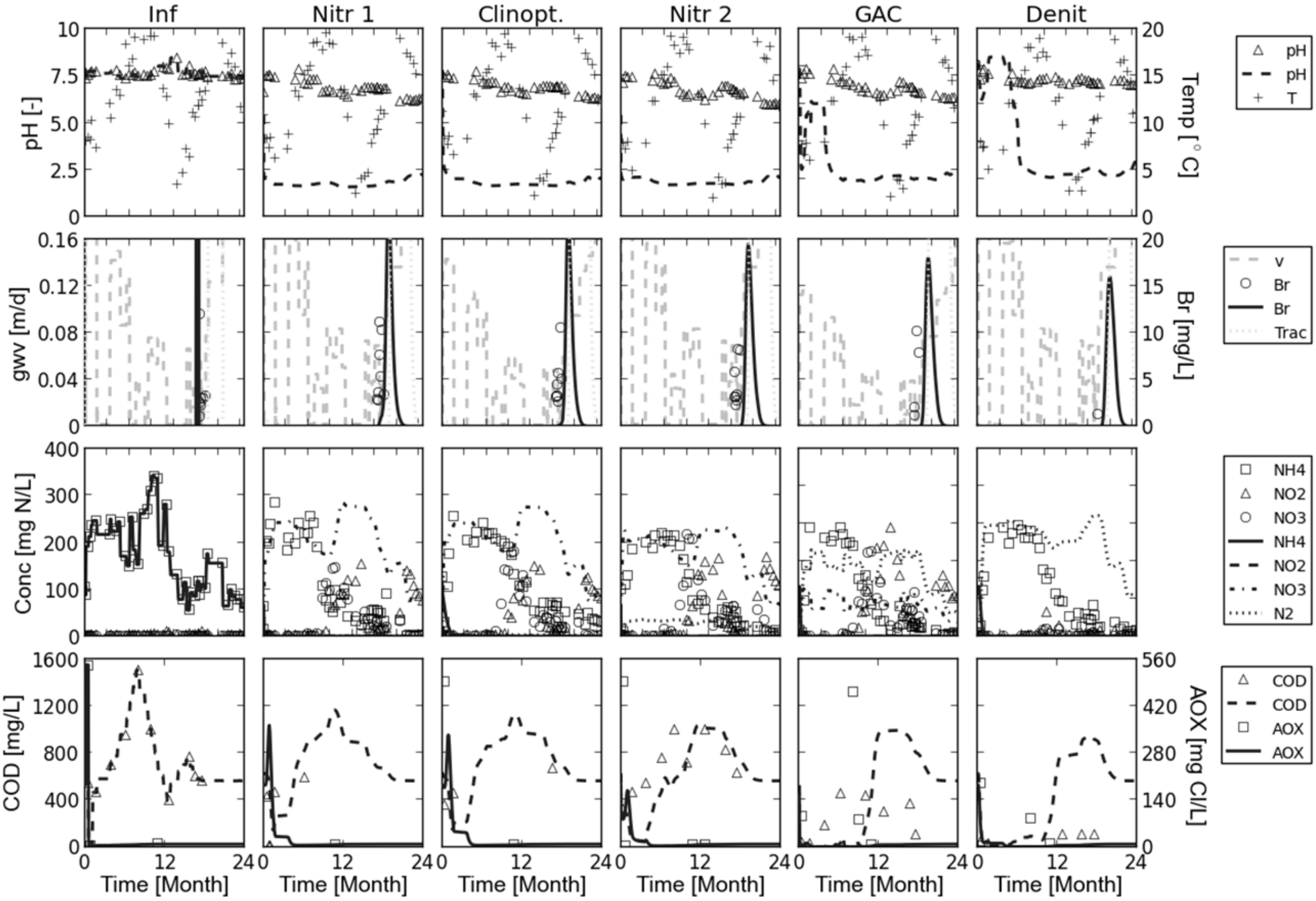

Figure 3: The simulation of contaminant dynamics in the multifunctional permeable reactive barrier treating landfill leachate (simulated: lines, observed: dots). The barrier consists of five different compartments: nitrification, ion-exchange (clinoptinolite), nitrification, sorption (granular activated carbon) and denitrification to remove ammonium, halogenated aliphatics (AOX) and other organic compounds (COD) from the landfill leachate. The top graphs show the pH and temperature profiles throughout the barrier. The second row of graphs show the pore water velocity (v), and the bromide tracer. The third row of graphs show the different nitrogen components and the bottom row indicates the observed and modelled concentrations of AOX and COD.

CONCLUSIONS

The HP1 program provided significant improvements over the PHREEQC code in simulating time-variable boundary conditions for flow, heat and mass transport. The concurrent simulation of the three processes allowed to highlight variables of interest in the experimental design of a multifunctional permeable reactive barrier. Results showed that lab-scale degradation constants should be used with care to simulate pilot-scale reactions. And potential effects related to temperature changes could not be adequately approximated using the Arrhenius equation. The model results indicated that the buffering and sorption capacities of the media should be experimentally determined since they could exert a great effect on the barrier’s performance. Finally, the hydrological regime in the multibarrier could play a significant role during the start up of the test or have an influence by preferential flow paths. The numerical model can aid in the experimental design of tracer tests to obtain more information for the physical characterisation of the barrier.

ACKNOWLEDGEMENTS

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Electrochemically-assisted biodegradation of chlorinated solvents with electrodes serving as electron donors/acceptors

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In situ bioremediation of chlorinated aliphatic hydrocarbons (CAHs), such as trichloroethene (TCE), typically occurs via sequential reductive/oxidative pathways that requires the subsurface injection of an electron donor (e.g. an H_2-releasing substrates) to stimulate the reductive dechlorination (RD) of highly chlorinated hydrocarbons, coupled to the downgradient injection of an electron acceptor (e.g. O_2) to promote the oxidation of (less-chlorinated) RD products. This approach can suffer from a lack of reliability due to difficulties in controlling the rate and extent of biodegradation processes taking place in the subsurface. To overcome these limitations, in the frame of the European Project Minotaurus (www.minotaurus-project.eu) a novel bioelectrochemical approach to remediate CAHs has been developed, which relies on the use of polarized electrodes as both electron donors and acceptors (either direct or indirect) for the RD of higher chlorinated CAHs or oxidation of less-chlorinated RD products, respectively. As for the RD step, lab-scale studies showed that a fine-tuning of the cathode potential allows gaining a direct control over the rate of TCE dechlorination and competing methanogenesis. Notably, with the cathode poised at -250 mV vs. SHE, the RD process, though quite slow, was highly efficient, with methanogenesis being fully suppressed. The set cathode potential highly influenced the microbial composition of the cathode with unidentified *Chloroflexi* being the dominant members of the community at -250 mV and *Dehalococcoides* spp. being the dominating members at more reducing potentials (< -450 mV). Further insights into the involved electron transfer mechanisms between the cathode and the dechlorinating bacteria are being explored by gene expression studies and compound specific isotope analysis (CSIA), both on pure and mixed dechlorinating cultures. As for the bioelectrochemical oxidation step, lab-scale studies revealed that *cis*-DCE, product of TCE dechlorination, can be oxidized using an anode polarized at +1.5 V as electron acceptor. At this potential, *cis*-DCE oxidation was likely sustained by O_2 generated at the anode from water oxidation. Molecular analysis of the culture showed the selective enrichment of a *Bacillus* sp., providing an indication that this microorganism was responsible for *cis*-DCE degradation. Based on lab-scale investigations, a field study has been initiated with a scaled-up (10-L) bioelectrochemical system, which is being operated with true groundwater from a contaminated site.

An alternative for regular zero-valent iron in permeable reactive barriers: Laboratory research

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The current study describes the research on an alternative for regular zero-valent iron called GRANUL-X®. The objective was to determine the reactivity of GRANUL-X® using artificial and site specific ground waters and find out if GRANUL-X® is suitable for use in permeable reactive barriers (PRB's). During experiments a comparison between GRANUL-X® and regular zero-valent iron was made.

GRANUL-X® is an material based on cracked reactive expanded clay granules (0-5mm) with excellent hydraulic properties. The high porous clay grains have a large internal surface area in which tiny reactive iron particles are incorporated. GRANUL-X® is therefore expected to be a very suitable material for use in passive groundwater remediation such as permeable reactive barriers.

In the context of two groundwater remediation projects (Lier in Belgium and former landfill Kanaalpolder in the Netherlands) laboratory-scale column test are performed to determine the reactivity of both GRANUL-X® and zero-valent iron (Gotthart Maier) and give more insight in efficiency, suitability and needed residence time. For the project Kanaalpolder column tests are still running and conclusions are not available yet. The column tests are expected to be finished in September 2013.

For the project in Lier two glass columns (length 20 cm) were filled with GRANUL-X® (23g) and two columns were filled with a mix of zero-valent iron (58g) and filtersand (101g). one of each column type was fed (1,75ml/h) with artificial groundwater (TCE, 1900µg/l) and one of each type with site specific groundwater (cis-DCE up to 11.000 µg/l). The results indicated a significant higher reactivity and lower accumulation of harmfull degradation products in the presence of GRANUL-X® compared to zero valent iron.

Finally in Lier, based on the lab-results and available field data, a 220m PRB with GRANUL-X® was designed and installed with a wall thickness of 30cm and a depth of 8,5 below gs. In areas with high concentrations the PRB was performed double. The PRB was constructed using the continues trenching technique. Unlike other PRB applications of zero valent iron, no mixing with filtersand was necessary to create a homogeneous filled PRB which is profitable in many ways.

Poster Presentations

Novel Activators for Persulfate Chemical Oxidation: Combined Remedy Approaches

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Activated persulfate has been shown to be an effective, chemical oxidation technology to treat a wide range of organic compounds of concern. Several activator systems have been demonstrated at field scale, including use of metals and chelated metals, hydrogen peroxide and high pH (or alkaline) activation. Recently, large scaled applications of persulfate activated by cement in once instance, and electrical resistive heating in another, have been performed. This presentation will discuss these projects and demonstrate that the activation methods may be ideal for certain sites heavily contaminant with recalcitrant contaminants.

Cement can play several roles as an activator for persulfate. Firstly, when applied with additional lime, cement can provide alkaline activation at a pH above 10. Secondly, due to pozzolonic reactions, heat will be produced, providing an in situ source of heat activation. In addition, addition of cement will provide a source for in situ stabilization of the soil, providing a combined approach incorporating in situ chemical oxidation and in situ stabilization of the target contaminants. This technology was recently demonstrated at the Turtle Bayou Superfund site in Texas (USA). The site contained many chlorinated and semi-volatile compounds of concern, including vinyl chloride. Over 345,000 kgs of persulfate were applied at this site through deep auger mixing, becoming the third largest persulfate application to-date. A combination of cement and lime were utilized.

Recently, heat activation, which has been performed in the laboratory on many occasions, has gained increased interest for application in the field. The use of electrical resistive heating as a source of persulfate activation was demonstrated on a large scale at the Port of Seattle, Washington (USA), to treat pentachlorophenol in a background of petroleum hydrocarbons. Heat was applied to the site for a period of a two months, followed by the application of 115,000 kgs of persulfate. Average site groundwater temperatures of 40 – 50 C were achieved. Reduction of the primary contaminant, pentachlorophenol, to below the clean-up targets were achieved at all monitoring wells with no observable rebound.

The impact of H_2 on SRB activity and removal of heavy metals from groundwater

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In situ bioprecipitation (ISBP) seems to be one of the most promising processes for immobilization of metals in saturated zone. Indirect ISBP is mainly performed by Sulphate Reducing Bacteria (SRB), that are anaerobic heterotrophs utilizing a range of organic substrates and sulphates as a terminal electron acceptor. Sulphides produced from sulphates reduction form insoluble complexes with a metal, and result in metal sulphides immobilization. SRB can be stimulated by the addition of various carbon – sources. The significant impact on bioprecipitation of heavy metals in saturated zone has selected parameters. Zero-valent iron (ZVI) is considered as a potential remediation agent for the elimination of numerous heavy metals from contaminated groundwater. The anaerobic corrosion of ZVI causes a decrease of oxidation state and formation of hydrogen. The formed H_2 is a potential e-donor for SRB and accelerates sulphate reduction.

The aim of this study was to evaluate the ISBP performed by SRB and ZVI for removal of selected heavy metals from groundwater. Batch tests were performed with aquifer materials and a synthetic groundwater containing Zn, Ni and Cd. In the research pure ZVI (in the form of powder and filings) and ZVI from foundry (in the form of chips and pellets) were used. The results showed that H_2 is efficient in stimulating sulphate reduction and removal of heavy metals, however it strongly depends on the type and particle size of ZVI. The highest production of H_2 was observed in microcosm amended with pellets but it did not improve the ISBP, and the precipitation of Zn, Ni and Cd.

Simplified models to predict long-term efficiency of Fe^0 permeable reactive barriers

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Effective prediction of Permeable Reactive Barriers (PRBs) longevity requires a solid understanding of the site-specific hydrogeological and biochemical conditions. Column tests able to reproduce site conditions can be performed to predict the long-term efficiency of a particular PRB installation. The data collected during these tests can be integrated in complex models able to simulate contaminant degradation and PRB deactivation. After the calibration of the complex model using the lab data and fast inflow rates, the long-term efficiency of the PRB can be predicted by lowering the inflow rates, reproducing the real site conditions. However, the predictions provided by complex numerical models can be highly uncertain, due to the empirical description of the deactivation mechanism. In this context the use of simplified models to predict the long-term efficiency of Fe^0 PRBs might be justified.

In this study two simplified models describing contaminant degradation and mineral deactivation in PRB systems are proposed. The first model is based on a modified version of the spatial temporal simulation model (STS) proposed by Kouznetsova et al. (2007). In the STS model the parameters controlling the mineral deactivation front were determined only from contaminant concentrations measuraments. Despite this simplification, the STS model still requires the user to prepare a detailed numerical input.

An extreme simplification of the deactivation mechanism under field conditions is proposed in the second model, which is based on the plug flow concept. The front velocity relative to effective groundwater flow was determined by the calibration of the geochemical model to the column data. The second simplified model provided estimations of the long-term efficiency that were comparable to those estimated by the geochemical model and that can be easily calculated for different design criteria.

Survival and activity of Sphingomonas sp. KN65.2 in a pilot scale activated drainage system

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One possible method of removing pollutants from contaminated groundwater in a fractured aquitard is via a draining system intersecting the fractures, in which biodegradation is enhanced. The polluted groundwater in the fractures is drained into channels filled with gravel, creating a porous environment where pollutants can be biodegraded by either planktonic or sessile microorganisms. In this study we investigate the ability of introduced and indigenous microorganisms to degrade a model pesticide, carbofuran, in saline groundwater. The salinity of the drained water ranged between 18.8 and 20 mS/cm.

The ability of a carbofuran degrading *Sphingomonas* sp. KN65.2 that was isolated from Vietnamese soil to degrade this compound was first tested in defined medium, under different salinities. This strain uses carbofuran as a sole source of carbon and energy, and in our hands, was able to degrade the compound at concentrations of 2% NaCl as well as in unfiltered groundwater from the contaminated site.

For a field test 3 L of strain KN65.2 was grown in TSB medium until reaching early stationary phase This starter was inoculated into a column containing clean gravel give a final concentration of 10^9 CFU per liter of column pore volume. Carbofuran concentration in influent was 5 mg/L and its depletion in the inoculated column was determined by HPLC. *Sphingomonas* sp. KN65.2 is naturally resistant to streptomycin, so we used this characteristic as a selective marker. Effluent samples were collected from the C-new column, and bacterial counts were performed on Tryptic Soy Agar (TSA) plates for enumerating total aerobic bacteria and on TSA plates amended with 200 mg/L of streptomycin for enumerating KN65.2. HPLC revealed that during the first four days from inoculation, carbofuran concentrations were steadily depleted in the inoculated column. However, from the fourth day onwards, the depletion rate decreased correlating with the decline of the bacterial counts.

Although under laboratory settings the KN65.2 strain exhibited satisfying performance, it is suggested that in the pilot column the bacteria were not able to compete with native microflora (as seen by the rapid decline in KN65.2 bacterial cell count) and was not able to colonize the chalk matrix. In addition, it is also possible that temperature and dissolved oxygen concentration in the pilot-scale system were not optimal for this strain. In conclusion, we propose that it would be more effective to activate the drainage system by adjusting the conditions (such as O_2 concentrations) in the pilot-scale system and stimulating the existing native microorganisms, rather than by bio-augmentation with exotic bacteria.

Compound specific isotope analysis (CSIA) to evaluate and quantify degradation of chlorinated compounds by micro-organisms and ZVI

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Compound specific isotope analysis (CSIA) is a tool that is being used to trace the degradation of compounds, like for instance chlorinated ethenes (CE). In particular, the enrichment of ^{13}C carbon isotopes in primary contaminants (PCE, TCE) and metabolites (cDCE, VC) can be used to quantify complete dechlorination, provided that compound-specific isotope enrichment factors are known. Mostly, these factors are not known for specific sites, and data from literature is used for the calculation.

Not only for biodegradation processes CSIA can be used, but also for abiotic reductive dechlorination of compounds by zerovalent iron (ZVI). Up to now, quantifications of degradation extent were based on theoretical considerations on overall isotope enrichment regarding maximum/average/minimum isotope fractionation. However, because of this variability the derived intensity of degradation can exhibit a wide range. Moreover, the concept is limited when applied for complex reaction patterns as they occur for CE degradation by ZVI.

Within AQUAREHAB (GA 226565), in a first phase, controlled lab scale experiments were performed to derive compound-specific isotope enrichment factors for several chlorinated compounds (PCE, TCE, cDCE, VC and/or 111TCA) during degradation by 2 different zerovalent irons and a CAH-degrading bacterial enrichment culture. This resulted in a valuable data set to support the classical CSIA-approach.

In a second phase, in order to confine the quantitative assessment of complete dechlorination of PCE and TCE by ZVI, we empirically determined lumped carbon isotope enrichment factors for this degradation process, which was treated as a black box. Therefore, besides compound-specific enrichment factors (ε_{PCE}, ε_{TCE}) also lumped isotope enrichment factors (ε_L for PCE and ε_L for TCE) were derived for two types of elemental iron and the bacterial consortium. In some situations, for instance when ZVI is involved, empirically determined lumped isotope enrichment factors may achieve a better approximation to (semi)quantify elimination of the chlorinated compounds.

Session 7

Waste Water treatment

Oral presentations

Wastewater treatment in Flandres: future challenges

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No input received

On-line control of an industrial SBR

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ABSTRACT: On-line control of the biological treatment process is an innovative tool to cope with variable COD and nutrient concentrations in industrial wastewater. In the present paper we propose a dynamic control strategy based on the redox potential profile (ORP) and the oxygen uptake rate (OUR) to determine the duration of the anoxic feeding phases and the subsequent aerobic phases in a nutrient-removing SBR. As a result, the F/M load to the SBR is adapted to the activity of the activated sludge and the actual characteristics of the wastewater.

INTRODUCTION

Quite a number of industrial wastewaters are characterized by a high degree of variability in composition, load and degradability (Eckenfelder *et al.* 2009). Since treatment plants have a fixed volume, large safety factors are applied in the design phase to guarantee an effluent quality within the discharge limits. As a result, the water treatment process in many facilities is often not very efficient. By introducing on-line control schemes, the wastewater treatment process may adapt itself dynamically to the varying influent conditions (Olsson *et al*. 2005). Such an approach offers great potential to save energy and time. In the present study, we design a dynamic control strategy based on signals from 2 common low-cost and reliable sensors, i.e. dissolved oxygen (DO) and oxidation reduction potential (ORP).

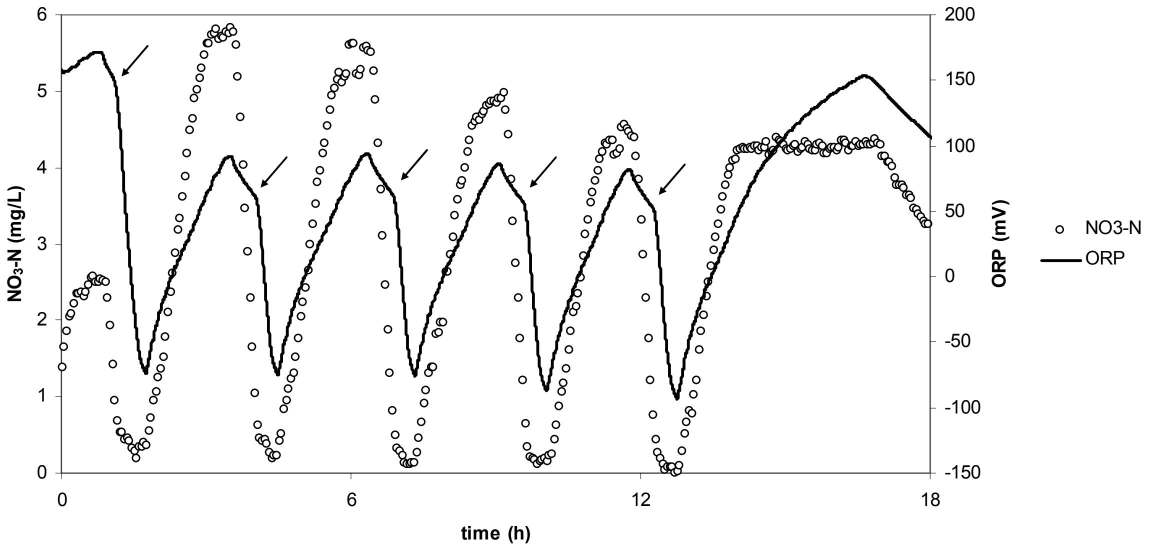
MATERIALS AND METHODS

A lab-scale SBR (total volume = 20L, volume after discharge = 12L) treating highly variable tank truck cleaning wastewater was set-up to validate the control strategy. The SBR was inoculated with the nutrient-removing activated sludge from the full-scale industrial wastewater treatment plant. The reactor was equipped with pH, ORP and DO sensors from Hach-Lange, connected to a SC1000 transmitter. The SBR process operation was controlled by a Siemens PLC connected to I/O modules from WAGO Kontakttechnik. The operator interface, including visualisation of sensor signals and the process control settings, was programmed using LabView software (National Instruments). The SBR was operated in a step-feed mode consisting of a number of consecutive anoxic feeding and aerobic reaction phases.

RESULTS AND DISCUSSION

The principle of the control strategy is illustrated in Figure 1 for a typical SBR cycle. The duration control of the anoxic feeding phases was based on the on-line detection on the “nitrate-knee” in the ORP profile (Olsson et *al*. 2005). A sharp decrease on the ORP indicates the complete removal of nitrate.
The duration of the aerobic phases was based on the absolute value of the oxygen uptake rate (OUR), which was calculated online in the aeration tank. A “low” OUR value corresponds to complete nitrification and COD removal.

The result of the control strategy is a SBR cycle with variable length depending on the characteristics of the wastewater (such as nitrogen content) and the activity of the sludge (as indicated by the OUR).



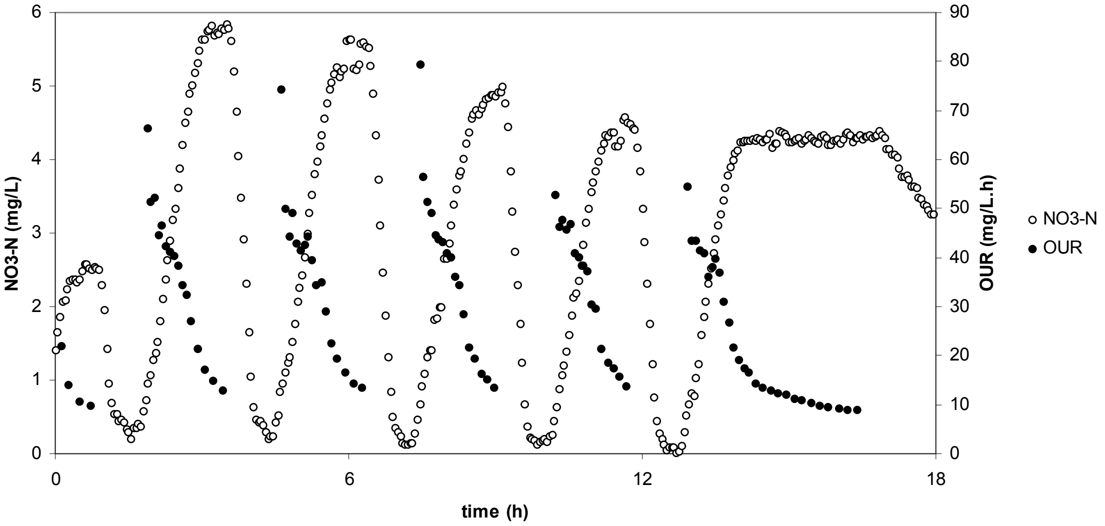


Figure 1: Online ORP (top) and OUR (bottom) profiles, and corresponding NO_3 cncentrations for a typical SBR cycle treating industrial wastewater; the arrows in the ORP graph indicate the "nitrate-knee"

CONCLUSIONS

Although reliable on-line nutrient sensors are available on the market today, they are very expensive and require intensive servicing. Therefore, on-line nitrogen monitoring is not a realistic option for most small enterprises. The results of the present study indicate that on-line control based on common and cheap sensors is a robust way to implement dynamic processes in industrial activated sludge plants.

ACKNOWLEDGEMENTS

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UV/H_2O_2, O_3 and (photo-) Fenton as a pre-treatment to GAC filtration of biologically stabilized landfill leachate

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Because of the specific characteristics of landfill leachates (high chemical oxygen demand (COD), low biochemical oxygen demand (BOD), especially for old landfills), biological carbon removal is limited, even with high external carbon dosages. Therefore, a treatment technique is needed that reduces the organic load and/or improves the biodegradability in an economically efficient way. As such, in this contribution, different AOPs (UV/H_2O_2, O_3 and (photo-) Fenton) where compared on lab-scale based on a systematic approach in which the effect of oxidation on the operation of the granular activated carbon (GAC) filter was considered. This should give an important insight in possible improvements to the current applied treatment trains.

Compared to untreated leachate, the GAC column tests showed that the GAC could be used substantially longer (up to 13 times) after Fenton treatment, compared to leachate treated by UV/H_2O_2 (no improvement) and O_3. The Fenton treatment (characterised not only by oxidation but also coagulation) led to a high removal of COD (up to 63%) mostly causing the extended GAC lifetime. Further, the Fenton treatment also resulted in an increased BOD/COD ratio of 0,17 (compared to 0,07 for untreated leachate) because of the high removal of COD. However, the sludge production should be taken into account to make an economical comparison between the different techniques. Photo-Fenton showed no improvement of COD removal and also no substantial reduction of sludge production (based on dry matter analysis) compared to regular Fenton was observed. With the UV/H_2O_2 process only minor COD (6.9%) and BOD (no changes) removal was observed. Most likely, the significant UV absorption of the landfill leachate hindered the production of hydroxyl radicals. Ozonation (66% BOD increase, BOD/COD ratio of 0,13), on the other hand, showed that there might be some potential in recycling the oxidized stream to the biological treatment unit to reduce external added carbon costs.

Potentials of Regional Industrial Symbiosis on Waste Material Valorisation and Pollution Prevention in West Flanders

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Rising prices of raw materials and growing awareness for environmental issues have led to changes in perception of the value of waste materials. Waste recycling and re-utilization are potentially favourable routes towards development of environment-friendly, sustainable and cost effective industrial processes. Therefore, it is of great interest to explore the possibilities of turning wastes into valuable products. Industrial symbiosis, aiming at the integration of industrial wastes for pollution prevention purpose, would greatly improve the economical and environmental wellbeing of the targeted region. This paper focuses on providing some technological evidences that could in turn encourage industrial symbiosis within the region of West Flanders by investigating inherently-formed iron-based water treatment residuals (WTRs) as alternative sorbents for phosphate (P) removal from contaminated process effluent from a potato processing plant. The WTRs were characterized, and their sorption efficiency and sorption capacity were tested using one- and two-stage treatment methodologies. The WTRs were capable of removing >98% of P from the effluent water. It was found that two-stage methodology improved the sorption efficiency significantly, reaching 90% removal level at less than half the one-stage sorbent dosage. WTRs are safe and economical sorbents for industrial waste water treatment, and constitute a good example where a waste product from one industry is used to remediate the waste stream of another neighboring industry.

Recent developments in the thermal treatment of saline waste water

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Thermal treatment of saline waste water has evolved in various industries during recent years into a feasible and economic way to fulfill many demands coming from the authorities to meet increasingly stringent environmental standards.

The possibilities that evaporation and crystallization offer for handling effluents containing inorganic as well as organic compounds have increased and provide new ways to handle industrial waste water in such a manner that not only is the volume significantly reduced, but also valuable and marketable products are recovered. Investing into a waste water crystallization plant is a major change for some industries resulting in an economic and environmental friendly solution.

Nowadays, the range of applications is wide and covers different industrial branches, such as:

- Chemical industry
- Mining
- Gas and oil industry
- Power generation
- Construction materials.

The benefit of thermal treatment is not only to reduce the quantity of waste water but in many cases to fulfill zero liquid discharge requirements. For such plants, the main target is the total evaporation of liquids therefore splitting the waste water into clean condensate and a dry salt, which, depending upon the composition of the waste water stream can either be marketed or disposed of.

If the waste water contains various components it is possible to recover the components separately through selective pretreatment and crystallization. The result is the recovery of clean water, several salts either as solids or as liquid products depending upon the actual waste water composition.

Products that can typically be recovered are NaCl, Na_2SO_4, KCl and $CaCl_2$ and the simultaneous recovery of more than one of the salts is also possible. SEP has an on-going development program to widen the range of applications and products continuously.

Based upon our wide experience in the crystallization of salts for the chemical, nutritional and pharmaceutical industries SEP are in a position to design waste water plants which to provide the optimum process concept using the most suitable equipment thereby resulting in high reliability and minimum down time.

Life cycle analysis of MINOTAURUS wastewater treatment technologies

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The FP7 MINOTAURUS project develops and tests environmental biotechnologies for treating wastewater and groundwater contaminated by specific organic pollutants and pollutant mixtures. These technologies are expected to bring beneficial effects for the environment through the elimination of (micro)pollutants, but may also cause environmental impacts during their production, operation and end-of-life disposal. Life cycle assessment (LCA) is a method to compare such environmental benefits and costs of a technology. In the study presented we assessed a MINOTAURUS technology that uses laccase-conjugated fumed silica nanoparticles in an ultrafiltration reactor to further remove Bisphenol A and other substances from biologically treated wastewater [1]. The procedures followed comply with ISO Norm 14040 for LCA studies. For the impact assessment of the systems the EDIP 97 method [2, 3] was used focusing on the impact category "chronic ecotoxicity in water".
The system boundaries and the analyzed subsystems of this technology are presented in Figure 1.

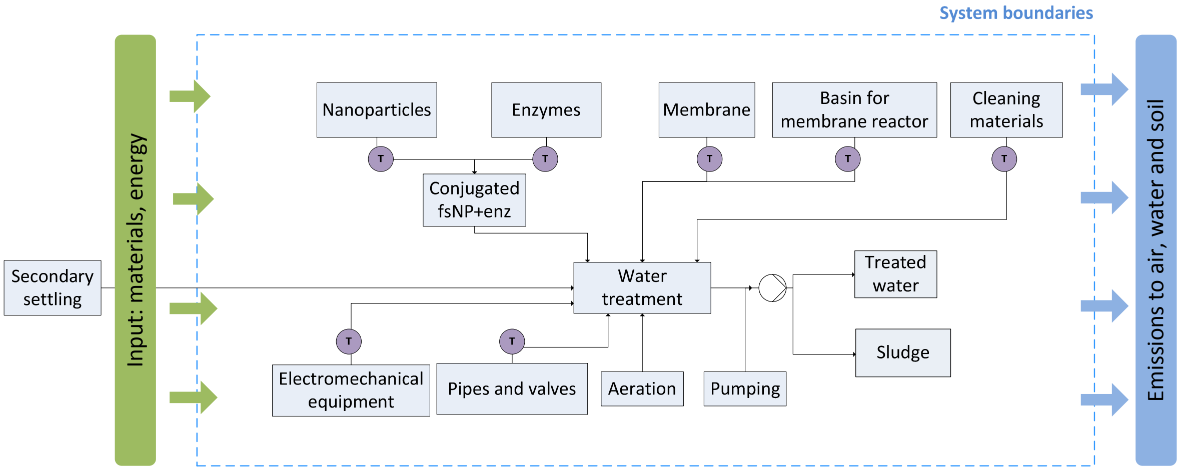

Figure 1 LCA boundaries for the MINOTAURUS enzyme technology

Preliminary results identified the production and use of the nanoparticles and enzymes and the membrane cleaning as processes causing the main impacts. A comparison with established technologies for micropollutants removal such as activated carbon technology or ozonation is on-going. In a next step the environmental costs and benefits of this technology will be compared with another MINOTAURUS technology, based on bio-augmentation of a ceramic MBR with bacteria specialized in BPA degradation.

LITERATURE

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Membrane Capacitive Deionization: An Economical Alternative For Water Desalination?

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Membrane capacitive deionization (MCDI) is an electrochemical desalination technology in which salt ions are removed from a water stream by storing them onto porous carbon electrodes by an electro-sorption process at low voltage. Once the electrodes are saturated, they are regenerated by polarity reversal, so that the ions are concentrated in a small waste volume. Ion-exchange membranes inserted in front of the electrodes enhance the efficiency of the process. Although MCDI seems a promising technology due to its low energy cost, environmental friendliness and low fouling and scaling risk, experience with the process is rather limited at the time.

In this project, the fundamentals of the MCDI process and the obtainable performance were therefore investigated in detail. A 2^4 factorial experiment design was used to examine the effects of different operating parameters (cell voltage, flow rate...) on the ion removal efficiency, the charge efficiency, the water recovery and the energy consumption of the cell. Experiments were performed with artificial NaCl solutions and a bench-scale MCDI test unit. The results of this experimental design showed that all operational parameters affected the process in some way. Moreover, the minimum and maximum values for the output parameters obtained in the experiment show that it is possible to operate MCDI at high ion removal efficiency (up to almost 100%), high water recovery (up to 88%) and/or low energy usage (down to 0.06 kWh/m³), depending on the selected settings. As such, the process is highly tunable to the specific prerequisites of each case. One very remarkable observation was the low charge efficiency at high cell voltage and low flow rates. Presumably this is due to the occurrence of concentration polarization phenomena under these conditions, similar to the ones in ED processes.

Ecotoxicity removal from industrial wastewater

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The wastewater originating form tank truck cleaning (TTC) activities is characterized by a high degree of variability in composition, degradability and toxicity. In a previous study with TTC wastewater, we found significant residual toxicity in the treated and discharged effluent. The aim of the present study was therefore to investigate the removal of acute toxicity from TTC wastewater by different key unit operations applied in industrial wastewater on a laboratory scale.

During a 5-month period, we collected influent wastewater samples from a TTC company in the harbour of Antwerp. In the lab, the samples were sequentially subjected to (1) chemical coagulation with increasing concentrations of $FeCl_3$, (2) biological treatment with activated sludge originating from the full-scale plant and (3) sorption with powdered activated carbon. Before and after each unit operation, we determined the chemical oxygen demand (COD), and assayed the acute toxicity with the 30min *Vibrio fischeri* bioluminescence inhibition test. The toxicity of final effluent samples was also measured with the 72h algal growth inhibition test using *Pseudokirchneriella subcapitata*.

The global average COD and sCOD of the raw wastewater were 5485 mg/L and 4160 mg/L respectively. The wastewater influent caused a significant reduction in bacterial bioluminescence, with average inhibition values of 92% for the unfiltered and 88% for the filtered samples. Chemical pretreatment by coagulation with $FeCl_3$ removed approx. 38% of the influent SCOD and reduced the inhibition by 11%. Activated sludge subsequently removed the biodegradable COD from the pre-treated wastewater which resulted in an average effluent SCOD of 700 mg/L. Biological treatment also significantly reduced the bioluminescence inhibition but the removal efficiency was highly variable. Activated carbon (at 10 g/L) almost completely removed the remaining COD and inhibition in all samples.
The response of the rapid bioluminescence inhibition assay (<2-9 Toxic Units) did not correspond to the algal growth inhibition test (886-5470 Toxic Units), indicating that the bacterial test may not always be suitable for effluent quality monitoring.

The findings from the present study suggest that conventional technologies such as coagulation and biological treatment did not suffice for complete removal of toxicity from TTC wastewater, and that advanced wastewater treatment technologies such as activated carbon filtration are required for the job of detoxification.

Selective removal of NaCl from an industrial brine using conventional and bipolar membrane electrodialysis

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Electrodialysis is an electrochemical separation technique by means of an electrical potential difference and ion-exchange membranes in order to separate ions in aqueous solutions. The application of conventional and bipolar membrane electrodialysis is examined on a purge of the brine circuit of the company INEOS ChlorVinyls. The research is part of the MIP-ICON project “Innovative Applications of Bipolar Membranes in electrodialysis – InToBiMem”. The concentrated salt stream contains high concentrations of chloride and sodium, respectively 90 and 64 $g \cdot l^{-1}$ and relatively small concentrations of sulphates and chlorates. The objective of the electrodialysis process is the selective removal of sodium chloride and the retaining of sulphates and chlorates.

For conventional electrodialysis, PC-SA (standard anion-exchange membranes) and PC-MVA (monovalent selective anion-exchange membranes), both in combination with PC-SK (standard cation-exchange membranes), are compared. Considering electrical efficiency and resistance, anion selectivity, pH requirements and solvent permeability, the best performance was achieved by the combination of PC-SA and PC-SK membranes. Experimental results show the perfect retaining of sulphates in the diluate. Simultaneously, a sulphate free concentrate with a NaCl-concentration of over 300 $g \cdot l^{-1}$ is obtained. However the selective retaining of chlorates by electrodialysis is not possible. The electrical efficiency for the removal of chloride and sodium varies from 80% to 100% and from 75% to 100%, respectively. The efficiency for the removal of chloride decreases with increasing desalination. No limiting current densities were observed for desalination up to 75%.

A long-term experiment revealed problems due to formation of Cl_2. The limited permselectivity of PC-SK results in leakage of chloride ions from the concentrate to the electrode rinse solution (ERS). Subsequently, Cl^- is oxidized to Cl_2 at the anode. The combination of chlorine and water is a strong corrosive mixture, which leads to oxidation of the stainless steel cathode (visual determination) and leakage of the terminal PC-SK membranes. Implementing two buffer compartments consisting of a Na_2SO_4-solution solves this problem. Another possible solution is the use of reinforced PC-SK as terminal cation-exchange membranes. This solution was tested during a five hour batch experiment.

Production of 2 M NaOH en 2 M acid by bipolar membrane electrodialysis is easily achieved. For this application PC-SK, PC-Acid 60 (anion membrane suitable for the production of monovalent acids) and PC-BPM (bipolar membranes) are used. Due to the absence of selectivity of PC-Acid 60 towards the different anions; the produced acid is a mixture of mainly HCl and lower concentrations of H_2SO_4 and $HClO_3$. The sum of the electrical efficiency for the removal of all anions is 70%. The efficiency for the removal of sodium is 72%. The produced acid and base are contaminated with 4% Na^+ and 2% Cl^-, respectively.

Session 8
Groundwater remediation: lessons learned from the field

Oral presentations

Reactive zones to remediate chlorinated hydrocarbons in urban environment: Comparing Oxidative & Reductive technologies in field applications

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In this presentation, we will outline, compare, and discuss results from 5 projects where chlorinated hydrocarbons were remediated in reactive zones created by injecting amendments into the groundwater. In 3 cases, a mix of zero valent iron (ZVI) and substrates was used, in one case only substrates were applied, and in one case activated persulphate was applied.
Three cases are full-scale remediation projects, whilst two cases are field-scale pilot projects. All cases are located in densely built-up urban environments, open to public use. Each case therefore is representative of today's challenges in urban redevelopment: how to address soil & groundwater contamination in Europe's most densely populated towns. All cases have produced sufficient data to analyze the different processes, the effects on the contamination and to draw conclusions on the respective technologies' applicability, including a review of costs. Three cases are nearing cases are nearing completion with regulatory approved closure.

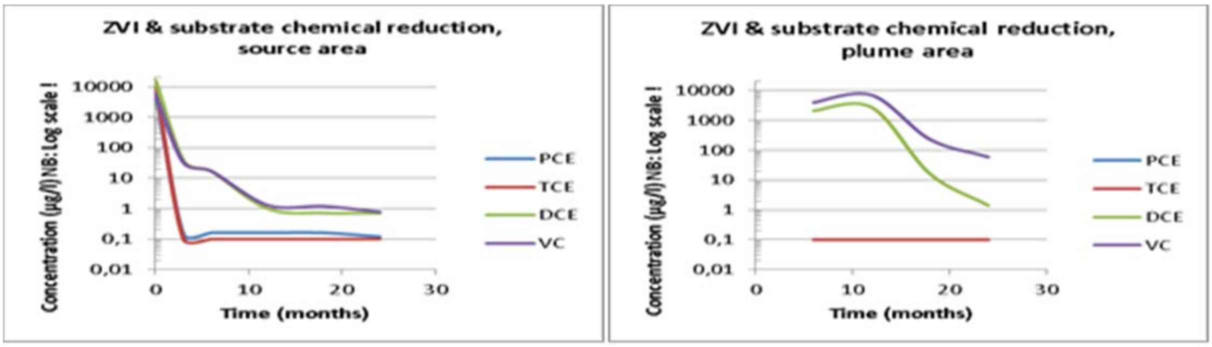

Figure 1: example data-set ZVI-substrate injection project

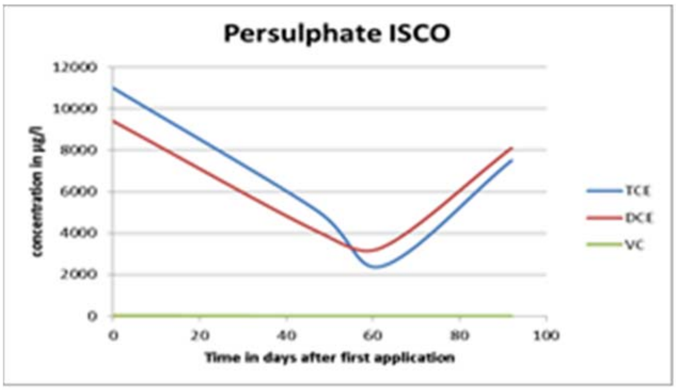

Figure 2: Interim results from Persulphate ISCO

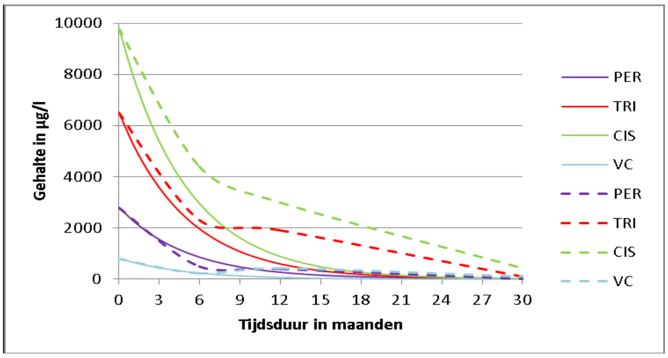

Figure 3: Results from a substrate-only anaerobic biodegradation project (solid lines are the predicted concentration decay curves based on modelling; the dashed lines are actually observed concentration decays), X-axis is time in months.

Injection of Guar Gum Stabilized Micro-sized Zero-valent iron via direct push – field study

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ABSTRACT: Within the FP7 AQUAREHAB project (GA 226565), injectable micro-sized zerovalent iron particles (mZVI) were developed and evaluated for in-situ chemical reduction of chlorinated aliphatic hydrocarbons (CAHs). mZVI particles have good reactive properties and a longer life-time than nano-sized particles (nZVI), but need to be stabilized during injection to prevent sedimentation in storage vessels and injection tubes. Earlier we reported on a field scale injection of guar gum stabilized mZVI that was performed in November 2011 as a joined endeavor of several AQUAREHAB partners. More recently, April 2013, an additional larger scale pilot test was performed at another CAH-contaminated site in Belgium, where findings of the first test and numerous lab scale tests were used to work out an improved approach.

At a PCE contaminated test site, 250 kg of mZVI was injected as 5 m³ of 0.45% guar gum stabilized suspension via direct push between 2 and 8 m bgs. The mZVI was injected in a test area of 3 by 6 m via 6 high pressure injections (MIP-IN technology) targeting a radius of influence of 0.5 m. Multilevel monitoring wells were installed at different distances around the injection point, along with temperature sensors and devices specifically developed to detect magnetic particles via measurement of electromagnetic susceptibility. Groundwater samples were taken before the injection and during several months after the injection. After the injection, also several undisturbed soil core samples were collected to evaluate the presence of mZVI (via susceptibility measurements & chemical analyses) and guar gum. The aim of the field test was: (1) to evaluate the feasibility to prepare guar gum stabilized slurry at a larger scale, (2) to evaluate the injectability of the within AQUAREHAB developed mZVI, (3) to determine the radius of influence of the injection, (4) to document the impact of the mZVI on the pollutant concentrations, and (5) to study the fate and added value of the guar gum after the injection.

This paper presents the results of the followed approach, as well as some practical considerations related to lessons learned.

INTRODUCTION

Chlorinated aliphatic hydrocarbons (CAHs) are among the most frequently detected groundwater contaminants representing a significant environmental concern due to indefinite life time and potentially carcinogenic and toxic effects on humans and environment (Henschler, 1994; Doherty, 2000). Since the early 1990s, zerovalent iron (ZVI), as a nontoxic material was used for in-situ removal of different CAHs creating well established permeable reactive barriers (PBRs) (Gillham and O'Hannesin, 1992; Mathenson and Tratnyek, 1994). In a PBR millimeter sized ZVI is installed in the subsurface in the form of a reactive wall requiring high excavation costs; moreover just shallow contamination can be reached. In contrast, mZVI particles (from 15 nm to 100 µm) can be injected directly into the subsurface, also at high depths, as aqueous suspensions. Particles can be released under pressure conditions (direct push) or/and gravity flow (permeation) creating an in-situ reactive zone (Li et al., 2006). In addition, the particles can be injected close to the source zone of the contamination, potentially leading to a large reduction of the time necessary for remediation. Nevertheless, due to the high density, mZVI particles are prone to fast sedimentation rate and can accumulate in tubes and injection wells, reducing the radius of influence and the contact area with contaminants. Therefore, to be used in field applications, mZVI particles must be stabilized. For this purpose, kinetic stabilization can be achieved by increasing viscosity of the suspension (kinetic stabilization) and as a consequence enhancing iron particles mobility (Xue and Sethi, 2012). Recent studies (Tiraferri et al., 2008; Tiraferri and Sethi, 2009; Xue and Sethi, 2012) proved that the green biopolymer guar gum is very effective and is able to provide an additional steric repulsion by adsorbing onto iron particles surface and reducing aggregation process.

This field study evaluated the feasibility of injecting guar gum stabilized mZVI slurry by direct push for remediation of CAH-contaminated site characterized by the presence of fine sand.

TEST SITE DESCRIPTION

The injection of guar gum stabilized mZVI took place at Site P (Belgium), which is an active industrial site. The spot selected for the pilot test is located near the source zone, where mainly PCE was present in concentrations ranging from 8.1 to 72.6 mg/L. The layer of 2-8 m bgs was the target of the pilot test. The water table is located approximately 2 m bgs.

The hydrogeological structure of the site consists of various tertiary and quartier sand (fine, light loamy sand 0-20 m bgs) combined in certain cases with sporadically clay layers. Empirical approximation of hydraulic conductivity was based on available data on grain size distribution (GSD). According to the GSD data, from 4.3-6.5 m bgs the estimated average K is 6.0×10^{-5} m/s, the hydraulic gradient is 0.000681 and the groundwater flow velocity is 7.4 m/year.

PRELIMINARY TEST

As previously reported (Velimirovic et al., 2012), preliminary laboratory tests were required in order to design the pilot tests. To examine the CAH-biodegradation potential at Site P batch experiments were conducted under anaerobic conditions using the soil and groundwater collected from the site with addition of guar gum as a potential electron donor. After two and the half months of monitoring, no indication of biodegradation was observed. The mass of iron needed for contaminants reduction was deduced from dose tests on lab scale under anaerobic conditions. The target mZVI concentration able to guarantee a fast reduction of the detected PCE was estimated by adding different mZVI concentrations into the soil and groundwater samples collected from the site. Based on the data of the dose test minimal concentration of mZVI for fast removal of PCE (7.3 mg/kg of slurry) is between 5 – 10 g/kg of slurry, while for high PCE concentration (57.5 mg/kg of slurry) a 5 times higher dose (mZVI concentration of 25 – 50 g/kg of slurry) was found needed. Finally, sedimentation tests were performed to estimate the guar gum (supplied by Rantec Corp.) concentration needed for efficient direct push injection of mZVI (d_{50} = 50 µm) supplied by Höganäs (Sweden).

FIELD-SCALE INJECTION TEST

The pilot scale test was performed on April 2013. Before the injection, 3 monitoring arrays were installed within 2 m radius around the planned injection points. Each array consisted of 3 sampling ports at different depths (approximately 5, 6 and 7 m bgs) and is provided with comprising groundwater sampling ports, temperature sensors and detectors for magnetic susceptibility (Figure 1 a), with one additional array with groundwater sampling ports.

The pilot test set up is shown in Figure 1 b. The field test consisted of several “top - down” injections at high pressures performed using Geoprobe 7822DT and MIP-IN system (Uyttebroek et al., 2012). A volume of 5 m³ of 0.45 % guar gum suspension was prepared in portions of 200l using Ytron ZC-0. 250 kg of mZVI particles were mixed with guar gum suspension at high shear rate for 10 minutes before each injection and injected at 6 different spots and several depths from 2-8 m bgs (depending on the MIP-IN data on pollutant concentration), creating a reactive zone.

Ten days after injection, 8 core samples (each 1-7 m bgs) were taken to evaluate the distribution of injected mZVI in the subsurface (Figure 1 a). At the same spots LEB-H enzymes (Rantec Corp.) were added to enhance guar gum degradation. The presence of mZVI in the core samples was evaluated through magnetic susceptibility measurements performed directly on the cores (Dalla Vecchia et al., 2009) immediately after their extraction. Chemical analyses performed on aliquots of soil from the dismantled soil cores confirmed high iron concentrations. The iron concentration was determined via hydrogen measurements after acid digestion of the mZVI particles present in the soil samples (Velimirovic et al., 2012).

GROUNDWATER SAMPLING AND ANALYSIS

Groundwater samples were collected 1 and 2 weeks prior to the mZVI injection to obtain baseline concentrations. Later on, 4, 8, 12 and 19 weeks after the mZVI injection, groundwater samples were collected to monitor the performance of the created reactive zone by connecting the PTFE tubing of the MLDS and conventional wells with a peristaltic pump. Field parameters were measured in a flow-through cell by a portable Multi 340i (WTW, Germany) equipped with pH and temperature electrode SenTix41, conductivity measuring cell TetraCon® 325 and

Liq-Glass redox potential (ORP) electrode (Hamilton- Nevada, USA). 20 ml of groundwater samples were collected for CAHs analysis in 37 ml vials capped with butyl/PFTE grey septa. Within 8 hours, the concentrations of CAHs, intermediate- and end-products were determined via direct headspace measurements using a Varian GC-FID. Guar gum present in the groundwater samples was quantified by phenol-sulfuric acid test using a colorimetric method (Dubois et al., 1956).

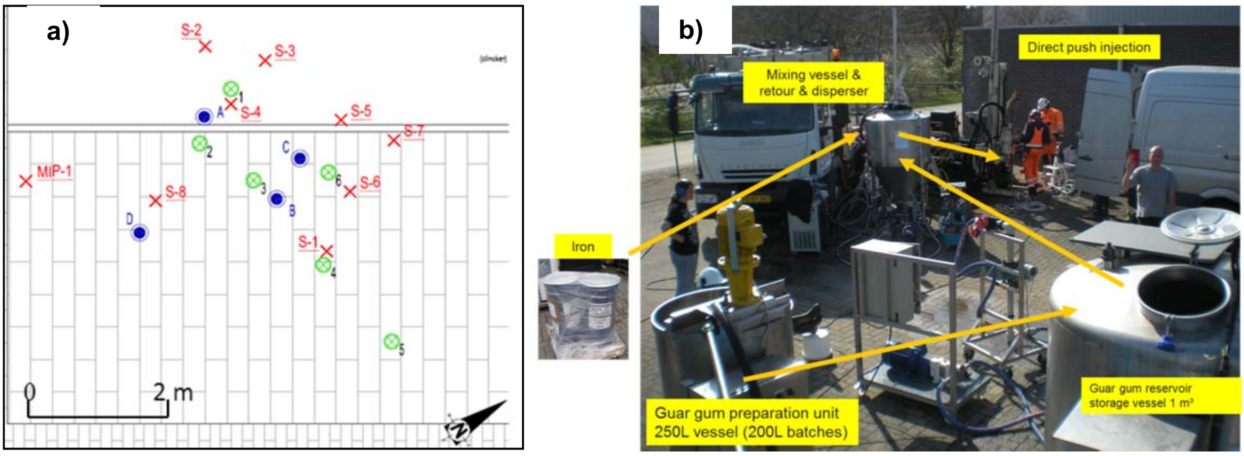

Figure 1: a) Injection and monitoring wells position in the test area. 1-6 injection spots (green), A-C VEGAS arrays (blue), D ground water sampling array (blue), and S-1-S-8 core samples (red). b) Direct push – configuration.

RESULTS

Injection pressure

During injection the pressure was continuously monitored using a pressure transducer connected to the injection pipe and a digital manometer which allows to monitor in real time the injection pressure over time (HD2124.1-Delta Ohm, Italy). In Figure 2 some characteristic pressure logs are reported.

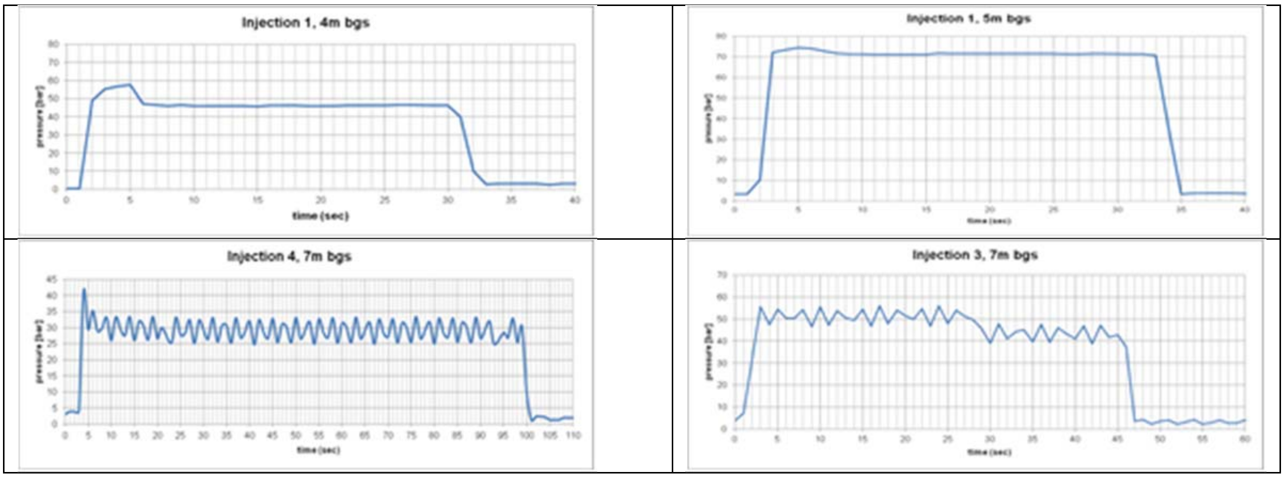

Figure 2: Pressure record during injection 1, 2 and 3 at different depths

The start and end of each injection can be easily identified on each pressure plot corresponding respectively to a sharp increase and subsequent decrease. Each injection took place in a very short time (from 30 s to 1/2 min). The generation of a fracture in the subsurface corresponds to a peak in the pressure plot and its intensity depends, as a general rule, on flow rate, viscosity and mechanical properties of the subsoil. The subsequent decrease in pressure corresponds to fracture propagation. Graphs show that very high pressures (ranging from 30 to 80 bar) were reached during injections; therefore, also due to the presence of pressure peaks, we can assume fractures generation occurred, giving rise to preferential flow paths. Comparing these results with magnetic susceptibility measurements, it is possible to affirm that in the vicinity of the injection point fractures propagates horizontally (see S1, S4 and S8 in Figure 3), becoming vertical as the radial distance increases (see S2 and S3 in Figure 3).

Iron distribution after direct push injection

The presence of mZVI in core samples determined via magnetic susceptibility measurements is presented in Figure 3. According to the data non-homogenous distribution of the particles at several different depths was observed. mZVI was clearly present in the core samples taken in the close vicinity (approximately 0.5 m) of the injection spots. mZVI was also detected close to the upstream well (at approximately 1.5 m from closest injection point) indicating that preferential flow paths were created. ZVI-concentrations obtained via the H_2 analysis were in agreement with these findings.

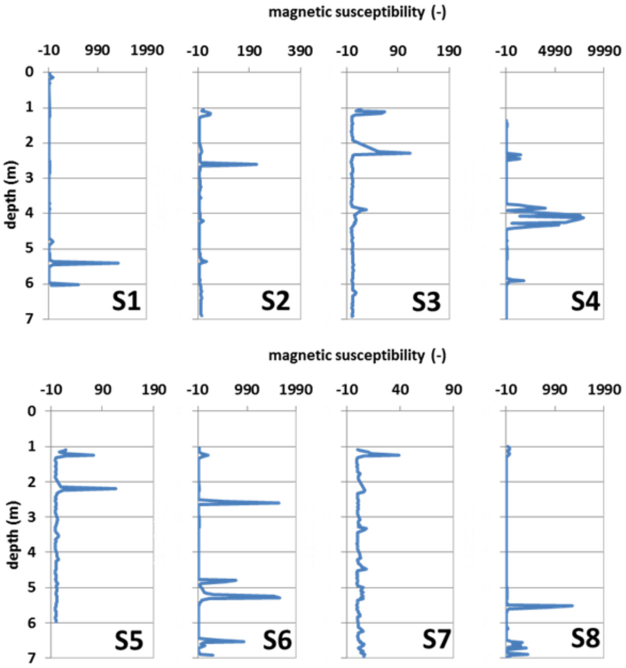

Figure 3: Magnetic susceptibility profiles of 8 core samples extracted close to the injection points.

Impact of injected mZVI on PCE reduction

Four weeks after mZVI injection, an average decrease of ORP from -1 mV to -41 mV was observed in the monitoring wells, while after 19 weeks a further decease of the ORP till -98 mV was observed. These data confirm that mZVI was delivered creating in-situ reactive zone. pH values were not changed drastically (average pH of 5.8-6.1), probably due to the buffering capacity of the aquifer.

Temporal changes of PCE concentration and degradation products (trichloroethene - TCE, cis-dichloroethene - cDCE, ethane and ethene – ETA+ETE) in monitoring wells are illustrated in Figure 4. Before injection, PCE was the predominant pollutant in all sampling points, and lower chlorinated compounds were nearly absent. One day after mZVI injection, the sampling ports were found to be clogged, probably by the guar gum. Four weeks after the injection, a guar gum concentration of 0.7 g/L was measured in monitoring well B at 6 m bgs. The sampling ports became available again over time, pointing towards degradation of guar gum (0-40 mg/L of guar gum was measured after 19 weeks) by the soil micro-organisms.

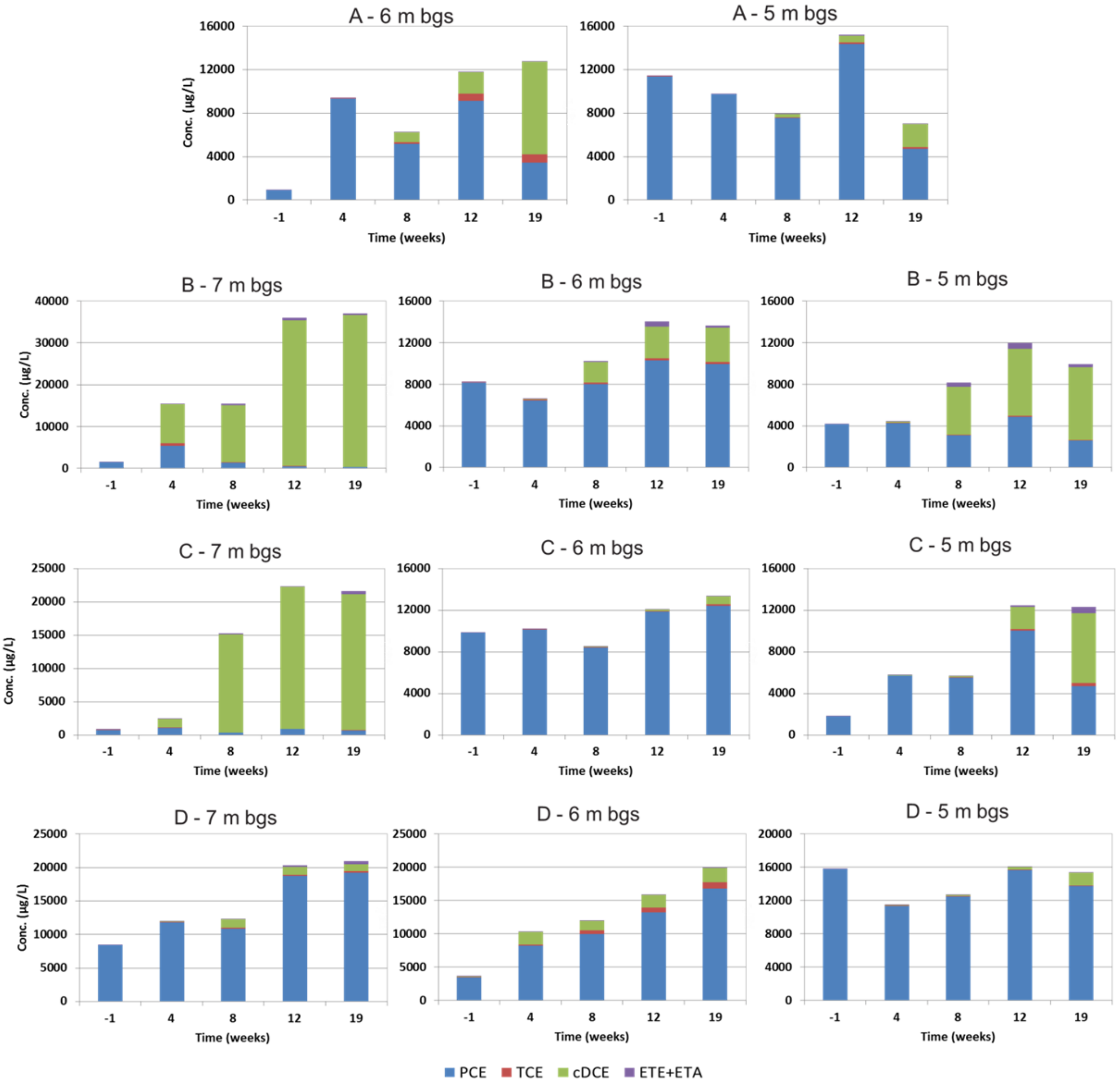

Figure 4: Temporal changes in PCE, TCE, cDCE and ETE+ETA concentrations in monitoring wells A, B, C and D at different depths. Please note different y-axis scale for different graphs.

Four weeks after mZVI injection, no PCE decrease was observed, even higher concentrations were observed in several sampling ports. However, degradation products started to appear indicating that the injection clearly induced degradation processes. Slightly increased concentration of acetylene observed 4 weeks after injection suggests that abiotic dechlorination occurred in the presence of delivered mZVI. Ethene and ethane as a final degradation products were also observed as presented in Figure 4. However, low concentrations of TCE with accumulation of cDCE after 8, 12 and 19 weeks was observed at several sampling points. Presented accumulation of cDCE is higher than expected when considering only abiotic dechlorination suggesting that biological processes were induced. Moreover, biological processes may have been initiated via pH increase, ORP decrease, guar gum degradation and hydrogen produced by the injected mZVI (Truex et al., 2011). For that reason groundwater samples were collected and microbial study was started.

CONCLUSIONS

The pilot test was performed in order to implement lessons learned from the pilot scale study reported by Velimirovic et al. (2012) and further optimize guar gum based mZVI slurry preparation and delivery for in-situ treatment of different CAHs. Presented data show that guar gum stabilized mZVI can efficiently be distributed within medium permeable aquifer using direct push techniques and consequently creating preferential flow paths.

Monitoring data show that after slurry injection PCE reduction included biodegradation processes till cDCE and possible reaction with iron.

Presented data indicate that guar gum stabilized mZVI slurry can be a viable option for in-situ remediation of CAHs instead of frequently used nZVIs. However, more monitoring activities are envisioned for appropriate evaluation of mZVI efficiency in degrading PCE within this pilot scale study.

ACKNOWLEDGEMENTS

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Robustness and reliability of an Inoculated Bioreactor for MTBE/TBA-Removal from Groundwater – pilot test

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ABSTRACT: Methyl tertiairy-butyl ether (MTBE) and Tert-butyl alcohol (TBA) are frequently used fuel oxygenates that have been released in the environment as a result of spills. As classical remediation methods for fuel contaminated groundwater (air stripping & sorption onto activated carbon) are not efficient for these compounds, a bioreactor technology was developed with bacteria that are specialised in the degradation of MTBE and TBA to CO_2. The performance of this inoculated bioreactor was evaluated at pilot scale (300L) under realistic conditions to test the reliability and robustness of the system. Within the FP7 MINOTAURUS project, the system was firstly operated at a chemical storage facility where the groundwater contained very high concentrations of MTBE (1-12 mg/L) as well as TBA (5-75 mg/L). Next, the pilot system was operated at a petrol gas station where the concentrations in the influent were lower. A good removal was observed, despite the multiple unfavourable conditions that were applied to the system. This shows that the inoculated bioreactor reactor technology is robust and reliable.

INTRODUCTION

Methyl tertiarty-butyl ether (MTBE) is a synthetic car fuel additive. However, it's use has resulted in widespread groundwater contamination (up to 830 mg/L) with MTBE. Tert-butyl alcohol (TBA), an intermediate in MTBE degradation, is often found in association with MTBE contamination. Both compounds are very mobile in the subsurface and are threatening capture areas for drinking water. They are, however, difficult to treat with existing pump and treat technologies (air stripping; sorption on activated carbon) due to their low sorption tendency, high water solubility and recalcitrancy. However, more efficient innovative technologies exist, which comprise biotechnology.

Earlier, an aerobic MTBE/TBA-degrading bacterial consortium (M-consortium) has been isolated and its use for treating MTBE/TBA-contaminated groundwater was demonstrated (Moreels et al., 2004, Bastiaens et al., 2004; Debor et al., 2010). An inoculated bioreactor for ex-situ MTBE/TBA-removal from groundwater, as part of a pump and treat solution, was developed at lab-scale and demonstrated successfully at pilot scale (Bastiaens et al., 2008). The technology realizes not only improved MTBE/TBA-removal, but is also more sustainable and eco-efficient in comparison with alternative methods, as the technology focuses on the destruction of the pollutants and not a relocation to other compartments (air, activated carbon).

The FP7 MINOTAURUS project (EU GA 265946) investigated the robustness and reliability of biotechnologies like the inoculated bioreactor, which is important to come to innovation, being the full scale applications. Earlier, results from lab scale tests showed (1) that bioremediation is a valuable option to remove MTBE/TBA from groundwater and (2) that the M-consortium has potential as bacterial inoculum to enhance MTBE/TBA and BTEX-biodegradation under aerobic conditions. Next, pilot scale tests were performed to evaluate the robustness and reliability of the system at larger scale under real conditions. The results of 2 recent pilot test are subject of this paper.

MATERIALS & METHODS

Inoculated bioreactor

An inoculated upflow bioreactor was developed by VITO for MTBE and TBA removal from groundwater. The prototype inoculated bioreactor is schematically represented in Figure 1. It concerns an upflow bioreactor where MTBE/TBA-containing water is pumped from bottom to top through a bed of specific biomass containing carrier materials. The bioreactor can be operated both as a fixed bed and floating bed bioreactor. A water recirculation loop returns part of the water from the top to the bottom of the reactor to (1) improve the homogeneity of the bioreactor and (2) to supply oxygen to the bioreactor. The outlet for the treated water is situated at the top of the reactor.

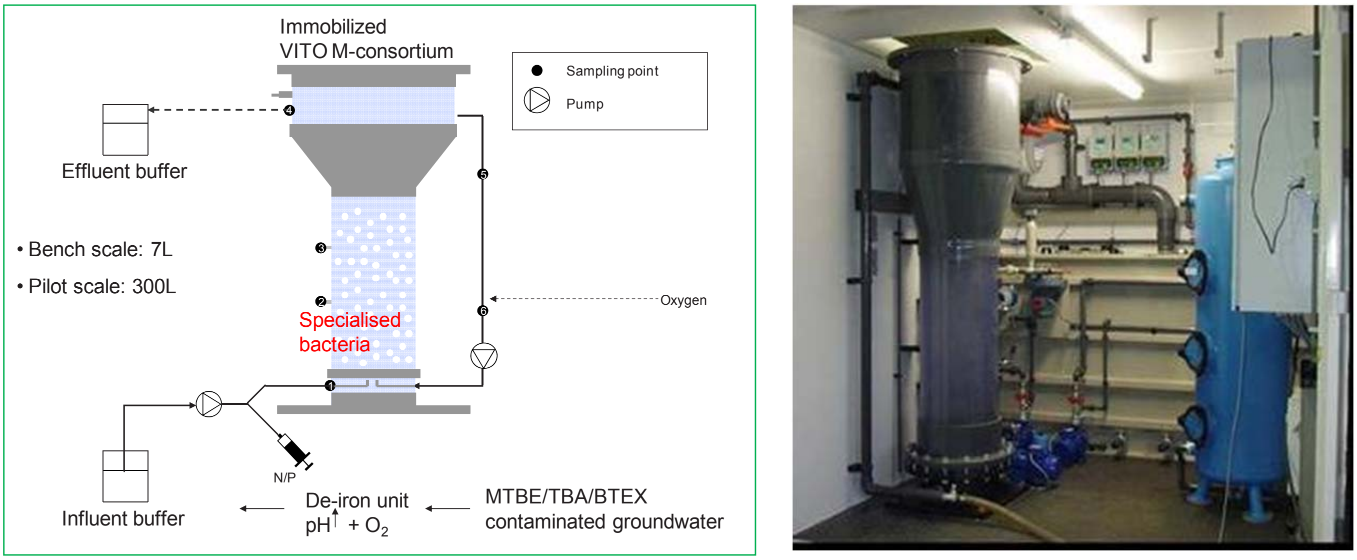

Figure 1: Schematic representation of the upflow inoculated bioreactor (LEFT) and photo of the bioreactor (RIGHT)

The beating heart of the bioreactor is the specialized biomass that is immobilized in the bed of carrier materials. The biomass consists of a mixture of bacteria, called M-consortium, that is able to degrade MTBE, TBA as well as BTEX-compounds completely to harmless compounds. The M consortium is cultivated in a fermenter to obtain the needed amounts of biomass, and is subsequently added to the bioreactor (= inoculation), where the bacteria can attach themselves to the carrier material. Besides addition of oxygen, a nutrient (Nitrogen & phosphor) addition system and pH-correction system are integrated to create more optimal condition for the bacterial activity.

The pilot scale bioreactor (up to 0.5 m^3/h) consists of an influent tank, a bioreactor with recirculation (Vtot= 300 L) and a polishing activated carbon filter. It is designed as a mobile unit which can be transported to the contaminated site for the required demonstration time, which is in the order of months. To avoid clogging of the bioreactor by the iron precipitates (originating from the dissolved iron in the groundwater), iron is removed from the groundwater in a first step.

Test sites & test conditions

The bioreactor was uploaded with the M-consortium off-site and was moved to the test site only after its MTBE and TBA –removal capacity was proven.
Test site 1 is an industrial site (chemical storage) in Belgium where the groundwater was heavily contaminated with MTBE (1-12 mg/L) and TBA (5-75 mg/L). In collaboration with the site owner an extraction well and test location was selected for the test, where high concentration of MTBE (300-5000 µg/L) as well as TBA (3500-10000 µg/L). were pumped.
Test site 2 is a petrol gas station in Belgium where high concentration of mainly MTBE (up to 8000 µg/L) and locally also TBA (up to 5000 µg/L) were measured in the piezometers. Existing extraction filters were used, which delivered groundwater with lower concentrations of MTBE (up to 2000 µg/L) and TBA (up to 300 µg/L).

Sampling & chemical analyses

The performance of the pilot system was monitored by sampling the groundwater at the entrance of the pilot system, at the effluent side of the bioreactor, and after the polishing activated carbon (GAC) filter (see Figure 2). Remaining concentrations of BTEX and MTBE/TBA were determined with an Interscience GC 800 Top gas chromatograph with headspace injection connected to a Voyager MS detection system. Temperature, pH and dissolved oxygen concentration were continuously logged.

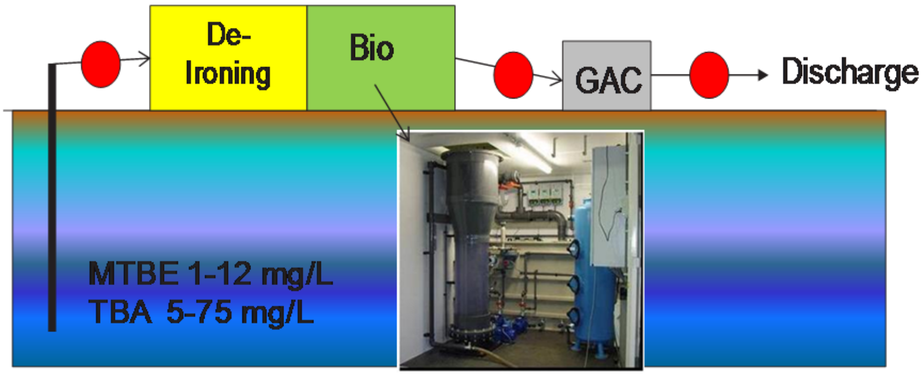

Figure 2: Schematic overview of sampling spots (red dots) used for the pilot test.

RESULTS

Pilot test 1

The bioreactor system was uploaded off-site and its reactivity was demonstrated during a 1 month of recirculation mode operation, and subsequently a 1 month of continuous operation (Hydraulic retention time = 10h) with groundwater artificially polluted with 8 mg/L MTBE and 4 mg/L TBA. An efficient removal (> 97%) was observed (results not shown).

Next, the pilot scale inoculated bioreactor (300 L) was transported to first test location, for a 5 month test period under different realistic test condition and operational situations. The pilot was operated at a chemical storage site where the pumped groundwater contained high concentrations of MTBE (up to 1-12 mg/L) as well as TBA (5-75 mg/L), which decreased in concentration during the test. Figure 3 shows the evaluation of the MTBE and TBA concentration over time in the influent of the pilot system and the effluent of the bioreactor (prior to the GAC step). The inoculated bioreactor was shown to remove these pollutants from the groundwater in an efficient and reliable way. Although a number of non-ideal but realistic situations were applied to the system (fluctuations of pH, temperature increases above 30°C, non-operational periods, fluctuation of flow, …), the system adapted fast and remained active without a need for re-inoculation.

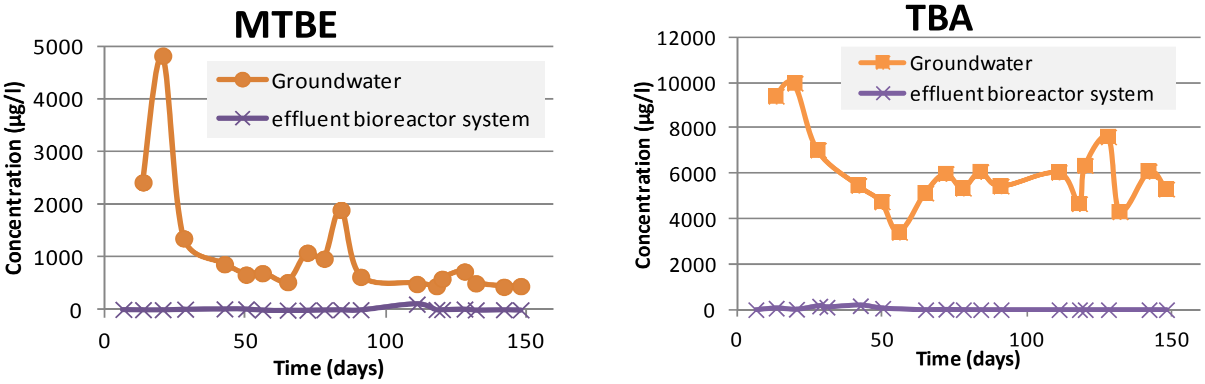

Figure 3: Efficient removal of MTBE & TBA by pilot inoculated bioreactor (prior to GAC polishing treatment)

More details on the MTBE and TBA concentration in the water before the GAC filter (= effluent bioreactor) and after the GAC filter are depictured in figure 4.. Generally, the bioreactor was able to reduce the concentration below the regulatory limit (100 µg/L). The GAC was shown to reduce the concentration further and proved to be only required as polishing step (police filter). As such the amount of GAC needed is limited.

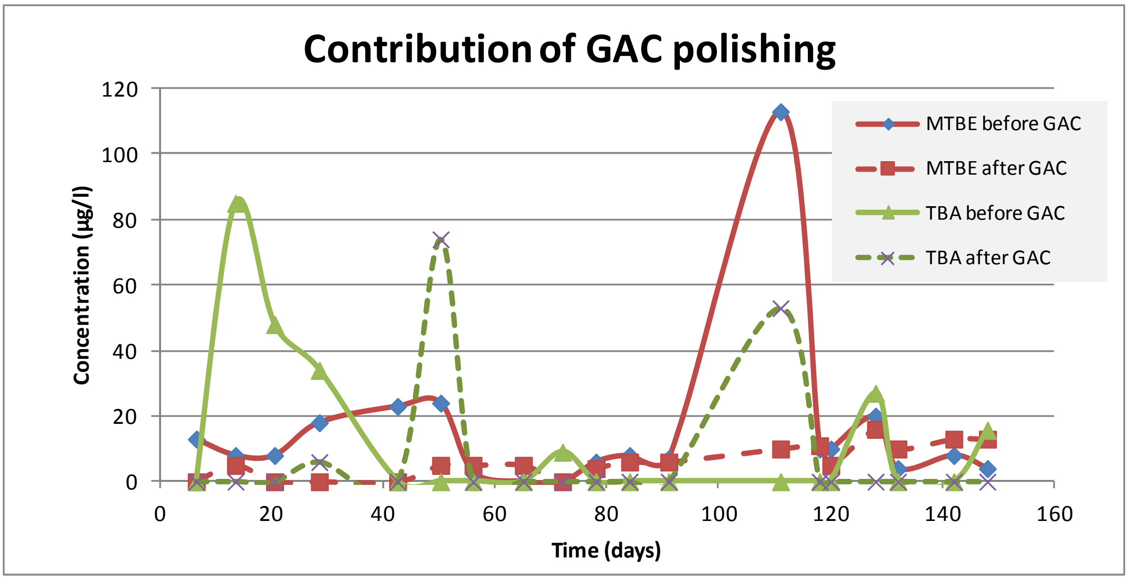

Figure 4: Evolution of the TBA-and MTBE-concentrations before and after the polishing activated carbon (GAC) step.

Pilot test 2

For pilot test 2, a different biomass carrier material was used in comparison with pilot test 1. An improved filling material to retain the biomass in the bioreactor was selected based on lab scale tests. Therefore, again, the reactor was uploaded off-site. Firstly, the bioreactor was operated in recirculation mode (no influent & effluent) and spikes of MTBE were regularly given as indicated in Figure 5. Once good degradation was obtained, MTBE was dosed continuously (5-30 mg/L/day) for another 30 days. All added MTBE was immediately degraded as proven by the low MTBE-concentration measured in the bioreactor (Figure 5). Next, the system was tested under continuous flow conditions (50 L/h) with artificially contaminated groundwater (5000 µg/L MTBE). The data indicated a good performance of the system with effluent concentrations below 100 µg/L.

Next, the system was transported and operated at a petrol gas station (Belgium) treating groundwater mainly contaminated with MTBE. Although high concentrations of MTBE, and locally also for TBA, were found in the piezometers, the existing extraction wells delivered lower pollution concentrations (100-600 µg/L). This is explicable by the different depths and larger filter screens of the extraction filters as compared to the monitoring filters, which led to dilution of the pollution. MTBE and TBA were removed efficiently in the system (100L/h, HRT = 3h) with bioreactor effluent concentrations below 25 µg/L. The system was operated for 40 days under these conditions.

Afterwards, it was decided to turn off the bioreactor system and make some modification to the groundwater extraction system with the aim to increase the influent concentrations. After a non-operational period of 2 months the system was restarted. In recirculation mode, it was observed that 8 mg/l was removed within 5 days, showing the bioreactor did not lose it activity. Currently, the system is being operated in continuous mode at 150 L/h (HRT = 2h).

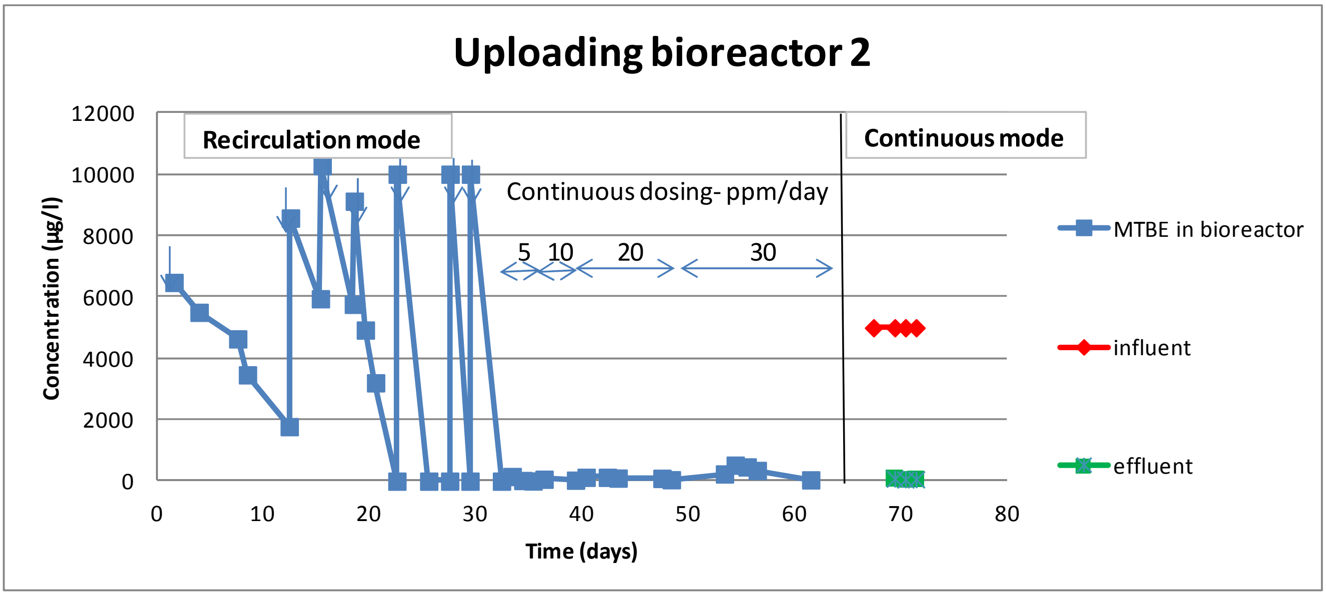

Figure 5: Uploading of bioreactor 2.

CONCLUSIONS

A pilot scale inoculated bioreactor (300L) was operated in the field under different circumstances. The prototype bioreactor was shown to be a relatively fast starting and stable system, removing MTBE and TBA from the groundwater in an efficient way, hereby meeting regulatory limits. High concentrations of MTBE and TBA are favourable for the system and were shown to maintain a well performing biofilm. In that sense, dilution during pumping of groundwater should be avoided as much as possible. It was experienced that it is realistic to pump only low MTBE/TBA-concentration at sites with high pollution level. Nevertheless, the system was shown to contain its activity, although limited contaminant concentrations are not favourable for the system.
Cost calculations have been made and indicate that the inoculated bioreactor technology is competitive with the less effective air stripping and subsequent sorption onto activated carbon for removal of MTBE (and TBA) from groundwater. This is especially the case with higher pollutant concentrations.

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Implementation of zerovalent iron for source zone treatment via soil mixing

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The soil and groundwater at a textile manufacturing site in West Flanders is polluted with chlorinated solvents. Trichloroethylene is found in the groundwater in very high concentrations (426 mg/l). Much less 1,2-dichloroethylene and vinyl chloride has been detected in the groundwater. The pollution in the soil is only trichloroethylene. A pure product layer has been detected at a depth between 7,2 and 7,6 m bgl. The soil consists of sandy clay and the permeability is very low. Practice has shown that the source zone can't be removed by traditional techniques such as pump and treat. Excavation would be complicated because the pollution is situated near a building and at a great depth. To excavate the pure product layer expensive measurements are required. Because of this, excavation is not BATNEEC. In situ chemical reduction of the DNAPL by injection of ZVI (zero valent iron) may be a solution.

The chemical destruction of the chlorinated solvents by addition of ZVI was examined by VITO in lab tests. These tests proved a degradation of more than 95% at the dose that was selected for field application. After a period of 8 weeks, a carbon source to stimulate biodegradation was added. With the C-source, a further decomposition of the chlorinated solvents was achieved.
On large scale, it is often a problem to keep the iron in suspension during injection and to distribute the iron equally over the polluted zone because of the great density of iron and permeability limitations of the soil. To counter this problem, the iron was suspended in a guar gum slurry which was distributed in the subsurface by soilmixing. During drilling, the ZVI-slurry is injected under high pressure and mixed with the soil at the same time, creating a soil mix pile. At this particular case, a total of 14 soil mix piles were executed successfully until 8,4 m bgl, whereby 3500 kg of fine sized micro scale ZVI was applied. The guar gum will be biodegraded in time with release of simple sugars. This is expected to stimulate the anaerobic biodegradation of the chlorinated solvents, which would complement the chemical reduction by the ZVI.

The first monitoring results of soil and groundwater concentrations are expected in October 2013.

This pilot has already shown that soilmixing may be a promising alternative to injection of ZVI by direct push or by injection in wells. The soilmixing can be a solution for the treatment of chlorinated solvents in high concentrations in dense soils and at great depth without removing a lot of soil.

In Situ chemical oxidation of carbon disulfide using activated persulfate

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Remediation of carbon disulfide (CS_2) poses multiple technical difficulties due to the chemical properties of the contaminant. CS_2 is a highly volatile and extremely flammable liquid with a wider explosive range in air than hydrogen. CS_2 can exist in the environment as a dense non-aqueous phase liquid (DNAPL). This project involved research and development of a completely novel remedial approach to destroy carbon disulfide *in situ*. Due to its explosive range conventional treatment options previously involved *ex situ* excavation, stabilization and disposal to landfill.

Persulfate is a thermodynamically powerful oxidant which is kinetically slow to react unless activated; therefore, the speed of the oxidation reaction and thus the potential to generate heat can be controlled making it a potentially ideal candidate for destroying CS_2 *in situ*. For mineralization of carbon disulfide, persulfate is activated by the addition of sodium hydroxide to achieve a pH of 10.5 in order that numerous radical species including the sulfate and superoxide radicals form. These radicals then cause progressive destruction of CS_2 to carbon dioxide, sulfate and water. The reaction kinetics involved are controlled by adjusting the concentration of both persulfate and sodium hydroxide, in order that oxidation proceeds without the production of heat or gaseous by-products.

ARCADIS undertook fundamental research to evaluate the potential for a safe, sustainable, cost effective in situ approach for the remediation of CS_2. Using the data from the laboratory work, regulatory approval was secured for a field pilot for the use of pH activated persulfate using to destroy CS_2. This successful pilot demonstrated the efficacy of the technology which then lead to a full scale application of this innovative technique.

Field scale applications of pH activated persulfate involved two techniques: (1) *in situ* injections and (2) soil mixing. This lead to the development of several new delivery systems, for example, a mobile oxidant delivery system was designed and constructed to allow bulk persulfate and activator to be mixed into solution in large quantities for co-injection to wells/rods or delivered to soil mixing equipment. During the field scale events health and safety was carefully considered and managed (particularly with soil mixing CS_2 impacted areas) and mitigation measures were developed and put in place to control any potential issues from vapor, dust, odor and temperature. For example, (1) dry ice was used to create an inert atmosphere for soil mixing and (2) an innovative CS_2 vapor management system was developed to capture and contain CS_2 vapors, which cannot be extracted by conventional soil vapor extraction systems.

Over the duration of the project, multiple application technologies for pH activated persulfate oxidation of CS_2 were proven to be successful in a variety of ground conditions. The technologies used could be effectively applied to a wide number of CS_2 impacted sites globally.

Bioaugmentation with in-situ culture propagation (BacAd)

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A metal processing site has a groundwater contamination with chloro-ethenes that has migrated 1 km. The groundwater has a high seepage velocity and is acidic. Laboratory tests have shown that enhanced natural attenuation by addition of a substrate induces partial dechlorination of PCE which stalls at DCE. The objective of the EU-LIFE+ sponsored project BACAd is to demonstrate that bioaugmentation can be achieved on full-scale in a cost efficient way by optimizing propagation of injected cultures.

Five microbial cultures and two electron donors have been screened with a laboratory microcosm test. The two best cultures were used for execution of two push-pull pilot tests. Each test was done with a specific culture and electron donor. Laboratory column tests were performed with these cultures and site materials to evaluate and optimize their migration in the soil. The culture that performs the best in the push-pull and column tests was injected on a larger scale to perform a pilot test with 4 injection wells. At the same time, a similar field test is being performed in an adjacent area with injection of groundwater from another site where complete dechlorination of PCE has occurred. Afterwards, the remediation has been scaled up-scaled to a reactive zone with 40 injection wells that covers the entire plume width. Full-scale bioaugmentation with transfers of the microbial population from the initial pilot test remediation areas to the reactive zone is scheduled in fall 2013. By doing this, the costs for the production and injection of the microbial culture may be decreased, improving remediation efficiency. The in-situ propagation of microbial cultures is monitored with QPCR and DGGE-analyses.

Laboratory microcosms have demonstrated complete dechlorination following bio-augmentation in the presence of the electron donors *Nutrolase* (a residue from potatoe processing) and glycerol. The column tests confirmed the need for bio-augmentation and the dechlorination capabilities of the two cultures that were used in the field. They have demonstrated the mobility of the cultures in aquifer material of the site.
The two push-pull test with cultures grown on *Nutrolase* and glycerol induced complete dechlorination in the field. Acidic groundwater conditions have slowed the process and required neutralization. Glycerol has proved to a better substrate than *Nutrolase*. The culture grown on *Nutrolase* was contaminated by pathogenic bacteria, which was caused by the substrate. The in-situ evolution of the pathogens has been monitored. The first small scale pilot test with injection of glycerol and a microbial culture has achieved complete dechlorination in the injection wells following bio-augmentation. The migration of the culture to the downgradient monitoring wells is currently being monitored. Full dechlorination has not been achieved yet in the injection wells of the second small-scale test in which groundwater from another site was injected. The installation of the full-scale reactive zone will be presented.

Poster Presentations

Shifts in bacterial diversity in the hyporheic zone of an eutrophic river after installation of an upstream wastewater treatment plant

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The microbial communities in hyporheic sediments depend on external supplies of nutrients. To this end, the installation of wastewater treatment plants (WWTPs) has the potential to significantly alter microbial communities due to its impact on nutrient concentrations. We investigated the effect of long-term decrease of organic carbon inputs due to the activity of a recently installed WWTP on the bacterial communities in the hyporheic zone of the Zenne River, Belgium. Pyrosequencing of 16S ribosomal RNA gene fragments was used to survey the dynamics of the bacterial communities in horizontal layers of sediments, collected in 2005 (2 years before WWTP construction), 2010 and 2011. Shifts in bacterial communities were associated with reduced organic carbon in the sediments of 2010 and 2011 compared with the samples of 2005. *Proteobacteria* was the most dominant phylum in the sediments of 2005 followed by the *Chloroflexi*. The relative abundance of *Chloroflexi* and abundance of organohalide respiring *Dehalococcoides mccartyi* (as determined by quantitative PCR) declined dramatically in sediments of 2010 and 2011 concomitant with substantial decrease of anaerobic vinyl chloride respiration potential in microcosms prepared from sediments taken during the three sampling campaigns. The more oxic and oligotrophic sediments of 2011 were associated with strong decrease of copiotrophic and anaerobic microbial groups including saprophytic members of *Firmicutes*, and sulphate- and nitrate-reducers, and concomitant enrichment of oligotrophic members of *Alpha*- and *Betaproteobacteria*. These results reinforce that microbial community dynamics can act as indicator for the ecological consequences of environmental disturbance, such as decreased organic carbon discharge in aquatic ecosystems.

Step-rate injection tests for the determination of the critical pressure for reagent injection in aquifers systems

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ABSTRACT: The determination of critical pressure through step rate injection tests plays a major role in environmental engineering (remediation of contaminated aquifer systems) as well as in oil and gas industry. Critical pressure is the pressure at which fracture is created in an un-fractured formation or it will widen an existing fracture in a formation. The determination of this value is crucial in oil engineering for better operation of water-floods and has extensively used to increase oil and gas recovery from tight reservoirs. Injection above critical pressure, not only produce an early breakthrough, poor sweep, reduced oil and gas recovery but also result in loss of costly injection fluids. On the other hand, injection far below the critical pressure decreases oil and gas recovery from reservoir. For groundwater remediation, the identification of the critical pressure is an important issue also for the design of field injection of reagents into the contaminated aquifers. Injection below the critical pressure results in permeation delivery of the reactants, and consequently fairly homogeneous distribution in the proximity of the injection point. In turn, injection above it causes fracturing of the porous medium, fluid delivery along preferential flow paths, even at high distances for the injection point, and a final non homogeneous distribution of the reactant. Permeation or fracturing injection can be preferred in specific cases.

To enhance the usefulness of step rate injection tests, the current paper presents a methodology for the determination of the critical pressure for reagent injection in aquifer systems and the interpretation of real tests conducted in a shallow aquifer system in Belgium. Although step rate injection tests have been frequently performed for several years in oil and gas industry by using Newtonian fluids (usually water) in order to access formation properties and to determine the critical pressure, for the first time this technique is applied here to aquifers systems and by using non-Newtonian fluids. This work was conducted in the framework of the AQUAREHAB project (FP7 - G. A. Nr. 226565).

INTRODUCTION

Step rate injection test is a basic method used to find out the critical pressure, that is, the pressure at which fractures open in an un-fractured formation during the injection of a fluid. It can be estimated from the combination of tensile strength of the rocks and minimum in-situ rock stress. When the applied pressure reaches, and overcomes, the critical one, a fracture opens, the tensile strength of the rocks vanishes and only the minimum in-situ rock stress acts to close the existing fracture. For this reason the minimum in-situ rock stress is also called closure pressure, and is usually determined from step rate injection tests (Nolte, 1982; Nolte, 1988).

Step rate tests are used in oil industry since over 60 years, and consist in the injection of a fluid in the oil formation, applying a constant discharge rate, which is then increased stepwise. The literature (Bennett and Clark, 1985; Felsenthal, 1974; Lacy and Hudson, 1995; Singh et al., 1987) available on the design, analysis and fracture evaluation in step rate tests is based on the use of Newtonian fluids (usually, water) and is related to reservoir engineer. In this paper the approaches for the determination of critical pressure and the interpretation of step rate injection tests are studied for non-Newtonian shear thinning fluids, and the application is extended to aquifers. In groundwater engineers, step tests are usually performed extracting water, and analyzed in order to determine the well characteristics or the aquifer properties (Sethi, 2011), while step injections tests are very limited.

In common approaches to the analysis of step rate tests in reservoir engineering, the critical pressure is determined from the results of step rate tests analyzed in terms of pressure at the well (p_w) vs injection flow rate (Q), measured for each injection step, when a steady state condition is achieved. A linear relationship (straight line) is observed between p_w and Q. When the injection pressure overcomes the critical one, than the slope of the p_w vs Q graph changes, due to the opening of fractures in the porous medium (Singh et al., 1987). When shear thinning fluids (i.e. characterized by high flow viscosity at low flow rates and lower viscosity at high flow rates) are used as injection fluids, the viscosity does not remain constant during the test, since it decreases with increasing flow rate (Tosco and Sethi, 2010; Xue and Sethi, 2012). Consequently, the determination of the critical pressure from p_w vs Q is not straightforward, since the relationship is not linear. The current paper presents a methodology to remove the non-linearity and determine the critical pressure. A relation between injectivity index and injection flow rate is presented. On the basis of this methodology, the paper also presents the interpretation of the an injection test conducted in a shallow aquifer system in Belgium in the framework of the FP7 AQUAREHAB project using a shear thinning guar gum solution.

MATERIALS AND METHODS

Removal of Non-linearity in Guar gum Injection

As discussed in the introduction, for step rate tests performed injecting a Newtonian fluid in a porous medium, there is a linear relationship between the pressure (p_w) at the steady state (that is, at the end of each injection step) and the corresponding injection rate (Q), following Darcy law (Darcy, 1856), up to the critical pressure of the formation. As soon as the critical pressure of the formation is reached, the slope of the line changes. For reservoir engineering, this behaviour assumes a steady-state Darcy flow in case of water injection and the pressure at the well can be calculated from the integral of Darcy law along the radial distance (Verruijt, 1970):

$$p_w = p_e + \frac{B\mu}{2\pi Kh}\left(\ln\frac{r_e}{r_w} + s\right)Q \qquad (1)$$

where p_e is the external (undisturbed) pressure of the reservoir or aquifer [$ML^{-1}T^{-2}$], *B* is the formation volume factor [-], μ is the viscosity of fluid [$ML^{-1}T^{-1}$], *k* is the permeability of the formation [$ML^{-1}T^{-2}$], *h is* formation thickness (m), r_e is the external radius of the aquifer or reservoir, r_w is the well bore radius (m), *s* is the skin factor [-], *Q* is the injection flow rate [L^3/T^{-1}], p_w is the wellbore pressure [$ML^{-1}T^{-2}$]. If the stabilized pressure measured at the well p_w is reported as a function of the discharge rate Q, a linear dependence is observed.

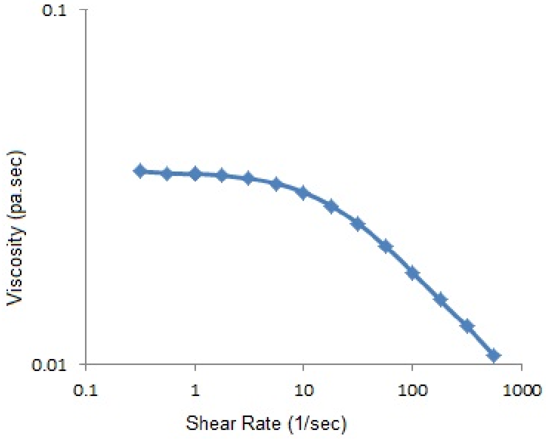

Figure 1: Viscosity as a function of shear rate for a guar gum solution (2 g/l)

For the application to aquifer systems, two simplifying hypotheses can be assumed, namely incompressible fluid and negligible variation of pressure between bottom hole and surface (*B=1*), and negligible head losses due to skin factor compared to head losses in the porous medium due to flow (*s=0*). Consequently equation (1) reduces to:

$$p_w = p_e + \frac{\mu}{2\pi Kh}\ln\frac{r_e}{r_w}Q \qquad (2)$$

Also in this case a linear dependence of p_w on *Q* is observed. The pristine permeability of the aquifer (i.e. before fracturing) can be calculated from the slope of the line interpolating the point of the graph p_w vs Q before the critical point.

In case of guar gum injection, the viscosity is not constant (Figure 1), and therefore the trend of p_w vs *Q* is not linear anymore. The injection pressure is given by

$$p_w = p_e + \frac{Q}{2\pi Kh}\int_{r_w}^{r_e}\frac{\mu(r)}{r}dr \qquad (3)$$

where the integral depends on the viscosity model of the injected fluid (i.e. on the law governing the dependence of the viscosity on the Darcy flow rate, which in turn depends on the radial distance from the well).

In a simplified approach, a linear relationship can be in turn assumed when reporting p_w on $Q{\cdot}\mu$ (Figure 2), provided that the viscosity at each step is an average viscosity, again dependent on the discharge rate. The point at which the slope of the straight line changes is the critical point as shown in Figure 2.

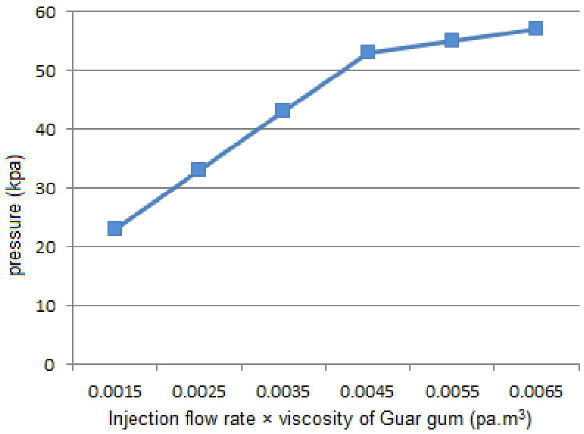

Figure 2: Well pressure (p_w) vs flow rate × viscosity ($Q{\cdot}\mu$) for the injection of a non-Newtonian fluid

Injectivity index

The injectivity of a well (*I*) is defined in terms of the injection rate (*Q*), pore pressure (p_0) and injection pressure (p_w) given by equation (2) (Newtonian fluids) or (3) (non Newtonian fluids):

$$I = \frac{Q}{p_w - p_0} \tag{4}$$

During the injection of fluid into the well in the Darcy regime, before fracturing occurs, the injectivity index remains constant. Conversely, an increase in injectivity index shows that fractures opened and the critical pressure was overcome. The point at which the injectivity of the injection fluid increases sharply is called the critical point (Figure 3).

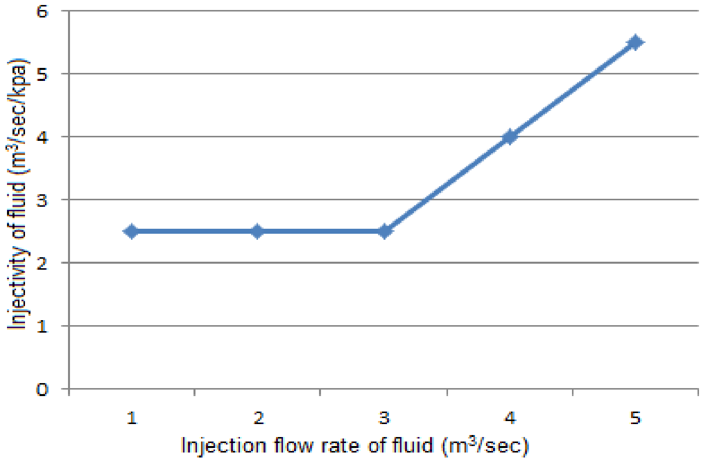

Figure 3: Example of injectivity index (I) vs injection flow rate (Q) for a step rate test with a Newtonian fluid

RESULTS

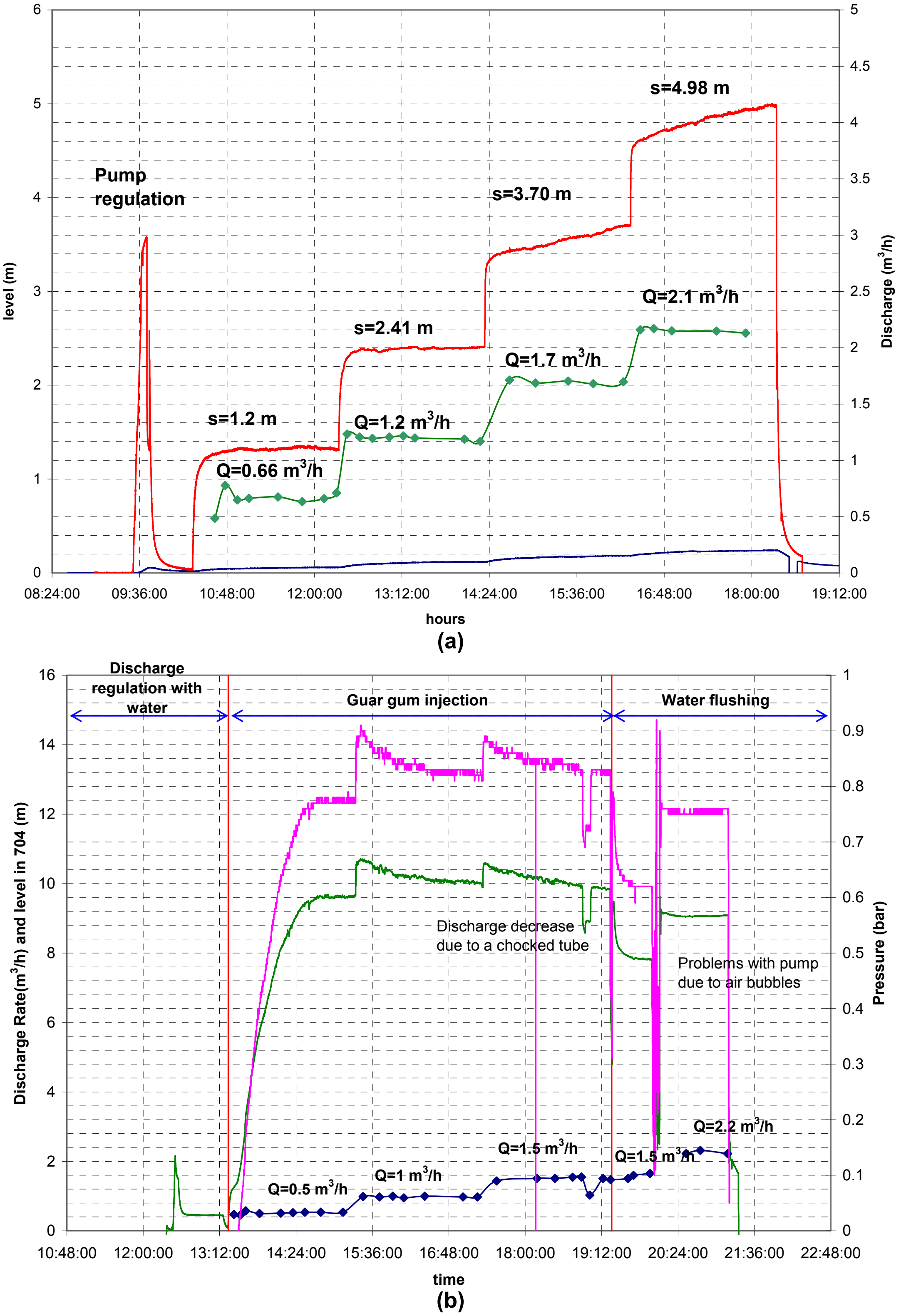

Figure 4: Discharge rate and water level during the water step test (a) and the guar gum step test (b)

The described methods for the estimation of the critical pressure were applied to two injection tests performed in an unconfined aquifer system. The first test was performed injecting water, while the second one was performed using a guar gum solution (2 g/l, viscosity curve reported in Figure 1). For the water test, fours step increases in

discharge rate were applied (discharge rate equal to 0.66, 1.2, 1.2, 2.15 m^3/h), while for the guar gum test three steps were performed (discharge rate equal to 0.5, 1 and 1.5 m^3/h). Each step lasted two hours. During the test, injection pressure and discharge rate values were monitored continuously. The experimental results for both tests are reported in Figure 4.
For the water injection test, the conventional p_w vs Q methodology provided the results reported in Figure 5.

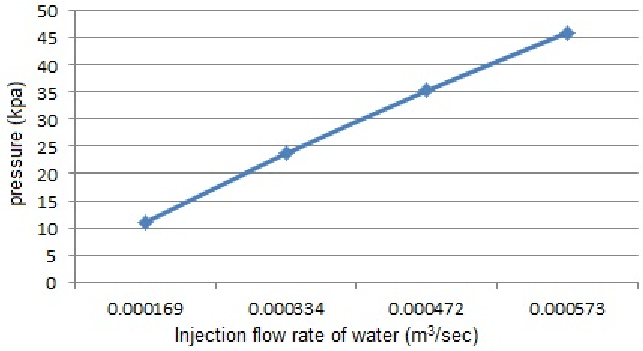

Figure 5: Steady state pressure p_w vs injection rate Q at the end of the water step injection test

During the water injection step rate test, there is a constant increase in the pressure with the increase in injection rate and no change occurred in the slope of the graph. This indicates that the critical pressure was not overcome during the test and the porous medium was not fractured. Conversely, during the guar gum injection step test, the first two steps show an increase in pressure with increasing $Q \cdot \mu$, while in the third step a decrease in pressure was observed (Figure 6). This is an indication, that fracturing occurred and the critical pressure was overcome in the last step of the test.
Similar results are obtained calculating the injectivity index. In case of the water injection test the injectivity index remains almost constant, which indicates that no fracturing occurred (Figure 7). In case of guar gum injection (Figure 8), at the beginning the injectivity index is constant in the first two steps, while it increases in the third one, which indicates that fracturing occurred and the critical pressure was overcome in the last step.

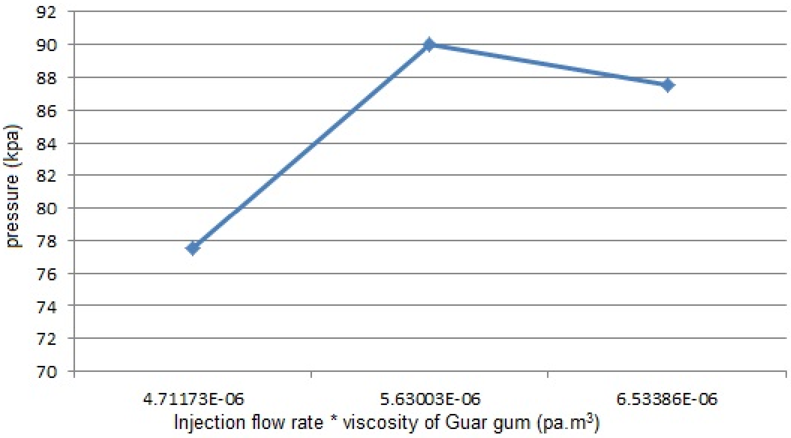

Figure 6: Pressure (p_w) vs injection rate×viscosity of guar gum ($Q \times \mu$) for the guar gum step injection test

CONCLUSIONS

In this work a method applied in petroleum engineering, based on step rate injection tests, for the determination of the critical pressure of a formation was applied to aquifer systems. The knowledge of the critical pressure is very important for the safe injection of reagents into aquifer systems. The method, developed for the analysis of step rate tests performed injecting Newtonian fluids (usually water) was modified for the interpretation of a step rate test performed injection a non Newtonian shear thinning fluid (a guar gum solution). The techniques developed in this paper have been successfully applied for the analysis of a field step rate injection test for guar gum in a shallow aquifer, indicating that the critical pressure of the system, above 90 kPa, is expected for a 2 g/l guar gum injection when applying a discharge rate higher 1 m^3/h and lower than 1.5 m^3/h.

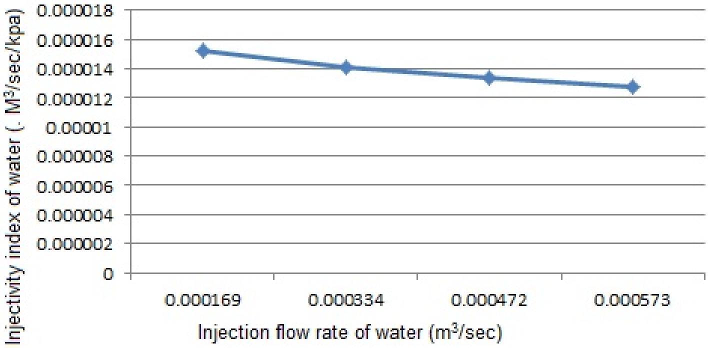

Figure 7: Injectivity index vs injection rate for water step injection test

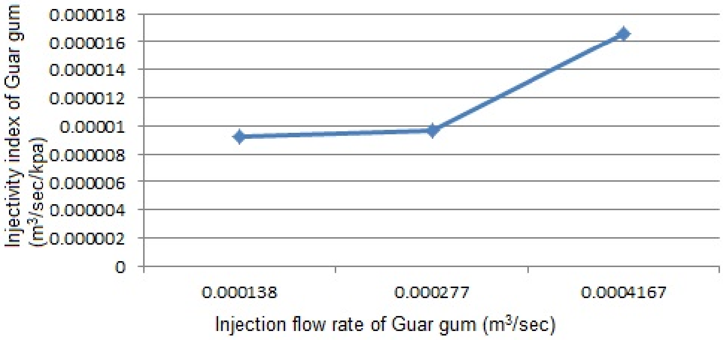

Figure 8: Injectivity index vs injection flow rate for guar gum step injection test

ACKNOWLEDGEMENTS

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Combining Bioaugmentation with In Situ Chemical Reduction (ISCR) for Remediation of Chlorinated Ethenes in Groundwater

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BACKGROUND/OBJECTIVES

The site is an operating manufacturing facility in New York USA, where historic operations have resulted in shallow groundwater being impacted by chlorinated volatile organic compounds (cVOCs). The main constituents of interest (COI) are PCE and cis-1,2 DCE that exceed the regulatory groundwater clean-up standards. The site geology comprises primarily of silty clay with intermittent layers of sand. The saturated zone impacts ranges between 1-4 m bgs.

APPROACH/ACTIVITIES

In situ chemical reduction (ISCR) is the combined effect of stimulated biological oxygen consumption (via "fermentation" of complex organic carbon sources), direct chemical reduction with reduced metals, and the corresponding enhanced decomposition reactions that are realized at the lowered redox (E_h) conditions. EHC® is a combination of controlled-release solid organic carbon and zero valent iron (ZVI) particles to yield a highly effective reductant for stimulating dechlorination of organic solvents present in groundwater, without accumulation of catabolic intermediates or aquifer acidification

A pilot test was conducted in February 2011 to demonstrate the site-specific efficacy of ISCR using EHC. Monitoring and sampling of groundwater within an EHC treatment zone and down-gradient thereof indicated significant reduction in the concentrations of target cVOCs within a period of three months. Full scale injections targeting the entire treatment area was implemented in July 2011, where a total of 3,700 kgs of EHC was injected over 24 injection points using direct push technology (DPT).

Given high historic concentration of DCE isomers and the lack of vinyl chloride (VC), naturally occurring microbial population was assumed to be catabolically limited. Hence, in theory the remedial process might benefit from the addition of inoculants with known abilities to rapidly biodegrade DCE and related compounds. Once favorable thermodynamic / redox conditions (low E_h, low DO) were attained following EHC addition, 12 L of *Dehalococcoides* (DHC) culture was added via DPT targeting a density of 5x10E6 cfu/ml DHC cells in groundwater within the treatment area.

RESULTS/LESSONS LEARNED

Monitoring and sampling of groundwater post full-scale EHC injection was conducted within the treatment zone and down gradient of the treatment zone over a period of nine months. Geochemical indicators such as ORP, total organic carbon, dissolved oxygen etc. were monitored along with COI concentrations to provide secondary evidence on the longevity of ISCR.

Remediation by Enhanced Reductive Dechlorination of a Chlorinated Solvent-Impacted, Strongly Aerobic Aquifer, France

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Key Words: Enhanced Reductive Dechlorination, ERD, Aerobic Aquifer, Chlorinated Solvents, PCE, TCE, Anaerobic Bioremediation, HRC®, 3DMe®, France, Full Scale

Objectives: Example of successful field-scale application of enhanced reductive dechlorination to remediate chlorinated solvent contamination in a naturally powerfully aerobic aquifer.

Innovative nature of proposed topic: Use of reagent-based treatment to create and maintain reducing conditions within a naturally aerobic aquifer without recourse to an on-going physical dosing system or engineering installations secures complete degradation of mixed chlorinated solvents through enhanced reductive dechlorination.

Enhanced Reductive Dechlorination (ERD), the destruction of chlorinated organic compounds through biostimulation of the indigenous microflora, is now a widely used and accepted remediation technology in many parts of the world. Extensive literature exists on the topic, especially concerning the biodegradation of chlorinated ethenes such as Tetrachloroethene (PCE), and Trichloroethene (TCE).

However, understandings vary as to under which conditions the technology can be effectively applied. Among these is the common assumption that ERD cannot be used in aquifers which are strongly aerobic under natural conditions and similarly aerobic prior to treatment.

Such naturally aerobic aquifers – these conditions often correlating with a high seepage velocity – characteristically do not to display evidence of natural attenuation indicators or parameters conducive to chlorinated solvent degradation such as presence of degradation daughter compounds, supportive geochemistry, or microbial indicators. Significantly, PCR tests can sometimes indicate that the required microbial groups (dehalorespirators) are not be sufficiently present. Often this is interpreted by remediation design engineers – quite understandably – as an indication that ERD is not feasible at that particular site.

Notwithstanding this, data from multiple sites displaying such conditions on which controlled-release electron donors (specifically Hydrogen Release Compound (HRC) and 3-D Microemulsion (3DMe) have been applied have shown that sustained reducing conditions conducive to microbial dehalorespiration can be created, and full contaminant bio-destruction can be successfully achieved, despite high seepage velocities and significant influx / recharge of competing electron acceptors into the treatment area. Sustained anaerobic / reducing conditions have been thus maintained over long periods of time (several years) by a single application event with the implication and indeed case evidence that ERD can be a cost-efficient, low-disturbance remediation technology on seemingly poorly conducive sites.

This paper succinctly reviews the above points and presents data from pilot and full-scale application of ERD through the use of controlled-release substrates on an active industrial site in the North-East France characterized by high seepage velocity (300 m/year), an extensive treatment area (20,000 m²) and notable through the presence of sensitive human and ecological receptors (site workers, down-gradient fishing lake) and on-going commercial activities throughout the impacted area (truck movements and general site activities). Key performance considerations from technical, commercial, regulatory and operational standpoints are discussed and the technology is critically evaluated.

It is anticipated that the discussion and case study will be of interest to site owners, regulators, consultants and remediation professionals alike.

Session 9
Nitrate & pesticide removal (in wetlands)

Oral presentations

Subsurface nitrate reduction in a reconstructed wetland takes place in a narrow zone beneath the peat

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The aim of our study was to determine the spatial distribution of potential nitrate reduction in a Danish reconstructed wetland. We installed screens in a 200-m transect spanning the riparian zone from Odense river to the adjacent fields at Brynemade, Denmark. The spatial distribution of nitrate, nitrite and dissolved organic carbon (DOC) was determined in water from the screens. Two intact soil cores (0-3 m) were collected from the denitrification zone. The cores were split in 10-cm slices for determination of nitrate reduction potential and for measurement of soil organic matter (SOM).

The potential for nitrate reduction decreased almost exponentially with depth in both cores. High potentials were found in the upper cores (0-99 cm) that also showed high concentrations of SOM in the form of peat. In this zone, the first-order rate constant (k) decreased with depth from a maximum of $6{,}8\cdot10^{-2}$ h^{-1} in the top to $1{,}3\cdot10^{-3}$ h^{-1} in the bottom, and with a mean of $1{,}2\cdot10^{-2}$ h^{-1}. The organic zone was succeeded by a 1-metre zone of lower and more variable nitrate reduction potentials with an overall mean of $k=1{,}5\cdot10^{-3}$ h^{-1}. Denitrification was detectable only in few samples from 200 cm and downwards with a mean of $k=1{,}3\cdot10^{-4}$ h^{-1}.

The spatial distribution of peat, DOC and nitrate suggest that nitrate and organic matter co-exist only to a very limited extend, and that denitrification takes place in a narrow zone beneath the peat where the DOC meets the nitrate. The limited spatial extend of nitrate reduction was verified by the distribution of the denitrification by-product nitrite, which closely mirrored the distribution of DOC. The high spatial heterogeneity does not correspond well with the general denitrification models (e.g. the Damköhler number approach), and should therefore be incorporated in denitrification simulations.

Long-term isoproturon and MCPA mineralization capacity in a recently restored wetland

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Diffuse pollution of surface waters by pesticides is difficult to handle. The recent trend of riparian wetland restoration however is considered as a promising technology for mitigation of diffuse pollution of surface waters by pesticides. Soil microbial communities that have been exposed to xenobiotics like pesticides have been shown to adapt in such a way that they can metabolize these compounds and mineralize them. In this study, we examined the potential of the microbial community of a recently (2009) restored wetland in Sint-Truiden, Belgium to mineralize the mobile pesticides 2-methyl-4-chlorophenoxyacetic acid (MCPA) and isoproturon (IPU) and to determine their long-term dynamics. We hypothesized that seasonal environmental disturbances such as freezing and drying can impact the pesticide degrading community and hence the kinetics of pesticide mineralization. Surficial soil samples (n = 30) were taken from the wetland during several sampling campaigns between August 2011 and May 2013 and were assessed for the mineralization of IPU and MCPA in the laboratory. Whilst mineralization of MCPA was fast in all samples (maximum rate ranging between 0.18 and 22.22 %/day and the mean and median were 8.33 and 7.27 %/day), the mineralization of IPU was much more heterogeneous within the wetland (maximum rate ranged between 0.00 and 20.26 %/day and the mean and median were 1.18 and 0.54 %/day). We found a significant difference between the medians of the maximum rate, the lag time and the extent of mineralization of samples taken at different time points for both IPU and MCPA mineralization. The lag times of mineralization were clearly shorter in May and August compared to the other months what might reflect differences in fitness of the pesticide degrading populations or in their density between colder and warmer months.

This research was funded by IWT (Flemish Agency for Innovation through Science and Technology) project 093003 and the EU project AQUAREHAB (EU grant n° 226565).

Subsurface hydrological flow paths and nitrate removal in flooded and non-flooded riparian zones: Conceptual models

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A numerical study has been undertaken to investigate the controlling hydrological and hydrogeological characteristics on subsurface flow processes and nitrate removal in flooded and non-flooded riparian zones. The conceptual models for the riparian zones are patterned after different Danish riparian zones. The study extends existing conceptual models by also including effects of flooding. Different system properties (e.g. peat layer and aquifer thickness, contrasts in hydraulic characteristics between peat and sand, flow boundaries, i.e. stream, seepage zones, floods, and connectivity with the upland) are evaluated in terms of how they spatially and temporally change subsurface flow paths and the effects they have on residence times and nitrate removal. The use of simpler (analytical) models – and when these simpler models are applicable – is evaluated, thus highlighting some of the key characteristics and parameters controlling nitrate removal in riparian zones.

Poster Presentations

Modeling of reactive behavior of pesticides including biodegradation in surficial wetland sediments

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Pesticides can enter wetlands through run-off, drainage or flooding where they can be degraded by micro-organisms. However, not much is known about the biodegradation of pesticides in wetlands. This study examines the reactive behavior of the mobile pesticides 2-methyl-4-chlorophenoxyacetic acid (MCPA) and isoproturon (IPU) in wetland surficial sediments. The surficial compartment of a wetland is a unique microbial niche since wetland sediments are often characterized by a high organic matter content and hence by a high sorption capacity and limited oxygen penetration in the sediment. Since pesticide degradation especially occurs under aerobic conditions this might affect pesticide reactive behavior in wetlands. Experiments were performed in dedicated laboratory microcosms that mimicked a wetland. We observed the mineralization of radiolabelled MCPA and IPU. The production rate of $^{14}CO_2$ from MCPA-IPU was 0.80-0.41 %/day at its maximum but decreased to a steady 0.09-0.04 %/day after 180 days of incubation. Based on these observations, we hypothesized that at the long term the rate limiting factor was not biodegradation but rather diffusion and sorption within the sediment. In fact, pesticides that bypass the aerobic surficial layer of the sediment will diffuse in and sorb to the sediment. However, depletion of the compound in the top layer due to degradation will drive the diffusion of the pesticide back out of the sediment. Based on this concept, we modeled the reactive behavior of these pesticides using HYDRUS-1D that provided for growth and decay of the pesticide degrading biomass. Experiments are currently going on to calibrate and validate the model by following MCPA and IPU degradation in columns packed with a layer of quartz sand inundated by a stagnant surface water, and inoculated with either an MCPA degrader or an IPU degrader.

This research was funded by IWT (Flemish Agency for Innovation through Science and Technology) project 093003 and the EU project AQUAREHAB (EU grant n° 226565).

Delineating Groundwater-Surface Water Interaction Using Temperature-Time Series Analysis Methods

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ABSTRACT: Groundwater-surface water interactions can play a crucial role in river-, riparian and wetland management. Their delineation and quantification at various spatial and temporal scales has become an important aspect in the study of contaminant transport and attenuation processes at the groundwater-surface water interface. One of the main parameters of interest is the groundwater-surface water exchange flux, which provides indications regarding stream-aquifer connectivity, the local flow regime as well as hydrogeological properties of the streambed. One of the methods to assess vertical exchange flux is through the analysis of temperature time-series. In this paper we delineate vertical exchange flux from temperature-time series collected at a Belgian River by comparing established numerical and analytical techniques with a novel approach. Results indicate a spatial variability of vertical fluxes over two orders of magnitude at the site.

INTRODUCTION

Over the last two decades the study of groundwater-surface water interaction has become increasingly popular. One major interest has been the delineation and quantification of exchange flux between aquifers and rivers. This information can be used to investigate the hyporheic flow regime (Buss et al., 2009) or assess the behavior of contaminant plumes within the hyporheic zone (Conant et al., 2004), i.e. the saturated transition zone between surface water and groundwater compartments that develops its specific physical and biogeochemical characteristics from active mixing of waters from both compartments (Krause et al., 2009).

Magnitude and direction of exchange flow are influenced by a variety of factors such as river-aquifer connectivity, i.e. gaining, losing or disconnected (Woessner, 2000), streambed morphology, stream channel planform and geometry, hydraulic properties of aquifer and streambed sediments, climatic conditions as well as anthropogenic factors such as near stream pumping or land use. These factors can interact on three distinct scales, the (i) the sediment scale, (ii) the reach scale and (iii) the catchment scale and are able to create a heterogeneous subsurface causing temporal and spatial variability in exchange flows.

Total exchange flow can commonly be divided into hyporheic exchange flow (HEF), i.e. stream water entering the hyporheic zone somewhere upstream and leaving it at some point downstream, and groundwater-surface water exchange flow, i.e. flow across the hyporheic zone (Hannah et al., 2009). In general, a separation of both flow types is difficult as this would usually require a hydraulic characterization of the subsurface and subsequent modeling so detailed that it is beyond the scope of most scientific studies. So far most studies consider vertical exchange flux (VEF) as a good substitute for groundwater-surface water exchange flux, especially in gaining/losing rivers with low horizontal intrabed velocities.

Exchange fluxes can be quantified in the field directly by seepage meter measurements (Rosenberry and LaBaugh, 2008) or indirectly by applying heat as a tracer (Anderson, 2005) and measuring temperatures within the riverbed (Essaid et al., 2008). In this study we use heat as a tracer to quantify the VEF at the Slootbeek, a small Belgian river. To estimate fluxes we make use of a newly developed method called LPML used to extract the frequency information contained in collected temperature-time series data. For one location we compare results obtained with the LPML to those obtained with established models as well as with seepage meter measurements. Afterwards we look at the spatial variability in vertical exchange flux and discuss future research possibilities.

METHODOLOGY

Study Site

Fieldwork was carried out at a small stretch of the Slootbeek, a category three lowland river and tributary to the Aa in Northern Flanders, Belgium, which is part of the Nete catchment (Figure 1). At the study site, the Slootbeek riverbed comprised a mixture of gravel and sand near locations ML169 and ML193, while at the other locations indicated in Figure 1 a larger part of the riverbed was formed by organic matter. Average channel width was 3.20 m and average flow velocity in the middle of the river amounted to 0.2 ms^{-1}. River stage ranged during the observation period from 0.15 m to 0.95 m due to climate influences as well as land use and irrigation practices on the nearby fields. Average discharge could roughly be estimated as 0.4 m^3s^{-1}. The local aquifer is described by Anibas et al. (2011) as consisting of heterogeneous sand layers with local clay inclusions. The lower boundary is formed by the Boom clay aquitard at about 80 m below surface where the Slootbeek flows into the Aa River. Aquifer hydraulic conductivities vary locally but average at 10 md^{-1}.

Field Work

Seven multilevel temperature measuring devices (sticks) from UIT, Germany, were installed at locations indicated in Figure 1 These sticks consisted of polyoxymethylene, in which several stainless steel temperature sensors were embedded. In our study we used a sensor configuration according to Figure 2C to record temperatures in 10 minute intervals over several months during 2012. River stage was monitored with a cera mini diver from Schlumberger. Additionally, two piezometers were installed into the riverbed and equipped with mini divers to record temperatures and pressures as shown in Figure 2. Groundwater temperature and level (around 1 m below surface) were monitored at the right riverbank. Vertical fluxes were also directly measured by means of three seepage meters (Figure 1 and Figure 2B) that were self-made based on discussions in Rosenberry (2008). Seepage meter measurements took place over several days.

Modeling

The general heat transport equation is often solved together with fluid flow (and contaminant transport) using complex physics-based coupled numerical models such as Hydrogeosphere (Therrien et al., 2010). These models can optimize hydraulic and thermal properties of the subsurface and represent complex fluid flow and heat transport patterns. A much simpler method is the quantification of the vertical exchange flux component only, assuming simultaneous vertical 1D non-isothermal advective-dispersive heat transport through a homogeneous saturated medium (Stallman, 1965), which can be represented by the following partial differential equation (PDE):

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial z^2} - q_z\frac{\rho_w c_w}{\rho c}\frac{\partial T}{\partial z} \tag{1}$$

T [Θ] represents the temperature of the subsurface dependent on position z and varying over time t [T], q_z [LT^{-1}] is the specific discharge or flux along the z-direction, c_w and c [$L^2T^{-2}\Theta^{-1}$] are the specific heat of the fluid and the fluid-rock matrix, respectively, while ρ and ρ_w [ML^{-3}] represent the density of the respective fluid-rock matrix and the fluid. Whereas variations in ρ_w and c_w in most hydrological settings can be considered negligible, ρc as the bulk volumetric heat capacity of the fluid-rock matrix strongly depends on sediment characteristics. D [L^2T^{-1}] denotes the effective thermal diffusivity (Rau et al., 2012b) and is in most literature sources described by

$$D = \frac{\kappa}{\rho c} + \psi|q_z| \tag{2}$$

with κ [$M^1L^1T^{-3}\Theta^{-1}$] as the bulk thermal conductivity representing the combined thermal conductivity of fluid and solid. The parameter ψ [L] is the thermal dispersivity and its importance for the determination of D is subject to ongoing scientific debate (see e.g. Anderson, 2005; Rau et al., 2012a). Its influence definitely increases with increasing exchange fluxes. In this study we considered it negligible. Analytical solutions to (1) have been developed e.g. in Schmidt et al. (2007) for thermal steady-state conditions as well as in Hatch et al.(2006), Keery et al. (2007) or Onderka et al. (2013) for transient conditions. Some of these have been integrated into automated software routines such as Ex-Stream (Swanson and Cardenas, 2011) or VFLUX (Gordon et al., 2012).

In our study we modeled temperature measurements taken over a 90-day period (17 February – 16 May 2012) using the frequency response contained in the temperature data considering the sensor on top of the riverbed (Figure 2C red circle) as the input signal that is (non)-linearly transported through the porous medium. For that we use the LPML, a newly developed method (Vandersteen et al., in preparation) that first determines the frequency responses using a local polynomial method, followed by a dedicate Maximum Likelihood estimator. Equation 1 can be re-written as the following PDE where the different parameters α, β and γ are constant.

$$\frac{\partial^2 T}{\partial z^2} + \alpha \frac{\partial T}{\partial z} + \beta T + \gamma \frac{\partial T}{\partial t} = 0 \tag{3}$$

The response of the system to a steady-state periodic excitation $T\,(0,t) = \Re(e^{j\omega t})$ can be represented as $T(z,t) = \Re(G(z,\omega)e^{j\omega t})$ with $G(z,\omega)$ as the frequency response from the input at the upper boundary. This frequency response function is extracted applying a local polynomial method (Pintelon et al., 2010) that uses the randomness of the input data and the spectral smoothness of the transient part $Tr(\omega)$ to separate $G(\omega)$, $Tr(\omega)$and the additive circular-complex normal noise. Applying a local polynomial method provides us with $G(\omega)$ and its uncertainty $\sigma_G^2(\omega)$, which allows for the development of an output error model that is equivalent to a Maximum-Likelihood estimator. Maximum Likelihood estimates are be obtained using nonlinear least squares minimization techniques such as Gauss-Newton or Levenberg-Marquardt optimization methods (Fletcher, 1980). As such, parameters α, β and γ in (3) can be optimized and their uncertainties can be determined. Combining equations 1-3, vertical exchange flux and thermal conductivity can then be deduced using $\hat{q}_z = \frac{\hat{\alpha}}{\hat{\gamma}} \frac{\rho c}{\rho_w c_w}$ (4) and $\hat{\kappa} \leftrightarrow -\frac{c\rho}{\hat{\gamma}}$ (5).

The LPML was implemented in MATLAB 2011b® (The MathWorks, Inc., Natick, Massachusetts, USA) and its applicability to solve (1) and provide meaningful flux estimates was tested on data from all seven locations shown in Figure 1. For location ML169 we also compared fluxes obtained by using the LPML to those obtained with VFLUX applying the method after Keery et al. (2007) and using only information from sensors two (on top of riverbed) and eight (lowest), as the latter method cannot incorporate information from more sensors simultaneously. Also, LPML results were compared to estimates obtained with the modeling software STRIVE (Anibas et al., 2009; Soetaert et al., 2002) that contains both a numerical solver after Lapham (1989) and an analytical solver after Stallman (1965).

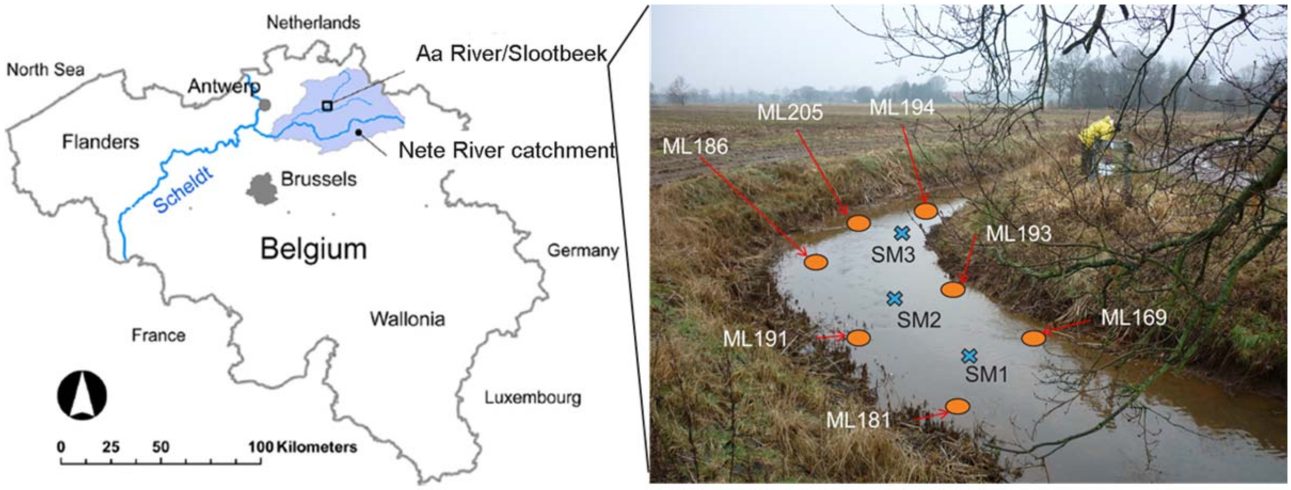

Figure 1: Slootbeek field site near Aa River. Right side roughly shows locations of temperature sensors (ML) and seepage meters (SM). At locations SM1 and SM3 piezometers as shown in Figure 2B were also installed. Left side was adapted after Anibas et al., 2011.

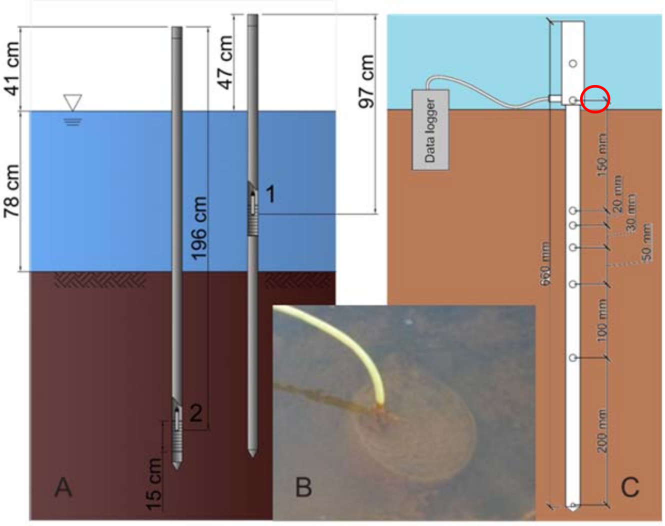

Figure 2A: Piezometer installed at location SM1. Location SM3 was equipped with a similar one. 2B: Picture of one of the self-made seepage meters used. 2C: Sensor configuration used for this study. Red circle indicates reference sensor on top of riverbed.

RESULTS

Riverbed temperatures ranged from 6.4°C to 15.4°C over the 90-day period and all ML measurement locations. Average temperatures at ML194 and ML205 are about 1°C above those of other locations. For all locations time-series profiles are similar to that of ML169 (Figure 3), with highly fluctuating surface water temperatures and decreasing temperature fluctuations with increasing riverbed depth. Using the ML169 temperature time-series data we calculated vertical exchange fluxes with the LPML and compared them to estimates obtained with STRIVE and VFLUX (Table 1). When using the information of all sensors simultaneously results obtained with the LPML (-52.3 mmd-1)are of the same order of magnitude as those obtained with STRIVE. However, if only information from sensors two and eight is used the flux estimated with LPML is reduced to only -2.9 mmd^{-1} while VFLUX even provides a small positive flux indicating losing conditions.

Additionally, the LPML was used to estimate fluxes for all other ML locations and results were compared to direct flux measurements by seepage meters (Table 2). As can be seen, fluxes estimated with the LPML vary from -19.4 mmd^{-1} for location ML193 to -648.5 mmd^{-1} for location ML186. For all flux estimations in this study thermal conductivity was fixed to κ = 1.8 Wm^{-1}K^{-1} and volumetric heat capacities were chosen as ρc = 2.90 x 10^{6} Jm^{-3}K^{-1} and $\rho_w c_w$ = 4.2 x 10^{6} Jm^{-3}K^{-1}. Results of seepage meter measurements also vary by one order of magnitude with location SM1 showing the smallest fluxes and similar values as obtained with the LPML at nearby locations ML 169, ML181 and ML193. In general, flux estimates from seepage meters and those applying the LPML are in good agreement. LPML results also indicate less groundwater inflow into the river at its right bank (ML169, ML193, ML194) than at its left bank (ML181, ML186, ML191, ML205).

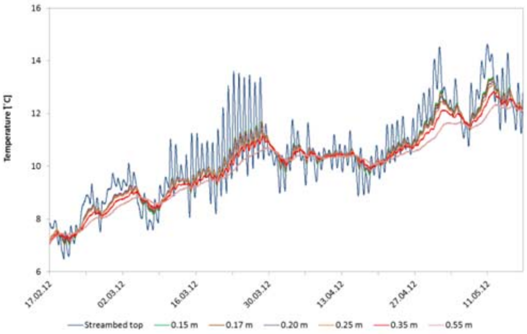

Figure 3: Temperature time series for location ML169 at various depths.

Table 1: Parameter comparison for Slootbeek using LPML and STRIVE

Parameter	Unit	STRIVE (numerical)	STRIVE (analytical)	VFLUX[b]	LPML	LPML σ
κ^a	$Wm^{-1}K^{-1}$	1.8	1.8	1.8	1.8	-
$q_z^{\mathbf{a}}$	mmd^{-1}	-23.3	-35.9	17.8	-52.3/-2.9	0.86

[a] κ was fixed to 1.8 $Wm^{-1}K^{-1}$ while q_z was optimized. Negative sign = flow from aquifer to river

[b] Solution after Keery et al., 2007 was used

Table 2: Vertical exchange flux calculated for several locations at Slootbeek

Location	q_z^a mm d^{-1}	Method
169	-52.3	LPML
181	-174.4	LPML
186	-648.3	LPML
191	-164.6	LPML
193	-19.3	LPML
194	-24.1	LPML
205	-276.5	LPML
SM1	-31.4	Direct
SM2	-378.5	Direct
SM3	-656.5	Direct

[a] κ was fixed to 1.8 $Wm^{-1}K^{-1}$ while q_z was optimized

DISCUSSION

Measured riverbed temperatures at the Slootbeek vary by location and depth. In general, advective and diffusive processes act simultaneously, causing differences in signal penetration depth depending on the upper boundary temperature at the riverbed top. Although measurements were taken during winter and early spring time with no in-channel vegetation and little plant coverage along the river bank, thus avoiding local shade effects and lower T at the riverbed top, average temperatures vary by almost 2°C. These variations could have been caused by locally increased amounts of upwelling groundwater with warmer temperature or by heterogeneous riverbed sediments (sand and gravel, sandy loam, varying organic matter content) and riverbed morphology that bring about variations in heat transport parameters and determine sediment scale water movement (hydraulic conductivity, flow velocity).

Considering temperature data of the entire 90-day period, averaged exchange fluxes estimated with the LPML indicate a gaining stream, as do seepage meter measurements where seepage was collected in plastic bags over 20-30 min intervals and several days. However, additional investigations on the same data shown in Vandersteen et al. (in preparation) indicate alternating gaining and losing periods depending on the location and length of the data set used.

Furthermore, fluxes estimated with the LPML in this study are limited in the sense that they were obtained while thermal conductivity was constrained to κ = 1.8 $Wm^{-1}K^{-1}$. This value is generally representative for sandy soils (Stonestrom and Constantz, 2003) but especially at locations near SM3 a higher organic matter content was encountered that due to its often high porosity shows a higher volumetric heat capacity and thus a lower thermal conductivity. In Vandersteen et al. (in preparation) this issue is further addressed and the LPML is applied to estimate vertical exchange flux and thermal conductivity simultaneously. In general, flux estimates obtained with the LPML coincide well with estimates obtained by other models. However, it has to be pointed out that flux estimates are dependent on the number of sensors used. This fact could lead to contradicting results as is the case with the LPML and VFLUX only using information from two sensors that alternatively show gaining or losing conditions albeit magnitudes of fluxes are close to zero. A larger number of sensors seems to improve estimates as uncertainties are reduced and flux results are closer to those obtained with seepage meters. Compared to transient methods that use only data with the frequency of one day and apply the amplitude ratios and phase shifts between two temperature sensors (Hatch et al., 2006; Keery et al., 2007) the LPML has the following advantages:

(i) It can make use of data from multiple frequencies and multiple sensors simultaneously.
(ii) The input signal can be non-linear or non-sinusoidal
(iii) The method provides uncertainties on the model as well as on the optimized parameters, using statistically-based Maximum-Likelihood modeling techniques without applying elaborate post-processing procedures (Shanafield et al., 2011).
(iv) LPML allows for a simultaneous optimization of fluxes and thermal conductivity under certain cases as discussed in Vandersteen et al. (in preparation).
(v) Computational efforts are minimal and the method is easy to use.

CONCLUSIONS AND FUTURE RESEARCH

In this work we calculated vertical exchange fluxes between a small reach of the Slootbeek and its connected aquifer using temperature time series using LPML. This method is a novel approach that makes use of the frequency response of the entire system to a known (non)-linear input signal at the riverbed top using a local polynomial functional model and a maximum likelihood estimator. For location ML169 fluxes estimates obtained with the LPML were compared to those obtained by other models and showed a good agreement. Estimates at six additional locations (Figure 1) show a spatial variability in fluxes ranging over two orders of magnitude on a scale of less than 50 m.

Future research will focus on estimating fluxes over different volumes (e.g. between sensors 1 and 2 or 1 and 3, etc.) at each location by assigning upper and lower boundary conditions. Additional temperature data can also shed more light on the temporal variability of fluxes in winter/spring and spring/summer periods.

ACKNOWLEDGEMENTS

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Bentazone mineralization in buffer strip soils adjacent to agricultural soils

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Bentazone is a widely used herbicide that however causes environmental problems. Indeed, it is often found at concentrations exceeding the drinking water limit in groundwater and surface water due to diffuse pollution from agricultural soil. This is explained by its low retardation in soil which is related to its low sorption capacity and high recalcitrance. Interestingly, bentazone shows a low DT_{50} in soil while its DT_{50} in water is high. Therefore, the impact of moisture content on bentazone mineralization was examined in soil from several grassed buffer strips adjacent to bentazone treated agricultural fields in Belgium. This was done by measuring the production of $^{14}CO_2$ from both ring labeled and side chain labeled bentazone in soil microcosms. A decreasing first order mineralization rate constant with increasing moisture content was observed for all soils. Mineralization extent with both ring labeled and side chain labeled bentazone reached up to 30%. However, at the long term, soils with the highest moisture content showed the highest mineralization extent. Fumigation and subsequent incubation of the soil did not result in increased $^{14}CO_2$ production suggesting that bentazone was not incorporated in microbial biomass during mineralization. Wet chemical oxidation of the soil showed that up to 30 % of the originally added tracer was bound to the soil as non-extractable residues. Our data show that bentazone degradation with production of CO_2 from the compound is possible in buffer strips but that this activity does not involve microbial growth but rather leads to degradation products that strongly bind to the soil.

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IN Situ Chemical Reduction (ISCR) for Remediation of Soil Containing Chlorinated Pesticides and Herbicides

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Introduction. A family of *in situ* chemical reduction (ISCR) products are available (i.e., soil amendments) for treatment of soils, sediments and other solid wastes contaminated with halogenated organic compounds. When the contaminants of interest are organochlorine pesticides (OCPs) or herbicides, the keys to this remedial approach are the composition of the soil amendment and application of repeated and sequential anoxic, then oxic, conditions to the contaminated matrix. The proprietary products are composed of plant fiber-based organic material and micro-scale elemental iron, which may be supplemented with sulfate in the form of alkaline earth salts.

Approach. Treatment proceeds *via* reductive dechlorination of the pesticides/herbicides followed by aerobic biodegradation of the partially or fully dechlorinated breakdown products. The soil amendment is typically applied at dosages of between 0.4% and 4% w/w and therefore causes very little, if any, increase in soil volume following treatment. Over the last 15 years, the technology has been used successfully for *in situ* and *ex situ* treatment of soils contaminated with a range of OCPs, including Chlordane, Lindane, DDT, Toxaphene, 2,4-D, 2,4,5-T, Atrazine, Dieldrin and Metolachlor at sites in North America, South America, Australasia and Europe.

Results. This presentation will include an overview of chemistry involved in OCP degradation using the ISCR products, along with case studies from several completed applications in the United States, Canada, and Europe, and provide a cost analysis.

Special session AQUAREHAB summaries

Poster Presentations

Development of Activated Riparian Zones for mitigating pesticides and nitrate diffuse pollution into surface water – AQUAREHAB WP1

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ABSTRACT: The paper summarizes the aims and main outcomes of the AQUAREHAB part that focussed on activated riparian zones to mitigate pesticides and nitrate diffuse pollution into surface water. The study comprises field work at two wetlands, as well as laboratory studies to derive degradation potentials and dynamics of the degradation process in function of seasonal chances.

INTRODUCTION

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 pesticide and nitrate diffuse pollution into surface water and how this could be activated and optimized. The processes contributing to nitrate and pesticide removal in wetlands were studied at the field and at lab scale., and the collected data were subsequently used for modelling the fate of nitrate 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).

Research work was performed by 5 institutes. The Geological Survey of Denmark and Greenland, Denmark (GEUS) and the University of Copenhagen, Denmark (UCPH) carryied out the hydrological and geophysical characterization as well as the field-monitoring of the selected field study site in the Odense River Basin. The Environmental Institute, Slovak Republic (EI) was surveying the ecological status of the river basin as a response to wetland restoration. The University of Leuven, Belgium (KU Leuven) and the CTM Centre Tecnologic, Spain (CTM) focused on the understanding of the processes involved in the removal of pesticides and nitrates in wetlands and the effect of season-bound changes on wetland pollutant removal activity, respectively, through dedicated lab work. UCPH was responsible for developing models which describe and predict the fate of nitrate and pesticides in wetlands using the selected field sites as model systems.

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 1). 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 compose 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 (i) the existence of a stable nitrate plume at the upstream locations near the agricultural field and of an aerobic-denitrification-iron oxidation zonation as the ground water flows to the river, and (ii) the absence of detectable pesticide concentrations. In contrast, the redox zonation at Skallebanke was very heterogenous with patches of oxygenated water with high nitrate concentrations along the transects. Also at Skallebanke, no pesticides were detected in the groundwater.

“Brynemade” site

“Skallebanke” site

Figure 1: Wetland field selected as study area within AQUAREHAB.

Information was obtained on pesticide biodegradation capacity and denitrification capacity via labscale 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 nitrate 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 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 (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 nitrate removal.

Site conceptual model

Based on all measurements, a hydrogeological model of the Brynemade wetland site could be proposed (Figure 2). 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.

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 nitrate reactive transport at the “Brynemade” site based on literature data regarding denitrification rates. The model was calibrated to the groundwater nitrate concentrations observed in the field. The model shows that the nitrate plume moves through the aerobic zone and that high denitrification rates in the anaerobic zone, ensure rapid nitrate removal.

The model can help to understand the fate of pesticides after ending up in a wetland by erosion, drainage or run-off.

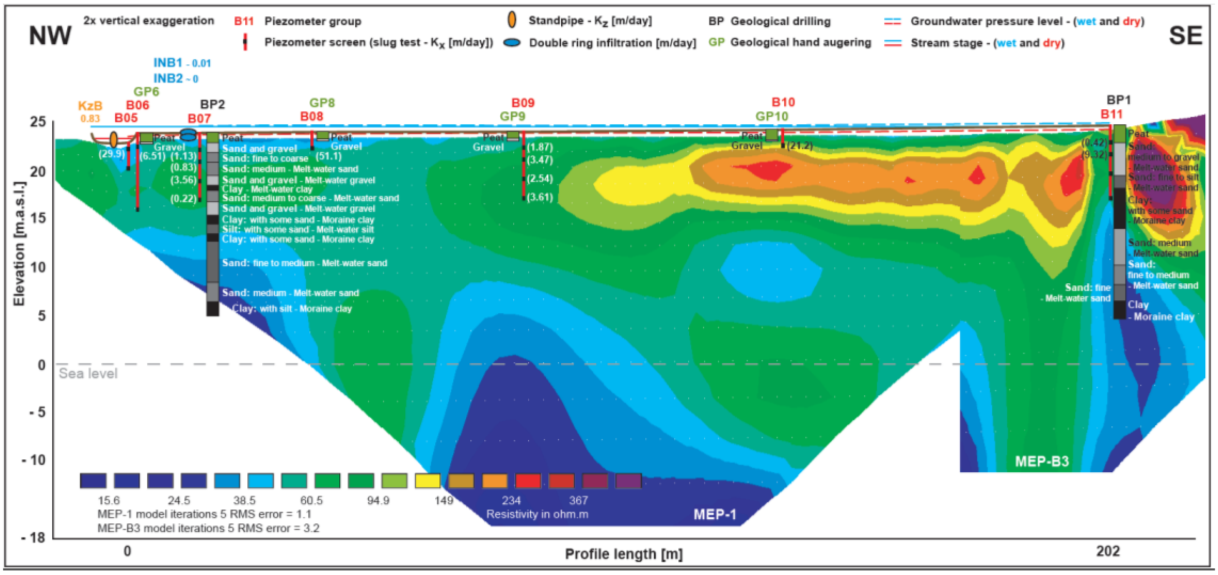

Figure 2: Hydrogeological model of the Brynemade wetland site. The main profile (B05-B11) 2x vertical exaggeration is shown. The profile shows inversion results on two performed MEP profiles with electrode spacing of 3 m, resistivity values are in ohm meters. Two deep geological wells with geology based on sample description for every meter (BP). Color scheme indicate apparent color and assumed hydraulic conductivity (Higher K-value with lighter color). Installed piezometers in groups of 1-4 with slug test results shown in brackets. Result 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).

Ecological status

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

PESTICIDE 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. Lab microcosm experiments showed the capacity to degrade/mineralize the pesticides isoproturon (IPU) and MCPA in the above surface compartment of a wetland (Figure 3). Based on the observed mineralization kinetics, the development of a conceptual model that describes the reactive transport of pesticides in the stagnant above surface layers of a wetland was initiated. The model can help us to understand the fate of pesticides after ending up in a wetland by erosion, drainage or run-off. Furthermore, indications for effects of seasonal disturbances on pesticide degradation were obtained but the experimental design needs to be improved to discriminate between 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.

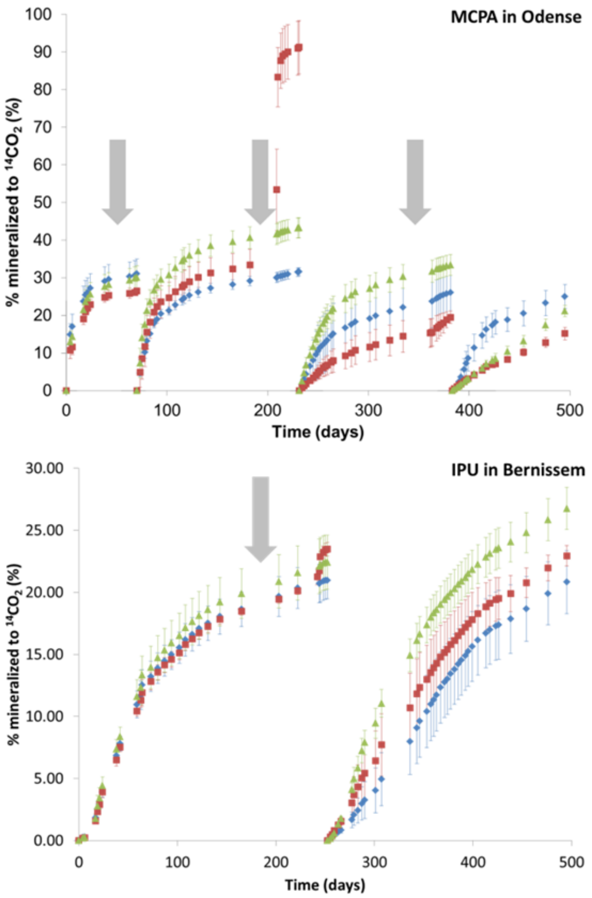

Figure 3: Cumulative mineralization of MCPA (left) and IPU (right) as a response to lab controlled disturbances. Disturbances (freezing and drying) are indicated by the vertical arrows. At the moments of spiking the microcosms with ^{14}C-herbicides, the cumulative mineralization curves were set to zero. The data shown are average from triplicate microcosms. Setups: drying (◆), freezing (■) and control (▲), with the error bars indicating the standard deviation.

NITRATE 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..

Surperficial 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 4). Results showed similar trend with elimination of more than 90% after 3 days of spiking.

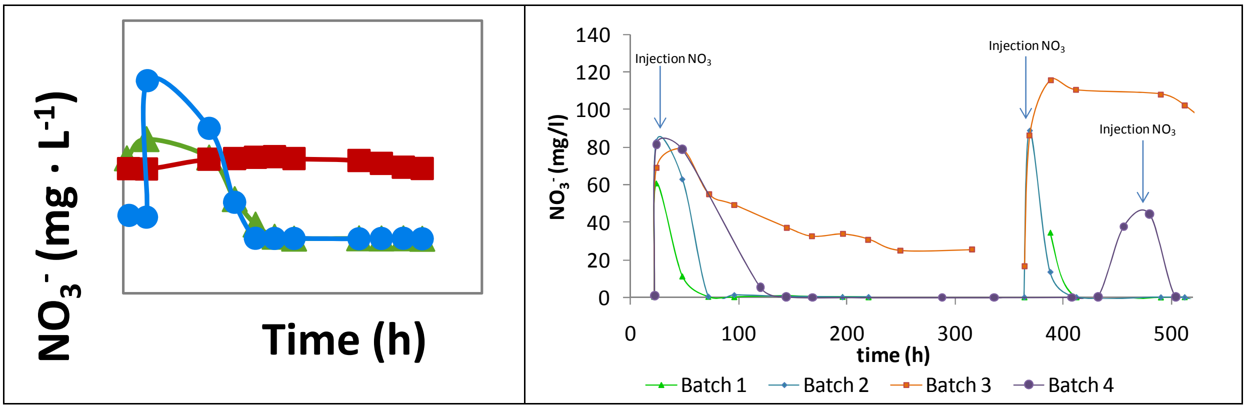

Figure 4: Denitrification batch tests with superficial soil from Brynemade (left) and Flix (right) showing the evolution of nitrate spiked in a stirred mixture of soil and water. Dead control are indicated by using squares (■)

Next step was a continuous wetland microcosm experiment were nitrate solution was run continuously in a sand bed that has the Flix peat soil in the upper part irrigated with water (Figure 5)

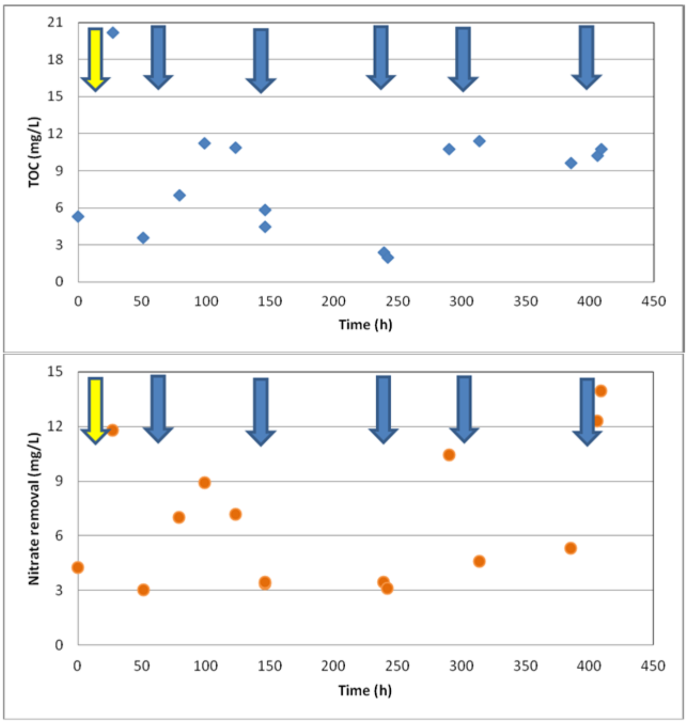

Figure 5: Continuous denitrification tests in sand bed with superficial Flix soil showing the evolution of DOC (mg C/l) and nitrate removal. Yellow and blue arrows indicate the time when peat soil was irrigated

Results shown a correlation between the removal of nitrate 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, 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 could 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 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 nitrate and nitrite will be eliminated from the groundwater. Based on the results, a concept (based on a combination of dedicated soil layers) was proposed for activation of riparian zones in order to allow efficient subsurface denitrification.

CONCLUSIONS

The removal of nitrate form wetland subsurface was studied at different wetland field sites by means of two complementary strategies. First, a reactive transport model succesfully described the behaviour of a nitrate plume in one wetland, taking into account denitrification rates and soil geophysical characteristics. Second, denitrification was studied in laboratory microcosms, clearly showing the role of the quality of DOC in the process. The mineralization of pesticides was shown to be influenced by the availability of oxygen, while seasonal changes did not affect the process to a large extent.

ACKNOWLEDGEMENTS

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Tailored carrier/bacteria technology for rehabilitation of areas with pesticide-containing pollution – AQUAREHAB WP2

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INTRODUCTION

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 1).

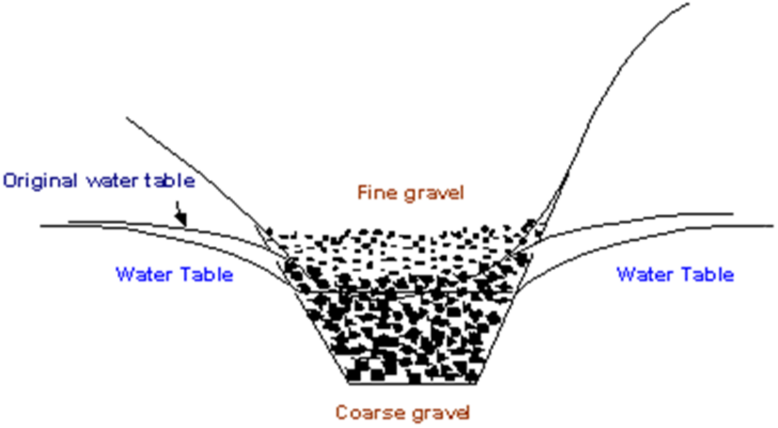

Figure 1: Cross-section of a drain with coarse carrier material, on which pollutant-degrading bacteria can form a biofilm that will degrade pollutants (pesticides) in the passing groundwater.

The research was carried out in three stages: (1) selecting the bacteria-carrier combination, (2) running lab-scale column experiments and (3) performing field-scale experiments.

SELECTION OF BACTERIA-CARRIER COMBINATIONS

We tested different bacterial strains for their interactions with both artificial and natural carrier material. 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), gray 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), gray 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 (mineral vs. organic, for example; Figure 2).

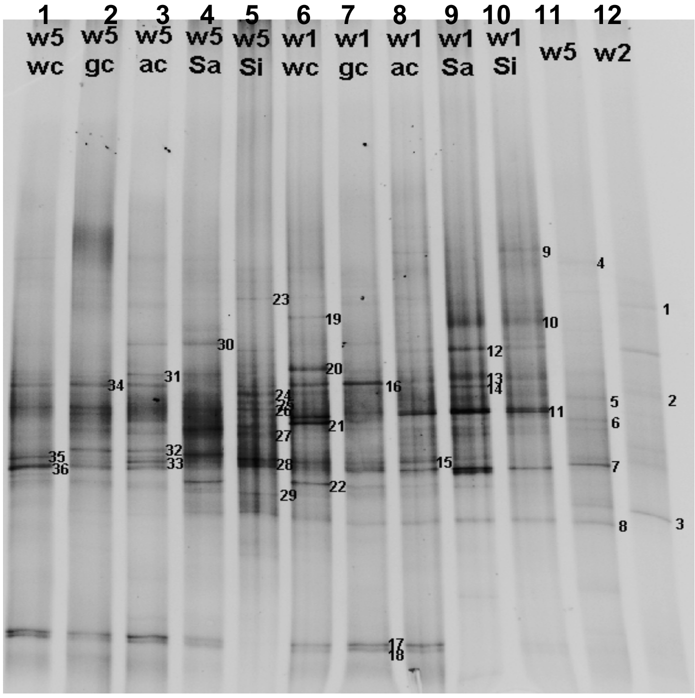

Figure 2: Photograph of the DGGE gel of 16SrRNA gene fragments extracted from the different incubated carriers' bags and the GR extracted from the site drainage channels. First row: lane number; second row: drain location; and third row: description of the carriers. Lanes 11 and 12 are of GR excavated from different locations along the drainage channels.

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 3).

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 (Figure 4). Promising bacteria-carrier combination that were identified comprise gravel and the resin XAD-7HP.

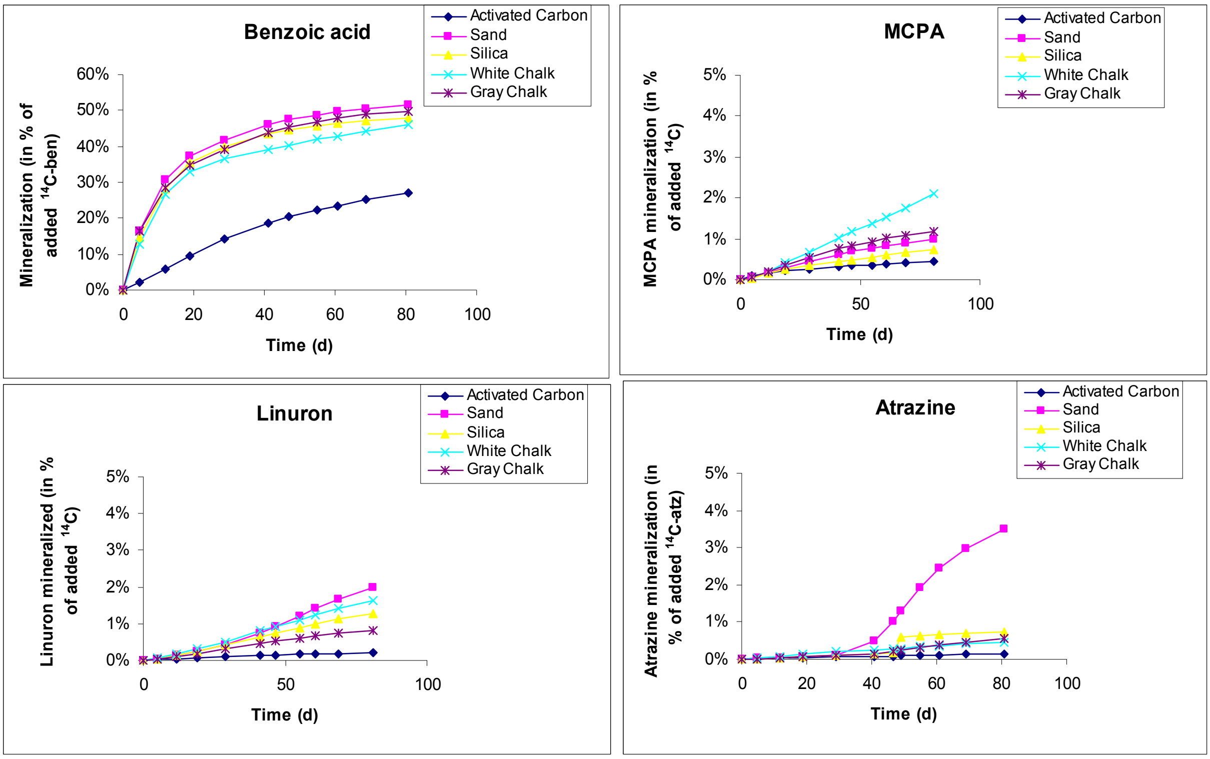

Figure 3: Mineralization of benzoic acid and selected pesticides by carrier incubated within the drained water in situ.

COLUMN EXPERIMENTS

Sand column experiments were set-up with different carrier materials (Figure 4). 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 pesticide 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 pesticide for a longer period of time. Switching back to the medium with the pesticide revealed that the columns with a XAD-7HP / sand ratio of 1:500 showed the most stable pesticide-degrading performance (Figure 5). 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.

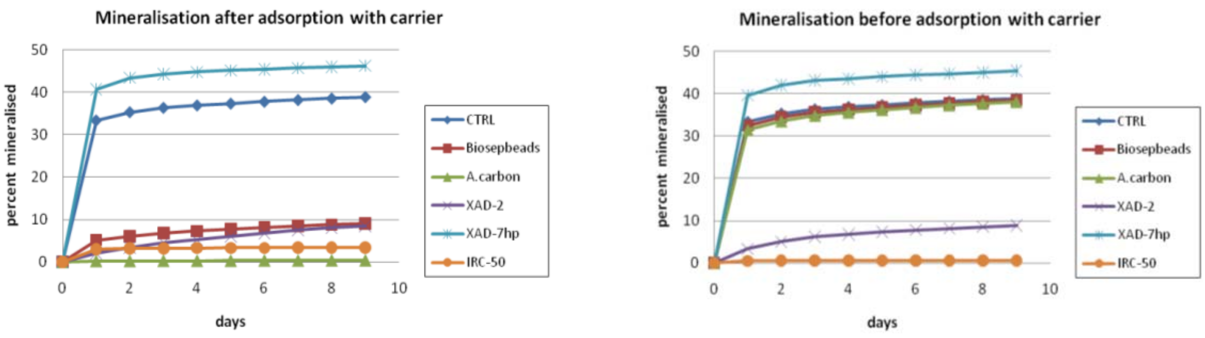

Figure 4: Cumulative mineralization of 14C-BAM by Aminobacter sp. MSH1 in the presence of different carriers. MSH1 was added either together with BAM (left-hand side) or after BAM had been sorbed to the carriers (right-hand side).

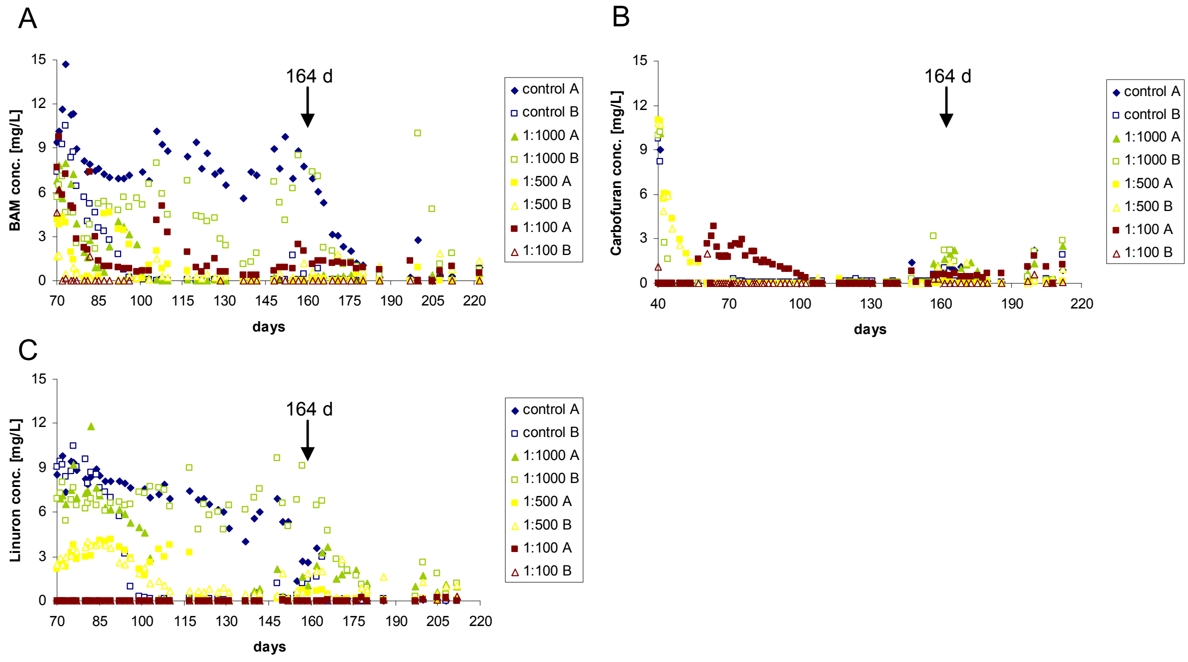

Figure 5: Effluent concentrations over time of (A) BAM, (B) carbofuran and (C) linuron in columns filled with sand (blue symbols, control) or Amberlite XAD-7HP and sand in a w/w ratio of 1:1000 (green symbols), 1:500 (yellow symbols) and 1:100 (brown symbols). Sphingomonas KN65.2 was injected on day 40, Aminobacter MSH1 on day 61 and Variovorax SRS16 on day 71. From day 164 on, only BAM and carbofuran were added with the influent medium (indicated by arrow). Figures show the two biological replicates.

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 real groundwater (Figure 6). 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.

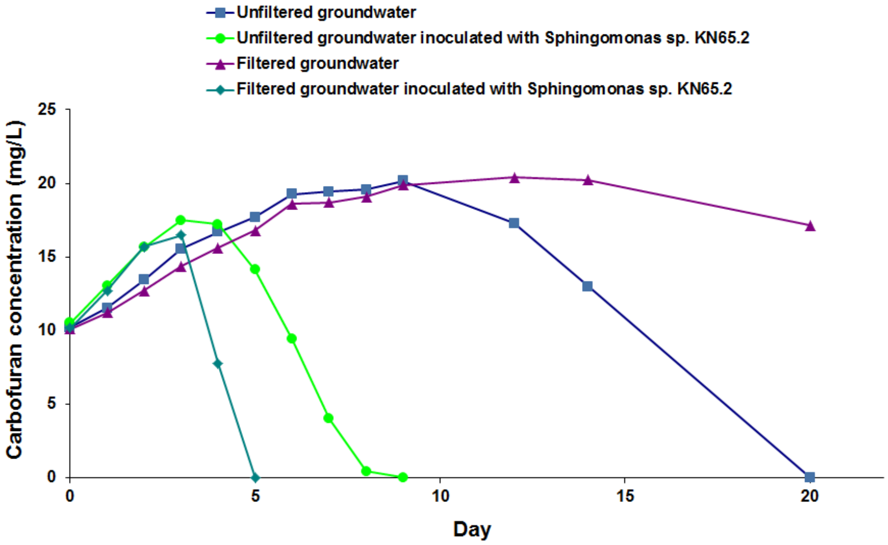

Figure 6: Biodegradation of carbofuran by Sphingomonas sp. KN65.2 with gravel as a carrier and with water from the site. The initial increase in concentrations is due to our inability to separate between carbofuran and degradation products.

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 7).

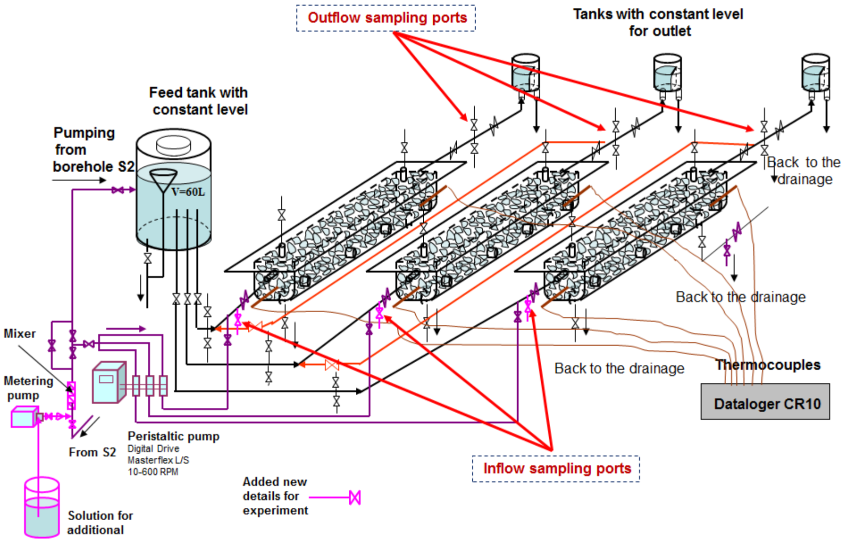

Figure 7: Scheme of the pilot system with the addition of the peristaltic pump and carbofuran container.

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, but the levels diminished with time (Figure 8).

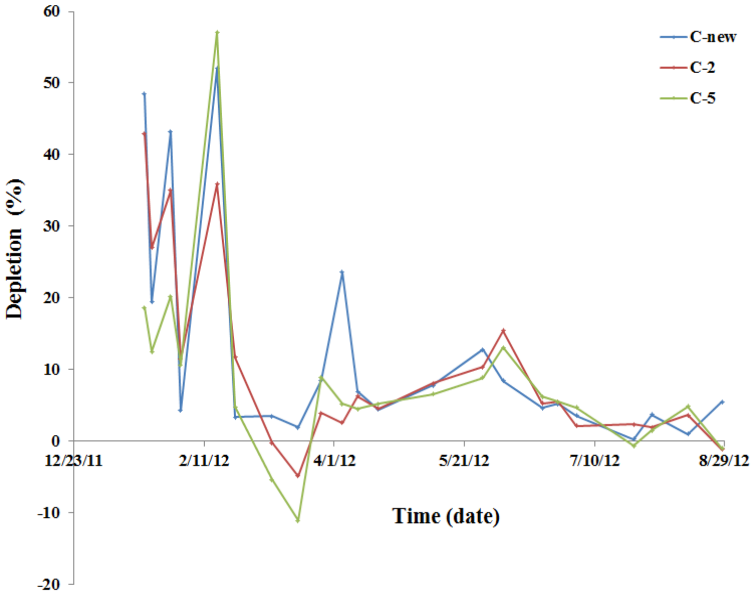

Figure 8: Carbofuran depletion percentage in the non-inoculated columns over time (from December 2011 until September 2012).

Introducing *Sphingomonas* sp. KN65.2 to the column resulted in a transient improvement in degradation (Figure 9). Attempts to oxygenate the water passing through the column failed because of clogging due to iron minerals within the contaminated water.

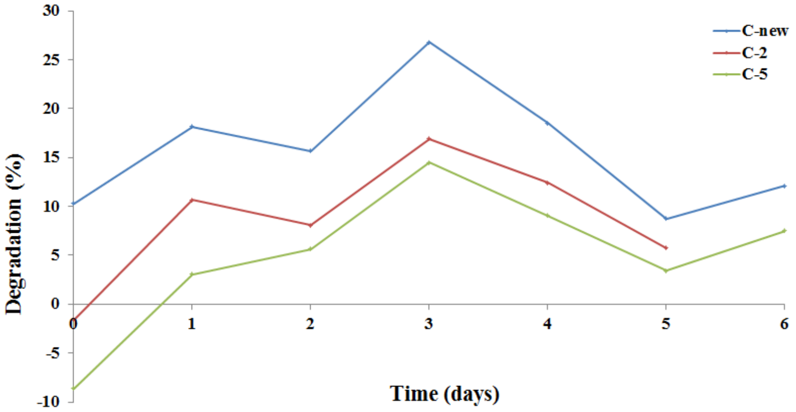

Figure 9: Carbofuran depletion (%) after inoculation with Sphingomonas sp. KN65.2

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.

Development of rehabilitation technologies to decrease pollutant influx between groundwater and surface water near river banks – AQUAREHAB WP3

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INTRODUCTION

In Work Package 3 of the AQUAREHAB project, the degradation of Chlorinated Aliphatic Hydrocarbons (CAHs) was studied in the sediment zone of the Zenne River and nearby aquifer at Vilvoorde in Belgium. This site is characterized by typical contamination problems of an urban and industrial nature which are discharging into the river, *i.e.* (i) municipal sewage from the city of Brussels and (ii) 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.

Our main aim was to select different remediation techniques to prevent the influx of CAHs into the sediment and finally the surface water of the Zenne River. More in particular, for the aquifer compartment, the injection of carbon sources was chosen to stimulate CAH biodegradation before reaching to the sediment while for the sediment compartment, capping of the sediment (rehabilitation) or the infiltration of oxygen by surface water into the sediments (natural attenuation) were investigated. In addition, the dynamics of the microbial and overall ecology of the river sediment was monitored over a period of 2 years (September 2009 till September 2011).

RESULTS

Stimulation of CAH degradation by carbon sources in aquifer compartment

The aim of this part of the study was to investigate the CAH degradation kinetics of the *Dehalococcoides mccartyi* population indigenous to a polluted aquifer discharging into the Zenne River using different carbon sources in batch cultures. Reductive dechlorination of trichloroethene (TCE) took place only when external carbon sources were added to microcosms, 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 1). A sensitivity analysis indicated that the inclusion of donor limitation 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.

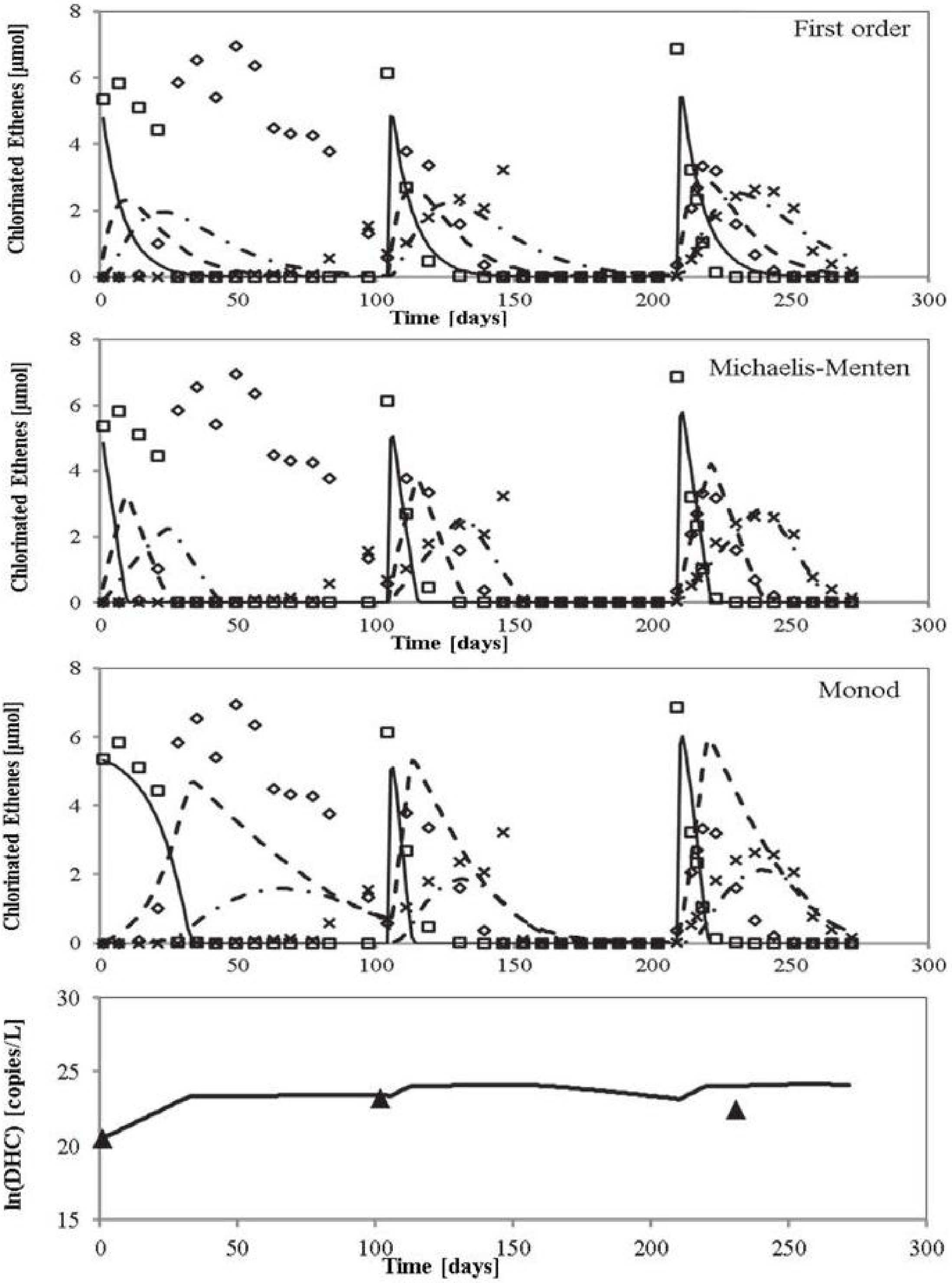

Figure 1: Model results using First-order (top), Michaelis-Menten (middle) and Monod (bottom) kinetics for the aquifer of one location to which sediment extract was added. Observed data: □ TCE, ◊ cDCE, × VC and ▲ 16S rRNA gene copy numbers of Dehalococcoides mccartyi. (DHC). Modeled data: — TCE, ---- 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.

Stimulation of the degradation of CAHs in the Zenne sediment compartment by capping or by oxygen infiltration from the oxygenated surface water

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 tophysically 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 amendement), it was clear that all tested capping materials had a positive effect on the degradation of VC and cDCE (Figure 2: 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.

). Tree bark was selected as the most promising capping material since it stimulated cDCE degradation for more than a year but also resulted in enhanced stimulation of *D. mccartyi* over methanogens as the main competitors.

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 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 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) of 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 (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 3).

The physico-chemical assessment showed a “less than good” status since insufficient oxygen level 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.

), and that oxygen distribution, as determined by sediment grain size and organic matter content, affects the local VC degrading bacterial community and VC biodegradation pathway.

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*.

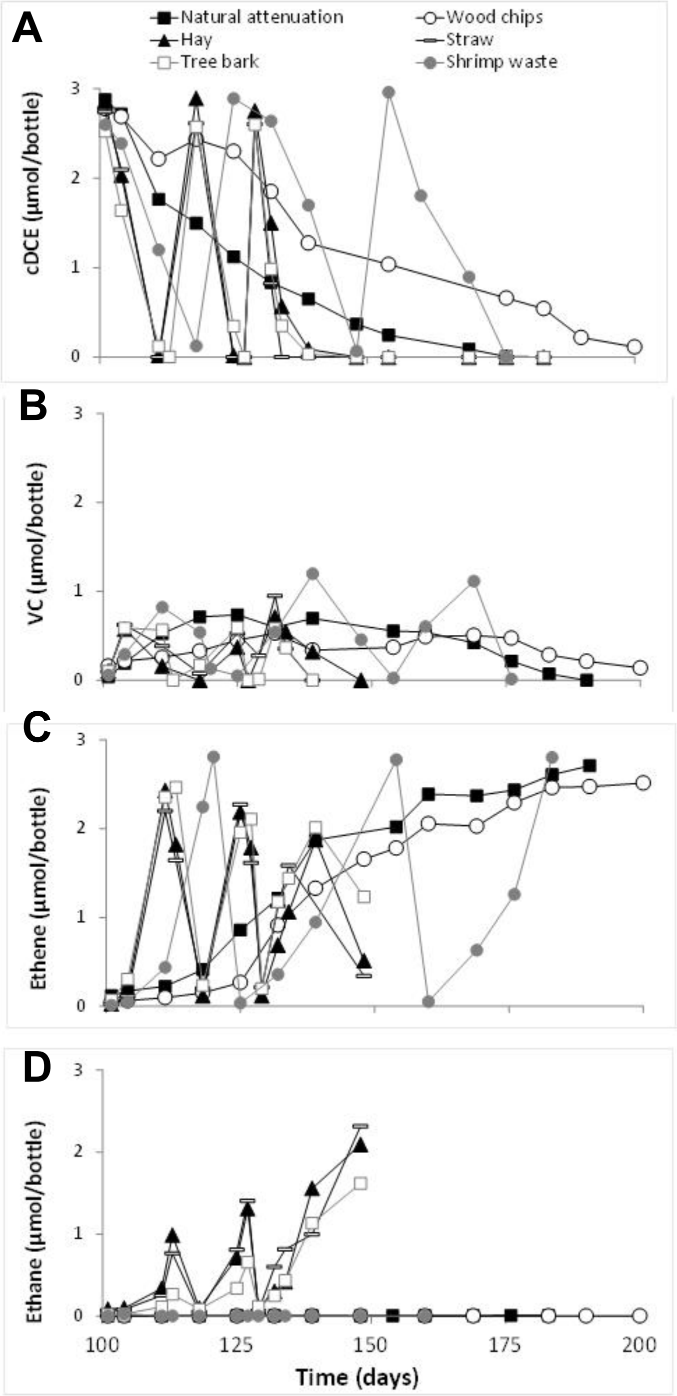

Figure 2: Anaerobic dechlorination of cDCE (A) to VC (B), ethene (C) and ethane (D) in sediment microcosms containing different SPOMs as a source of carbon and electrons. cDCE was added at day 100 when degradation of VC was completed in microcosms. Data shown are average values obtained from duplicate microcosms.

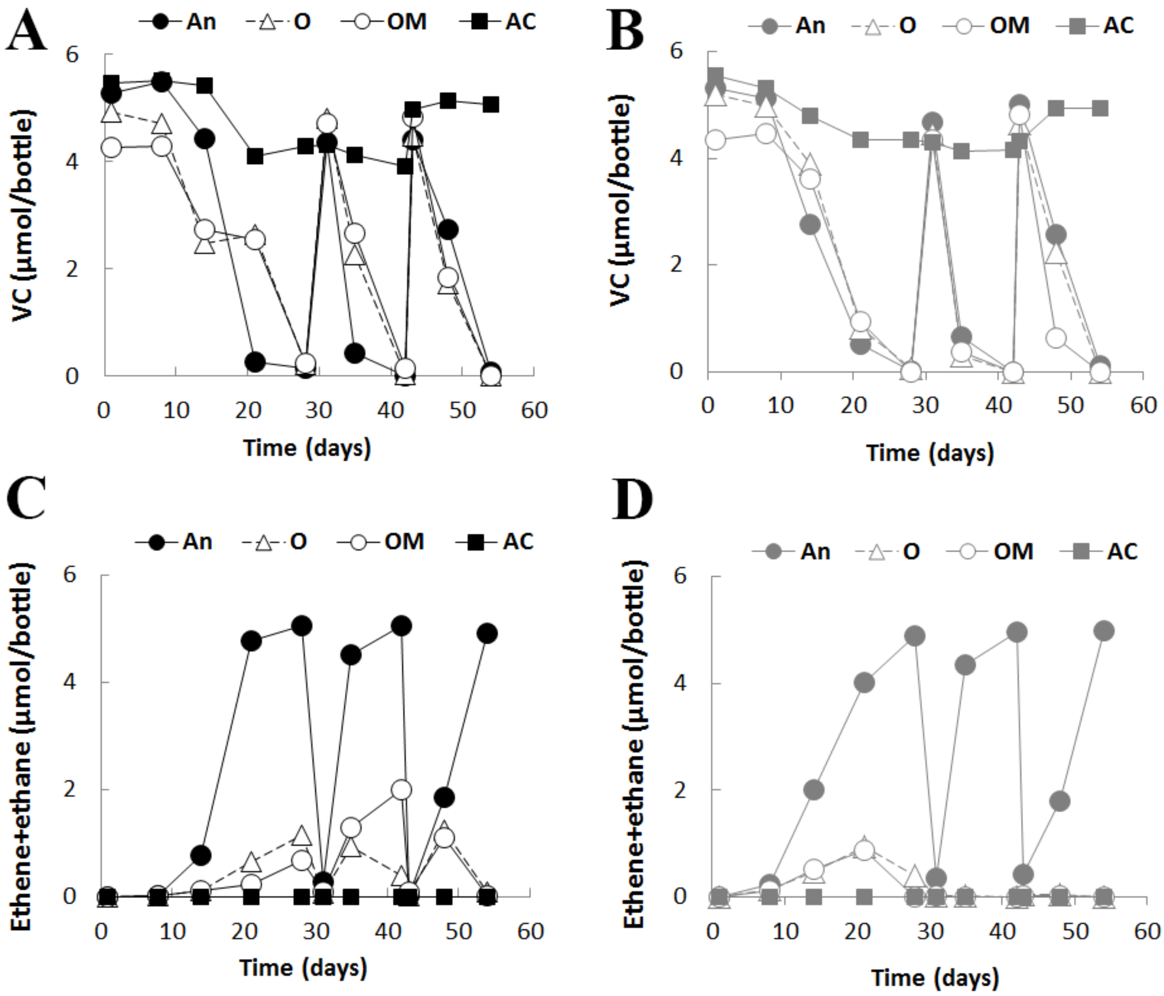

Figure 3: VC degradation (A and B), accumulation of ethene and ethane (C and D) in oxygen-exposed and anoxic microcosms containing sediment from location P26 (panels A and C) and P25 (panels B and D), respectively. An: anoxic, O: oxygen exposed microcosms, OM: oxygen exposed microcosms amended with methane, 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.

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 4).

The physico-chemical assessment showed a “less than good” status since insufficient oxygen level 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.

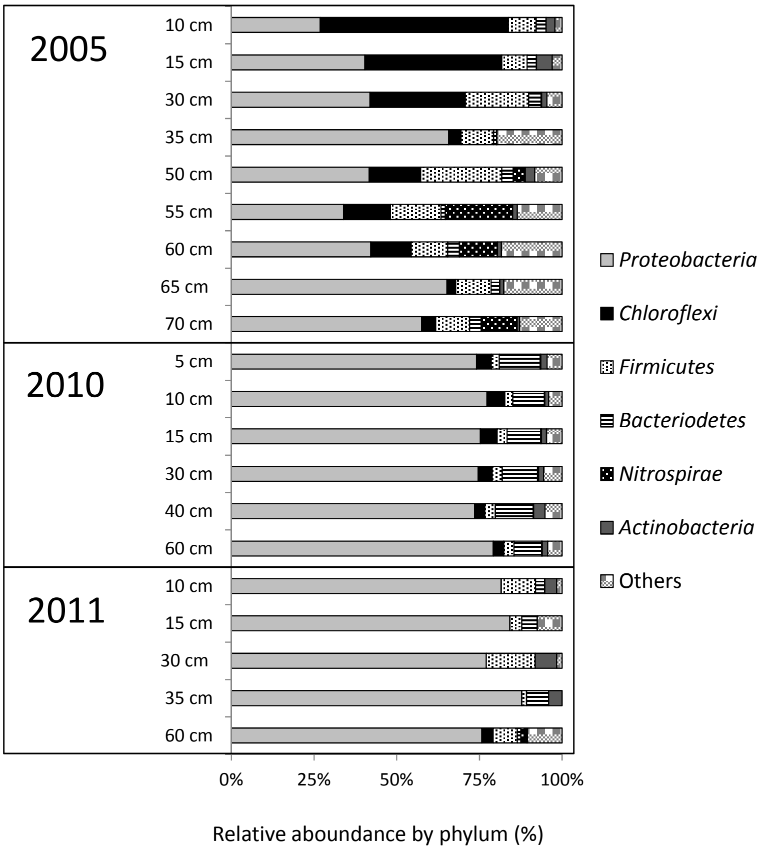

Figure 4: Relative abundance of the dominant bacterial phyla at different depths in the sediment core samples taken in 2005, 2010 and 2011.

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In-situ groundwater remediation by multibarriers: longevity, design parameters and interaction between different removal processes – AQUAREHAB WP4

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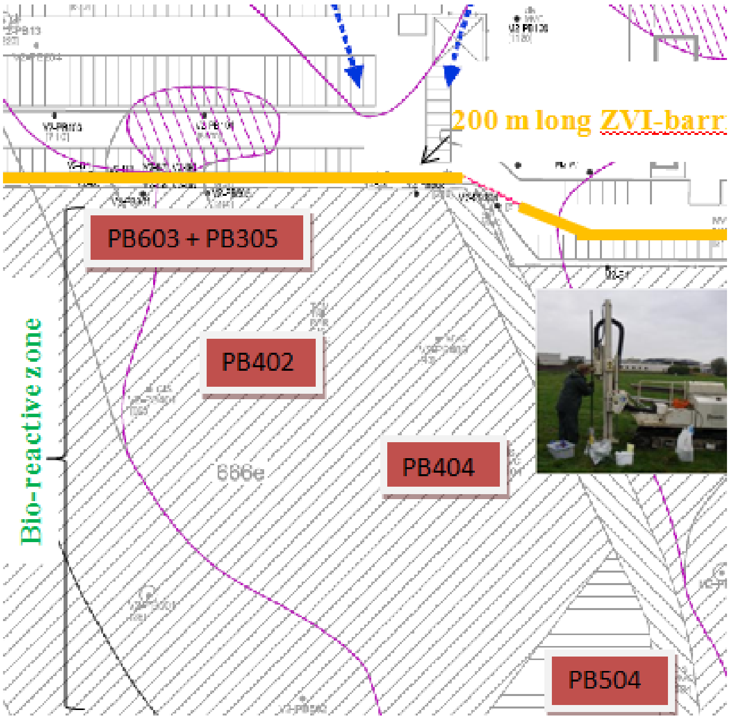
ABSTRACT: Within the FP7 project AQUAREHAB (GA 226565) WP4 was dedicated to multibarriers, an in-situ technology where different pollutant removal mechanisms are combined for treatment of groundwater contamination plumes with multiple pollutants or pollutants that require different degradation steps. The research focussed on identification and determination of crucial parameters to predict the short and long term impact of multibarriers on the environment on a local scale. Interactions between the different removal mechanisms within a multibarrier was also a point of attention. 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 injection of electron donor. Earlier this multibarrier concept was found suitable for an industrial site in Belgium (Scheldt river basin), where a full scale ZVI-barrier was implemented in 2005. Available field data were completed with numerous new field measurements. Data from lab scale tests were used to derive degradation rates and corrosion rates that were required as input for a numerical model that was developed with the aim to predict the longevity, i.e. the functioning of ZVI-barriers over time. New approaches to derive pollutant degradation rates were evaluated. In a later phase of the project, 2 additional multibarrier concepts were also considered to evaluate the generic character of the findings.

INTRODUCTION

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 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 function of the pollutants and site specific aspects.

Within AQUAREHAB, WP4 was dedicated to multibarriers, not with the aim to develop a multibarrier for a specific site, but to focus on identification and determination of crucial parameters to predict the short and long term impact of multibarriers on the environment on a 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 injection of electron donor (see Figure 1). Earlier this multibarrier concept was evaluated on labscale and 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.

In a first phase, 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 lab to derive these parameters; (3) determination of biodegradation rates via classical lab-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 focus on parameters that do influence the functioning and longevity of the multibarrier. There was a close collaboration between partners with a technological background and modellers, which was required to develop numerical technology models to predict the functioning of ZVI barriers & multibarriers. In a second phase of the project, the generic character of the approaches and tools developed were evaluated for 2 other multibarrier systems. This paper summarises the main achievements.



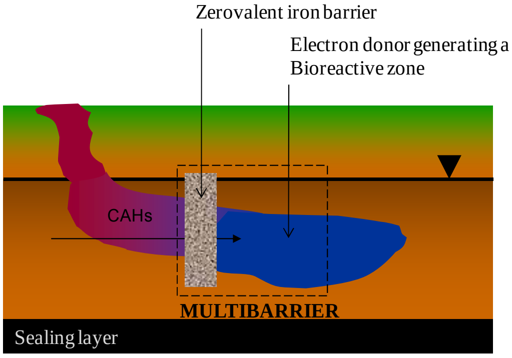


Figure 1: (Left) Multibarrier at site A comprising (1) a 200 long ZVI barrier and (2) a bioreactive zone with monitoring wells; (top) schematic representation of the multibarrier at site A.

RESULTS

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 lab scale experiment was performed during which hydrogen production by the ZVI was followed in time as 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 (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 scenario's, while the second phase corrosion rate is expected to lead to scenario's more close 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 lab 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. Generally, a column feasibility test is performed to deduce degradation rates of the pollutants and other parameters needed as input parameters for the design of the ZVI-barrier. Groundwater from the site, and the selected ZVI type are used in these tests. Minimal required contact times of the groundwater and the ZVI to meet the regulatory limits are calculated. Within the AQUAREHAB project, an improved test procedure has been elaborated which allows to deduce parameters related to the de-activation of the ZVI over time, enabling to estimate the life-time of the barrier for specific sites. The procedure is described in the generic guideline that AQUAREHAB composed related to ZVI-barriers and which will be made available via the AQAUREHAB website (vito.aquarehab.be).

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 a saturated groundwater model, advective-dispersive solute transport, and a comprehensive reaction network. 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 identifiability of the model parameters (see WP7).

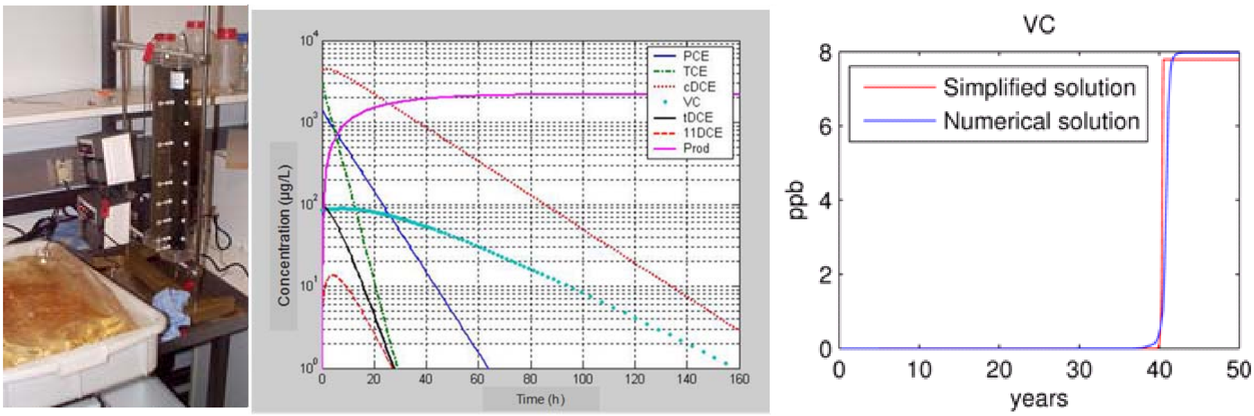


Figure 2: Column test setup (left), simulated evolution of CAH-concentration within a ZVI-barrier (middle), and expected CAH-concentration at the barrier effluent site predicting the longevity of a ZVI-barrier (right).

Bioreactive part of the multibarrier (at site A)

Degradation rates via labscale tests. Earlier batch-degradation experiments showed that a CAH-degradation potential is present at the site. New fed-batch experiments were started within AQUAREHAB in December 2009 to derive CAH-degradation rates for site A using aquifer samples at 4 different distances from the barrier (PB603/PB305, PB402, PB404, PB504, see Figure 1). At all locations at site A, a clear biodegradation potential for 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 0-10 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), CAH-degradation was observed. For the other spots, lactate addition was required to stimulate the CAH biodegradation. In poisoned controls no removal of CAHs was observed.

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). This approach allowed to link copy/transcript numbers with degradation rates. 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. For example reductive dehalogenase transcripts are high in the 305 and 603 batches but lower in the 504 and 404 batches. Secondly the 603 and 402 batches have gene copy numbers generally above 10^5 copies/g for all targets but in the other batches there is more variation of the gene copy numbers ranging from 10^2 -10^8 copies /g. Univariate analyses revealed a correlation between degradation rates of PCE and gene copy number (DNA-level) of pceA, tceA, vcrA and bvcA and TCE degradation rates were positively correlated with tceA and vcrA. No correlations were found between 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. Further biostatistical analyses was applied to investigate the correlations more in detail. 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.* 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.

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

Hydrogen formed by ZVI serves as electron donor for CAH-biodegradation. 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. Further, hydrogen produced during anaerobic corrosion of ZVI, may be used as electron donor for the CAH-degrading microbial population. Experimental prove was collected that CAH-degrading bacteria could use hydrogen as the final electron donor. As such, the hydrogen producing ZVI may be a good habitat for dechlorinating bacteria. This was experimentally proven (see angled core section below).

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 lab scale batch degradation experiment with PCE, TCE, cDCE and VC separately using artificial groundwater. Further, also site specific stable isotope fractionation factors for these CAHs during biological degradation were derived via laboratory experiments. Both degradation processes induced an enrichment of the heavier C-isotopes in the non-reacted remaining part of the pollution, which should be taken into account when evaluating field data. Although some differences were observed in the extent of the enrichment, 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).

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 are being 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. This 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. Repeated isotope monitoring revealed zones of constant and dynamic microbial degradation activity and located several secondary sources.

Divers were installed in June 2011 for continuously monitoring groundwater levels, temperature, and EC. The data will 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 meanwhile 6-year old ZVI-barrier to evaluate its performance over time. The samples comprise besides ZVI-barrier material also aquifer just before and just after the ZVI-barrier (Figure 3; Bastiaens et al., 2012). Its porosity and reactivity were examined, as well inorganics present. The ZVI-barrier was found to be still as reactive as the original ZVI and the porosity remained sufficiently high. No higher concentration 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 tag-pyrosequencing. A diverse microbial population was found present in the ZVI-barrier, comprising dechlorinating bacteria (Chloroflexi).

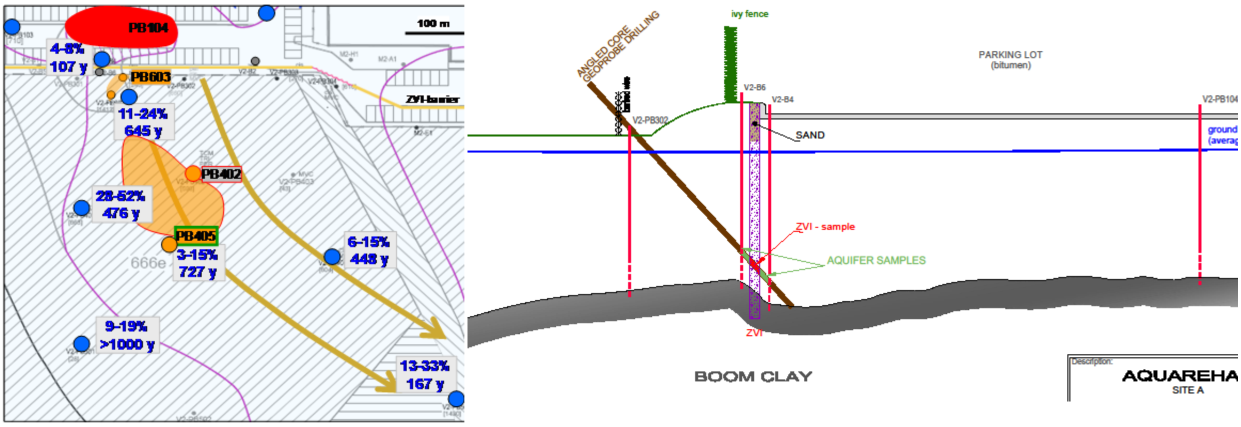


Figure 3 Conceptual site model derived from CSIA data (left), and scheme of angled core sampling (right).

Field numerical model. On the other hand, a theoretical approach was used based on numerical modelling (collaboration with WP7) aiming at predicting the functioning of the ZVI-barrier and the bioreactive zone over time. The data collected via lab 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 depictured in Figure 4.

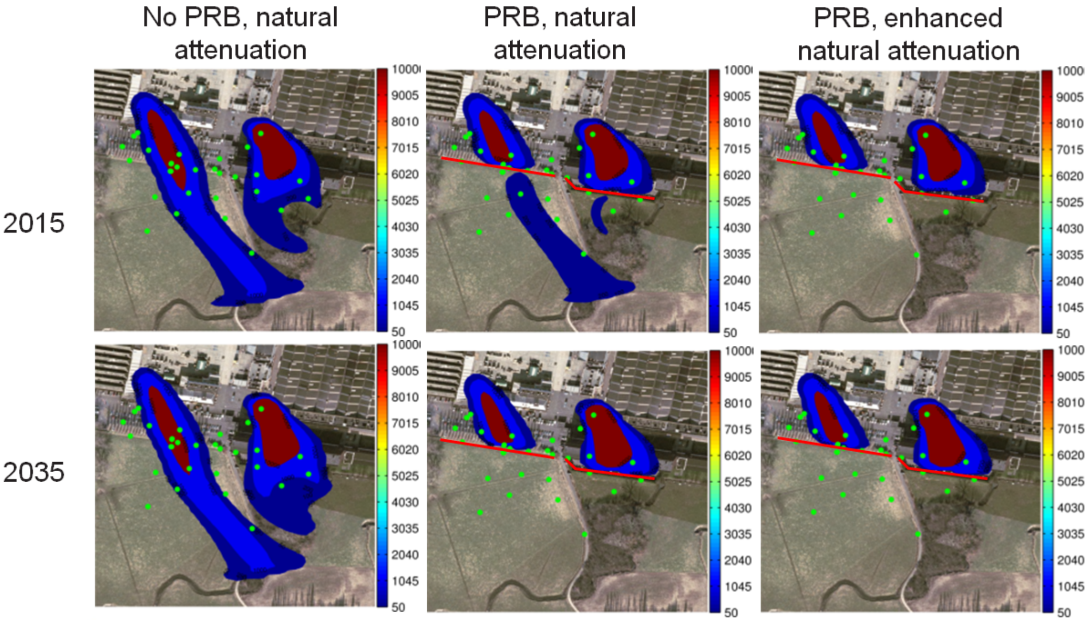


Figure 4: Simulation of groundwater plume evaluation in time under different scenarios.

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) lab scale test to verify the feasibility and derive design parameters, (4) design & dimensioning of a pilot/full scale, (5) implementation of the technology in the field, (6) monitoring and adjustments when needed, and (7) site closure. 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 also for other multibarrier concepts.
Therefore, in a second phase of WP4, 2 additional multibarrier concepts were considered:

- At site O, a pilot scale sequential multibarrier system was installed to remove ammonium (biologically via nitrification/denitrification and abiotically by ion exchange with zeolites) and COD and AOX (via sorption on GAC) (LIFE MULTIBARDEM).
- At site H, a multibarrier concept for a mixed contamination plume containing BTEX, CAHs and MTBE was considered. Lab scale feasibility tests showed that a multibarrier consisting of a ZVI-part followed by an inoculated aerobic zone has potential.

In respect to the generic character of the WP4 outcomes, it can be concluded that:

- ZVI-dedicated tests and model tools can be used for ZVI-parts of other multibarriers.
- For new type of barrier parts, the specific feasibility tests will be different, but the same logic can be followed.
- 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 5 shows the results of simulations for site H that were made based on kinetic parameters derived from previously performed lab scale feasibility tests.

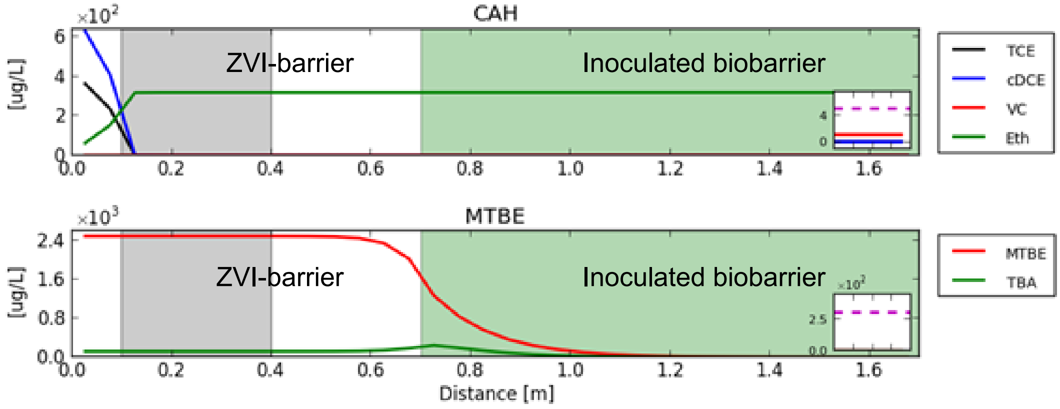


Figure 5: Simulation of the CAH and MTBE-concentration at site H as determined via the HP1 approach.

CONCLUSIONS

A combination of a good site characterisation, lab 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.

Within AQUAREHAB, generic guidelines were composed for ZVI-barriers, biological reactive zones and multibarriers, that can assist consultancies, contractors, site owners and authorities to evaluate the feasibility of a (multi)barrier application. These documents will be made available via the AQUAREHAB website (www.vito.be).

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Development of Groundwater Rehabilitation Technologies with Injectable Fe-based Materials – AQUAREHAB WP5

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ABSTRACT: 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 remediation efforts). Within the last four years, two strategies were pursued: (1) The use of reducing 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 oxidative 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.

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. Two mechanisms for pollutant removal were observed: sorption and degradation. 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.

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). 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 in the pores to 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 injection point.

For the 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.

SMALL LABORATORY-SCALE REACTIVITY, LONGEVITY AND MOBILITY TEST

Colloidal stability of Fe-based particles and guar gum rheology

Oxidizing Fe-based particles have typical size in the orders of few terms of nanometers and are sufficiently stable when dispersed in pure water. Conversely, reducing Fe-based particles, in a size range of 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 microns) 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 and of residual undissolved guar gum flakes, 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) evidenced 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 maximum it amounts approximately 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 for contaminant remediation (Fritzsche et al., 2012; Lee et al., 2012). Nanoparticulate ferrihydrite colloids sustained their high intrinsic reactivity and bioavailability also 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 on the microbial iron turnover in the environment, and on the potential for 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 desired not 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).

MODELLING THE TRANSPORT OF FE-BASED PARTICLES IN POROUS MEDIA

A software has been developed in this project for the simulation of the transport in porous media of highly concentrated suspensions of iron particles dispersed in non Newtonian fluids. The transport of iron particles is modelled 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, is modeled. Changes in pore velocity, viscosity, density and porosity due to the progressive deposition of iron particle are included. The influence of flow rate and fluid viscosity on the transport mechanisms is implemented as well. 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 microparticles 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 microscale via computational fluid dynamics (CFD) simulations (Tosco et al., 2013).

LARGE SCALE LAB EXPERIMENTS, CONSTITUTIVE RELATIONS AND MONITORING

Large scale lab experiments

Flow experiments on a radial flow domain performed with nanoiron 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 the injection can 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 transport of micro iron particles (2 µm) by permeation is not feasible for the given porous media. The microscale 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 did not get transported enough. 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 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:

- no clogging occurs during the injection, since it was proved that particle deposition rate is constant with time;
- micro iron in guar gum suspension is much more mobile than micro iron in water over a wide range of seepage velocities;
- particle mobility decreases as it travels farther from the well;
- 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;
- 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);
- micro particles in a weak suspension of guar gum can be distributed at a distance of 2m from the well using sufficiently high flow rates (example 0.004 m^3/sec);
- to design a field application, the relationship between injection rate and seepage velocity in the porous medium should be predicted.

Monitoring

A monitoring strategy including the necessary tools has been developed successfully. The tools include a master and slave system connected to a number of sensor arrays (Buchau et al., 2010). Each array consists of race-track coils to directly measure ZVI content, of temperature sensors to monitor temperature changes brought about either due to injection of slurry or due to chemical reactions and of 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 on the 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.

PILOT SCALE TEST, INCLUDING THE ENVIRONMENTAL IMPACT OF THE TECHNOLOGY ON THE ENVIRONMENT

All in all 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 1). The pilot test demonstrated that mZVI slurries stabilized with guar gum can be prepared at pilot scale and delivered in the subsurface (Velimirovic et al., under review). Direct push injection has been selected as 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.

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 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:

- the guar gum preparation method is applicable for small amount of guar gum. For larger quantities a different approach needs to be worked out.
- 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
- Observations made at the field indicate that further improvements of the iron sensor are needed to make it a reliable and functional system.

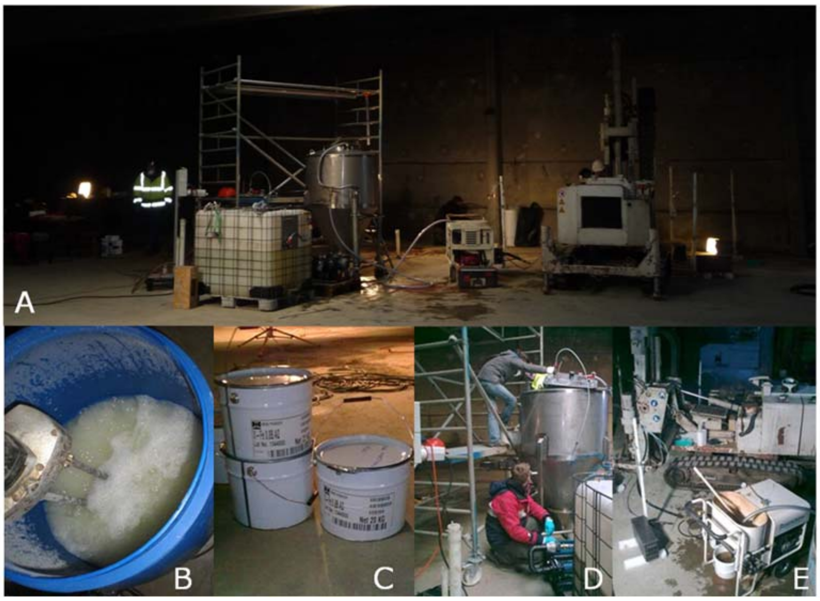

Figure 1: Iron injection set up. (A) injection area, (B) guar gum preparation, (C) mZVI, (D) mixing of guar gum and mZVI, (E) Geoprobe injection.

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 application. 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 minor and local scale of ecotoxicological impacts (few square meters for the worst case situations, in case daylightening of the injection fluid occurs).
An adenosine tri phosphate (ATP) bioluminescence assay was prepared to examine worst case scenario for CAH-degrading enrichment cultures. Stimulating effect on the bacterial activity have been observed as well as reduced activities when high doses were applied. It was found that nanoscale 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.
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.

CONCLUSION

The results of AQUAREHAB laboratory and field tests demonstrated that the use of guar gum stabilized mZVI slurries has potential for in-situ remediation of CAH-contaminated sites. In the alb it was show that mZVi can be stabilized by guar gum and does not impact the reactivity irreversible. A temporarily decreased reactivity can occur until break down of the guar gum. Further, it was shown that guar gum stabilized mZVI slurry can be relatively easily prepared at a pilot scale in the field, and with the appropriate equipment, full scale preparation is predicted to be feasible. Next, via direct push techniques, the slurry was found injectable in the subsurface. A controlled delivery of the product in the subsurface, on the other hand, is a challenge. Preferential flow paths of the injected iron slurry were created when applying high pressures. Consequently, a heterogeneous distribution of the iron particles was obtained. While the deeper layer (8-10.5 m bgs) was targeted, a significant part of the mZVI flowed upward in the shallow zone (4.5 m bgs) due to created preferential paths during high pressure and flow injection.

In conclusion, despite the fact that guar gum stabilized mZVI particles were delivered at a different depth than intended, delivered mZVI can degrade 1,1,1-TCA in the field. Further demonstration of this technology in zones with different CAH-pollutants and with more controlled delivery of the reagents has been performed within the Aquarehab project as an extrapolation case.

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The integration of watershed fate models, ecological assessment and economic analysis of water rehabilitation measures in the REACHER decision support system – AQUAREHAB WP6

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ABSTRACT: A decision support tool called REACHER was set up. It contains information derived from multiple calculation runs with watershed fate models (SWAT, SECOMSA) to assess (1) the effect on water quality at the outlet of catchments by implementing measures at different locations in the catchment, both related to point source reduction as well as to diffuse sources and (2) the contribution from groundwater to the surface water load and the concomitant time delay between applying a measure and the effect on the water status. The second important functionality of the decision support tool is the visualisation of ecological status or ecotoxicological effects related to estimated concentrations predicted by the watershed models or monitored concentrations by environmental agencies. An adapted Species Sensitivity Distribution ms-PAF approach was used to derive ecotoxicological effects from mixtures of chemicals and time dynamics. The third part of the decision support tool is the setup of scenarios with measures containing economic and performance data (costs, timespan, efficiency, applicability) of the measures. The REACHER tool is demonstrated for nitrogen in the Odense catchment (Denmark) and the Scheldt river basin (France, Belgium). Related measures to remove nitrogen by reduction of point sources (waste water treatment) and diffuse sources (cattle reduction, connection of households to waste water treatment, wetlands) were assessed based on scenarios with the watershed models and incorporated in the REACHER tool for the Scheldt basin. In this contribution, the setup of REACHER, the various components, and results for the case studies is shown.

INTRODUCTION

Water managers have to make decisions on the implementation of measures to improve the status of the aquatic ecosystem. The available information on innovative rehabilitation technologies, and more specifically groundwater remediation technologies, is complex and therefore difficult to incorporate in programmes of measures. Challenges related to the implementation of groundwater remediation technologies at the river basin or groundwater body scale are the upscaling from field to catchment scale, the interaction between groundwater and surface water, the time delay between action and effect due to the attenuation processes, and the assessment of the effects of multiple measures within one catchment. Often technologies act on just a specific set of chemicals whereas multiple chemicals end up in the groundwater or surface water and may cause adverse effects to ecology. Ecological effects of mixtures of chemicals arriving at different time periods in the catchment are difficult to assess. The policy context for decision support systems in water management in Europe is largely defined by the European Water Framework Directive (WFD). This Directive, adopted in 2000, sets ambitious objectives to meet 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, 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. The WFD also explicitly mentions the concept of a water body as the preferred scale, which can be quite detailed, depending on the Member State and the specific river basin. Member States need to report the amount of water bodies reaching good status now and in the future. The WFD requires that these plans include cost-effective programmes of measures. How to identify which measures are cost-effective is also an important target for a DSS. Developing web applications instead of desktop models also adds some additional complexities, especially if end users need to perform model simulations. Models need to be sufficiently simplified, have short calculation times and easy to operate to allow end users to perform so called "on the fly" calculations.

METHODOLOGY

REACHER DSS Architecture

The REACHER DSS architecture basically consists of three main components:

- Models
- Databases
- User interface

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 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.

Databases contain:

- data from literature (e.g. measures and costs), inventories (e.g. pollutant emission data), expert knowledge
- data from lab tests (performance of technologies)
- output data from models

The user interface allows for:

- User entries: choice of management options for a certain geographical unit, choice of evaluation criteria, …
- 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). WebDSS user interface is designed to communicate with the database following data transform standards.

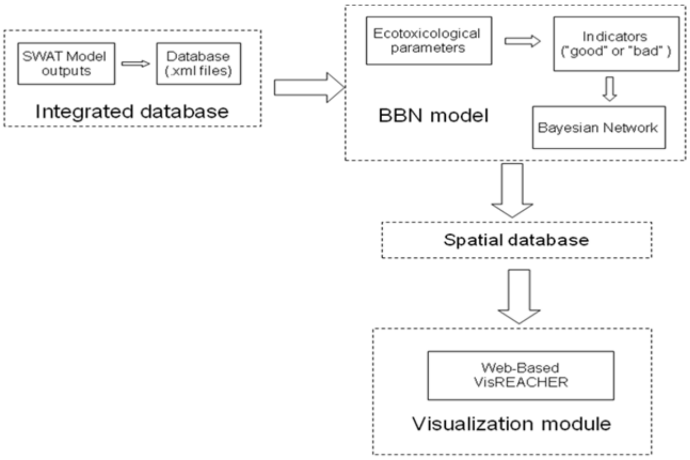


Figure 1: General layout of the DSS for evaluation of rehabilitation technologies in a geographical framework

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 (e.g. Figure 2). Besides SWAT, a new conceptual modeling 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 subbasin. The model was calibrated and evaluated for the Scheldt river basin.

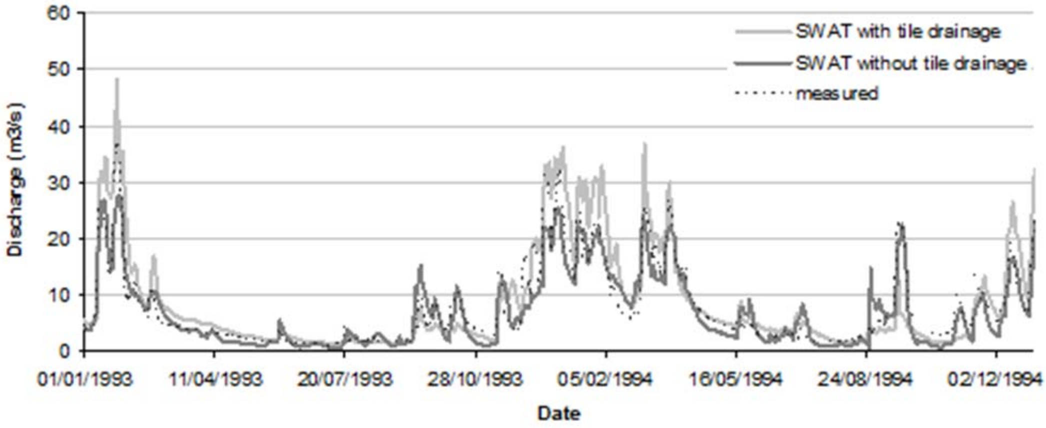


Figure 2: Evaluation of the performance of the adapted SWAT model for artificial drainage in the Odense catchment

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 be not 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 subbasin, a database with total annual costs, total annual load reduction (kg/year) 2015-2021-2027 is composed. Depending on the selection of measures and the selected year, the sum of all costs and load reductions for all selected measures per subbasin is made. Results are shown in additional columns in a tabular view. One column displays all costs per subbasin, one column displays all load reductions per subbasin. 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.

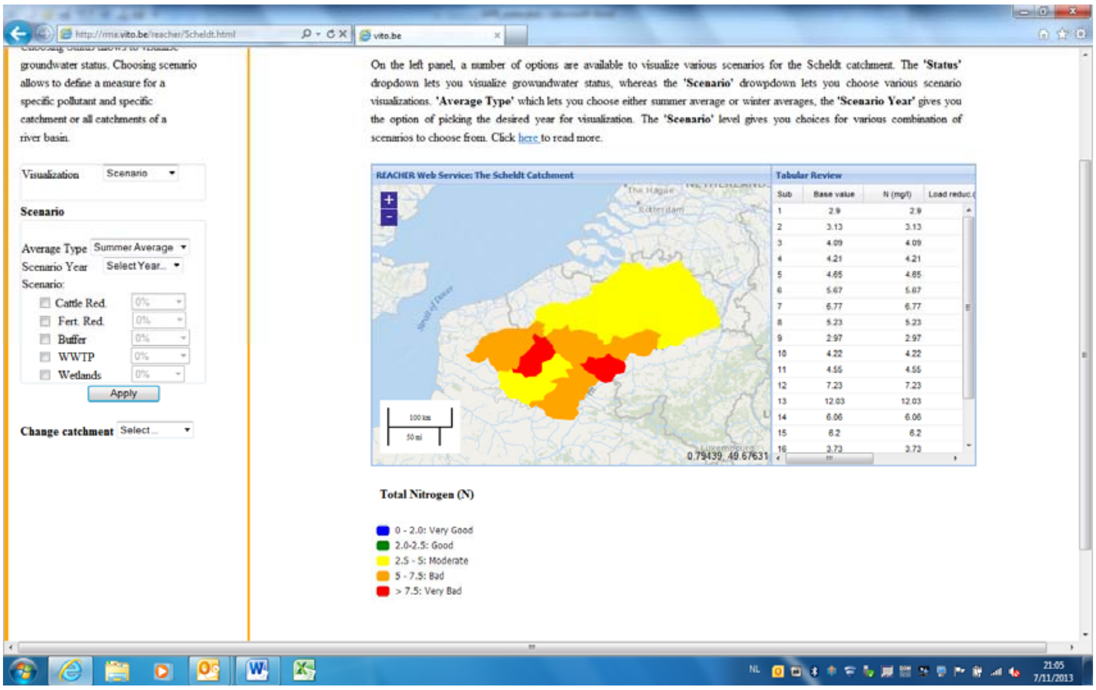
Ecotoxicological criteria are derived for specific chemicals based on the Species Sensitivity Distribution (SSD) approach resulting in PAF, ms-PAF or weighted mean PAFs. If single chemical concentrations are measured for a certain river basin (site, locality), concentrations can be translated into the 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).

Use case

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.

RESULTS AND DISCUSSION

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 3). The user can select a scenario by applying one or multiple measures (cattle reduction, fertilizer reduction, buffer strips, waste water treatment, or wetlands).



groundwater status. Choosing scenario allows to define a measure for a specific pollutant and specific catchment or all catchments of a river basin.

Visualization: Scenario

Scenario

Average Type: Summer Average
Scenario Year: Select Year...
Scenario:
☐ Cattle Red. 0%
☐ Fert. Red. 0%
☐ Buffer 0%
☐ WWTP 0%
☐ Wetlands 0%

Apply

Change catchment Select...

On the left panel, a number of options are available to visualize various scenarios for the Scheldt catchment. The **'Status'** dropdown lets you visualize growundwater status, whereas the **'Scenario'** drowpdown lets you choose various scenario visualizations. **'Average Type'** which lets you choose either summer average or winter averages, the **'Scenario Year'** gives you the option of picking the desired year for visualization. The **'Scenario'** level gives you choices for various combination of scenarios to choose from. Click here to read more.

REACHER Web Service: The Scheldt Catchment

Tabular Review

Sub	Base value	N (mg/l)	Load reduc
1	2.9	2.9	
2	3.13	3.13	
3	4.09	4.09	
4	4.21	4.21	
5	4.65	4.65	
6	5.67	5.67	
7	6.77	6.77	
8	5.23	5.23	
9	2.97	2.97	
10	4.22	4.22	
11	4.55	4.55	
12	7.23	7.23	
13	12.03	12.03	
14	6.06	6.06	
15	6.2	6.2	
16	3.73	3.73	

Total Nitrogen (N)

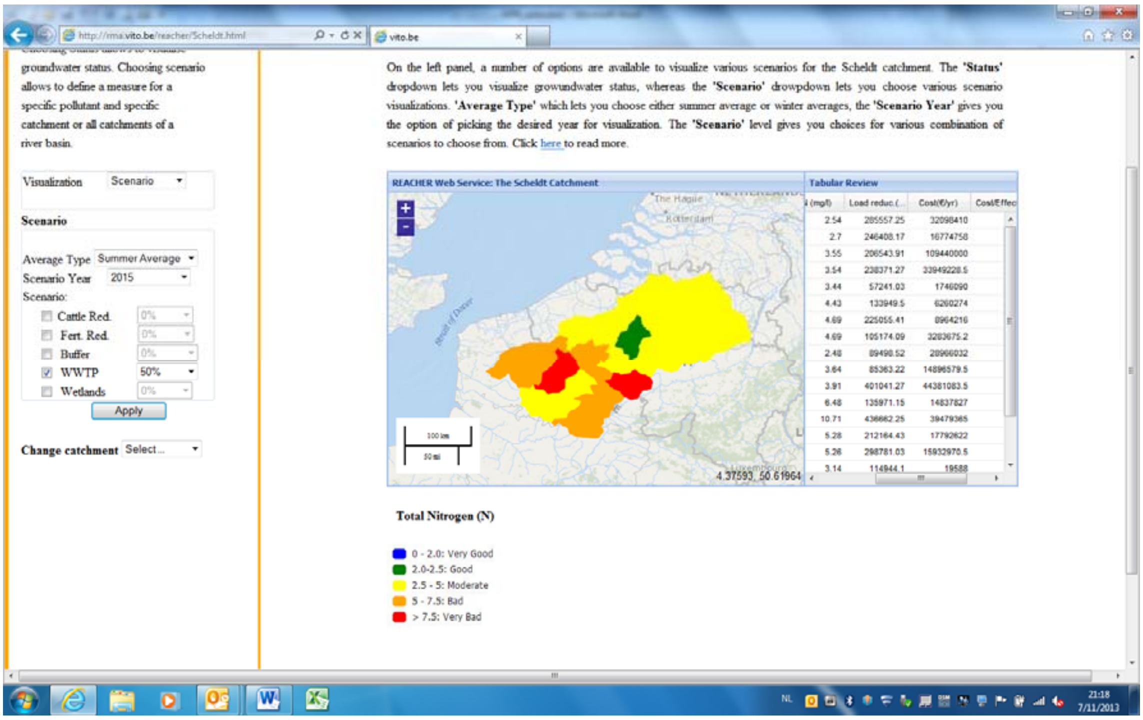
- 🟦 0 - 2.0: Very Good
- 🟩 2.0-2.5: Good
- 🟨 2.5 - 5: Moderate
- 🟧 5 - 7.5: Bad
- 🟥 > 7.5: Very Bad

Figure 3: Surface water status visualisation in the REACHER DSS. The status window consists of a geographical delineation of subbasins and colour coded classification of the N status at the outlet of the subbasin. The N concentration values are given in tabular view for each subbasin.

The effect of implementing one or multiple measures is displayed geographically and in tabular view. The table shows the load reduction in each subbasin achieved with implementation of a measure, the associated cost and the cost-effectiveness ratio (Figure 4). 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 punctual locations in a river basin.

The prototype REACHER DSS for the Scheldt is fed with data from precalculated runs with the SECOMSA model for the different scenarios (Haest et al., 2013). The SECOMSA predictions were evaluated using discharge measurements and nitrate concentrations for various subbasins in the Scheldt catchment.



groundwater status. Choosing scenario allows to define a measure for a specific pollutant and specific catchment or all catchments of a river basin.

Visualization: Scenario

Scenario

Average Type: Summer Average
Scenario Year: 2015
Scenario:
☐ Cattle Red. 0%
☐ Fert. Red. 0%
☐ Buffer 0%
☑ WWTP 50%
☐ Wetlands 0%
Apply

Change catchment Select...

On the left panel, a number of options are available to visualize various scenarios for the Scheldt catchment. The **'Status'** dropdown lets you visualize growundwater status, whereas the **'Scenario'** drowpdown lets you choose various scenario visualizations. **'Average Type'** which lets you choose either summer average or winter averages, the **'Scenario Year'** gives you the option of picking the desired year for visualization. The **'Scenario'** level gives you choices for various combination of scenarios to choose from. Click here to read more.

REACHER Web Service: The Scheldt Catchment

Tabular Review

(mg/l)	Load reduc.(...	Cost(€/yr)	Cost/Effec
2.54	285557.25	32098410	
2.7	246408.17	16774758	
3.55	206543.91	109440000	
3.54	238371.27	33949228.5	
3.44	57241.03	1746090	
4.43	133949.5	6260274	
4.69	225055.41	8964216	
4.69	105174.09	3283675.2	
2.48	89498.52	28966032	
3.64	85363.22	14896579.5	
3.91	401041.27	44381083.5	
6.48	135971.15	14837827	
10.71	436662.25	39479365	
5.28	212164.43	17792622	
5.26	298781.03	15932970.5	
3.14	114944.1	19588	

Total Nitrogen (N)

🟦 0 - 2.0: Very Good
🟩 2.0-2.5: Good
🟨 2.5 - 5: Moderate
🟧 5 - 7.5: Bad
🟥 > 7.5: Very Bad

Figure 4: A scenario with connection of 50% unconnected households to a waste water treatment plant and effect on summer average N concentration, obtained load reduction and associated costs in 2015

CONCLUSIONS

The REACHER DSS prototype is developed as a generic software tool to assess the effects of rehabilitation measures on water quality. It contains fate model calculation functionalities, cost effectiveness economic analysis, and visualization options for status visualization in a geographical context. Depending on specific user requirements, the tool can be further developed (user specific classification criteria, spatial detail, measures and scenarios of measures, economic analysis).

ACKNOWLEDGEMENTS

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Development of groundwater remediation technology models for use in water management strategies at the river basin scale – AQUAREHAB WP7

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ABSTRACT: Reactive transport models were developed for reactive smart carriers treating contaminated groundwater in drains of an industrial site, for Fe-bearing material either implemented as a reactive barrier in the subsurface in combination with natural attenuation or as injectable micro-scale particles, for a reactive zone between groundwater and the river, and for groundwater-fed wetlands that were periodically flooded. The reaction models were calibrated for nitrate removal (wetlands) and removal of CAHs (Fe-based barrier + NA, groundwater-river interaction zone), using reaction parameters determined in independent lab batch or column tests. The hydrological model is calibrated using hydraulic heads determined in the respective fields, by estimating the hydraulic conductivity field. Model results for the field applications of the different technologies are shown. Lessons learned from setting up the models were the importance of estimating the source term of the pollution, the determination of the heterogeneous flow field and the limitations of using lab-derived reaction constants to simulate the contaminant plumes. Another objective of the work package was to use the reactive transport models to set up parsimonious models for estimating removal rates for various technologies. These parsimonious models can be used in water management models at the river basin scale to evaluate the effect of using multiple groundwater remediation technologies at the scale of a water body. WP7 developed and evaluated calculators for estimating the lifetime of an Fe-based barrier, a plug flow reactor model for wetlands, and a tanks in series model for the removal of contaminants in a groundwater river interaction zone. The parsimonious model structures performed adequately well under specific circumstances in representing the removal, in comparison to the more complex reactive transport models.

INTRODUCTION

The performance and longevity of groundwater remediation technologies under field conditions can be predicted using reactive transport models. 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 WP 7 of Aquarehab is to use reactive transport models to design lab and field experiments for evaluation of the technologies, to model field application of the technologies and to reduce reactive transport models for inclusion in water management at the catchment scale.

METHODOLOGY

Optimal experimental design

Figure 1 shows the optimal experimental design strategy for groundwater technology assessment. 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 modelers (the mathematical/IT experts that implement the processes in a computer code). An example of a conceptual model is shown in figure 2. 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 of 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 6). In optimal experimental designs, this usually refers to maximization of the information content and minimization of costs.

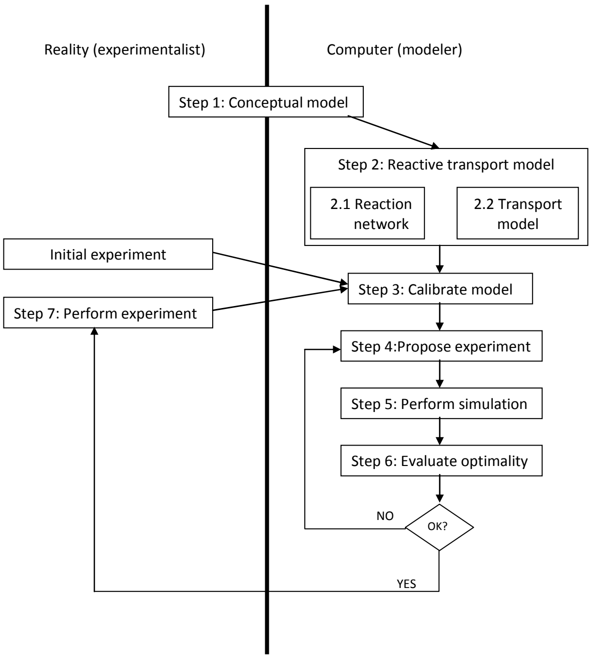


Figure 1: Optimal experimental design procedure for groundwater remediation technology performance assessment

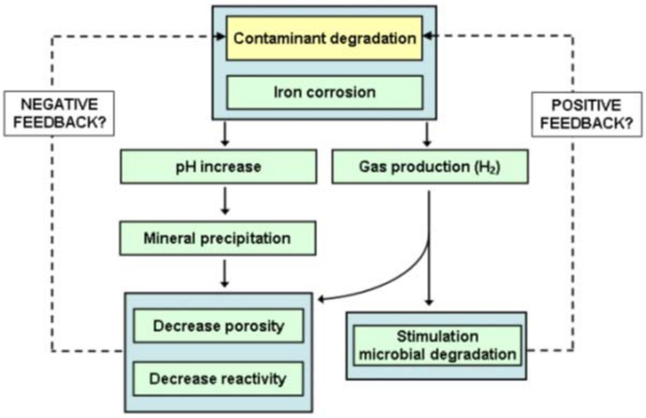


Figure 2: Conceptual model for the reaction network of an Fe^0 reactive barrier

Reactive transport models

Smart carriers in field drains

The basic idea of the rehabilitation technology is to treat the pollutants in trenches that drain intercepted contaminated groundwater and that contain tailored materials as support for microbial biofilms which degrade the pesticides in the passing contaminated drainage water. The model is programmed in Hydrus-1D (Simunek et al., 2013) and contains the following processes:

-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.

Wetlands

The wetland-aquifer systems were modelled using FeFlow (Diersch, 2005). The model has the following main characteristics: (i) 2D variable-saturated steady-state flow and multi-species transport and (ii) 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. Feflow 6.0 was used to simulate 2D flow and reactive transport. Feflow is a commercially available from http://www.feflow.info/

Groundwater river interaction zones

A model was developed to describe the groundwater-river interactions in the hyporheic zone and to estimate the attenuation before the groundwater discharges in the Zenne river. The flux exchange between the groundwater and surface water across the stream bed interface was initially estimated by using a two-dimensional, finite difference variably saturated, groundwater flow and heat transport model (VS2DH) (Healy and Ronan, 1996). A first-order model in PHREEQC containing advective-dispersive solute transport with first order degradation was developed to represent the degradation of VC in the river sediment. These two approaches were finally combined in the HP1 model to facilitate data management and processing using only one software tool for the simulation of the processes near/in the hyporheic zone. The HP1 code is fully incorporated into the HYDRUS-1D software package which can be downloaded from the link below. The user manual and notes on how to use HP1 can be found on http://www.pc-progress.com/en/Default.aspx?hydrus-1d [available on-line, 03/05/2013].

(multi)Barriers

The reaction model used to predict barrier longevity simulates groundwater flow and multi-component reactive transport. Fifty three aqueous complexation reactions and 3 mineral phases were included. Sixteen dissolved species were also included in the model to 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. The field model was tested developed in MODFLOW-RT3D, PHAST and MIN3P. MIN3P is a geochemical model, particularly suited for lab-scale applications under simple flow conditions. Model Muse, is a free MODFLOW and PHAST interface, http://water.usgs.gov/nrp/gwsoftware/ModelMuse/ModelMuse.html. PHAST is a PHREEQC based geochemical model with an internal flow solver, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/. PHREEQC models geochemical process and 1D contaminant transport. On line guide and download instructions can be found at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/. RT3D is a customizable reactive transport model which uses as flow input the MODFLOW output, http://bioprocess.pnnl.gov/rt3d.downloads.htm.

Injectable iron

A PHREEQC model was developed to simulate observed geochemical changes from a batch experiment performed with one iron type. The model was subsequently applied in a 1D transport model to simulate the iron injection and transport process, where the iron (gFe0 L-1) is distributed along a short distance from the injection point. The iron concentration in the soil matrix was simulated by the model MNM1D (Tosco T. et al., 2010), which was used as input for the reactive transport model. PHREEQC models geochemical process and 1D contaminant transport. On line guide and download instructions can be found at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

Reduced models for water management

The implementation of reactive transport models in catchment scale water management and rehabilitation, is not straightforward and limited by data availability and computational effort. Reactive transport models require process understanding at the microscopic scale and extensive parameterisation, which is not feasible at the catchment level. One way to upscale reactive transport models to the catchment scale is to derive simplified model structures from the more complex ones. The performance of these simplified model structures are verified with the complex model structures. The reduced model outputs can be plugged into decision support tools.

Wetland plug flow reactor

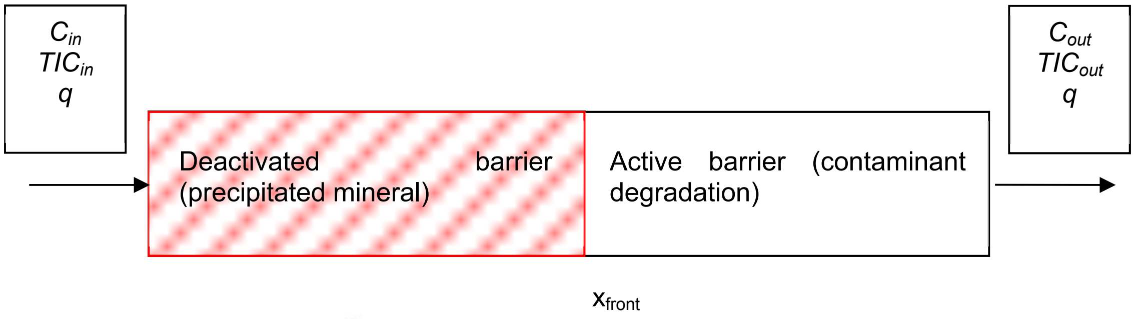
The steady-state relative concentration of a plug flow wetland reactor with a flow residence time of τ_G and first-order decay (with rate λ) is:

$$C_r = \frac{C}{C_0}\exp(-\lambda\tau_G)$$

where C_0 is the concentration of water entering the wetland and τ_G is the hydraulic residence time. The efficiency of a wetland in reducing mass can also be expressed by a mass reduction ($M=1-C_r$).

Reactive barrier lifespan calculator

The simplified model assumes that a mineral front develops in the PRB under low flow velocities (field conditions) and that before the front all the reactive surface area is depleted. Hence, only behind the deactivation front contaminants are actively degraded. The mineral front advances with the aging of the barrier according to the formula reported in Figure 3.



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

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

Tanks in series model for groundwater-surface water interaction

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

$$C_n = \frac{C_0}{(1+D_i)^n}$$

Where C_n is the concentration leaving tank *n*, C_0 is the concentration entering the series of tanks, D_i is the Damköhler number for tank *i* (from Eq. 5), *n* is the number of tanks. Any layer with its specific Damköhler number can be included in the analysis.

SELECTED RESULTS

Optimal experimental design

An example result for the use of models in experimental design is taken from lab experiments with zerovalent Fe to remove CAHs from groundwater. The model validation results are shown in Figure 4. The model was used to define further experiments for the assessment of the performance of the technology. It is useful to do an independent characterization of iron corrosion rate in a separate batch experiment. Biotic degradation rates should be assessed independently using batch experiments. In order to determine which mineral contributes most to the iron deactivation process (iron-carbonate or calcium-carbonate), a separate column experiment without Ca would be an option. Another option is to perform a more quantitative microscopic mineral characterization, e.g. comparison of coating thickness and extent for various minerals.

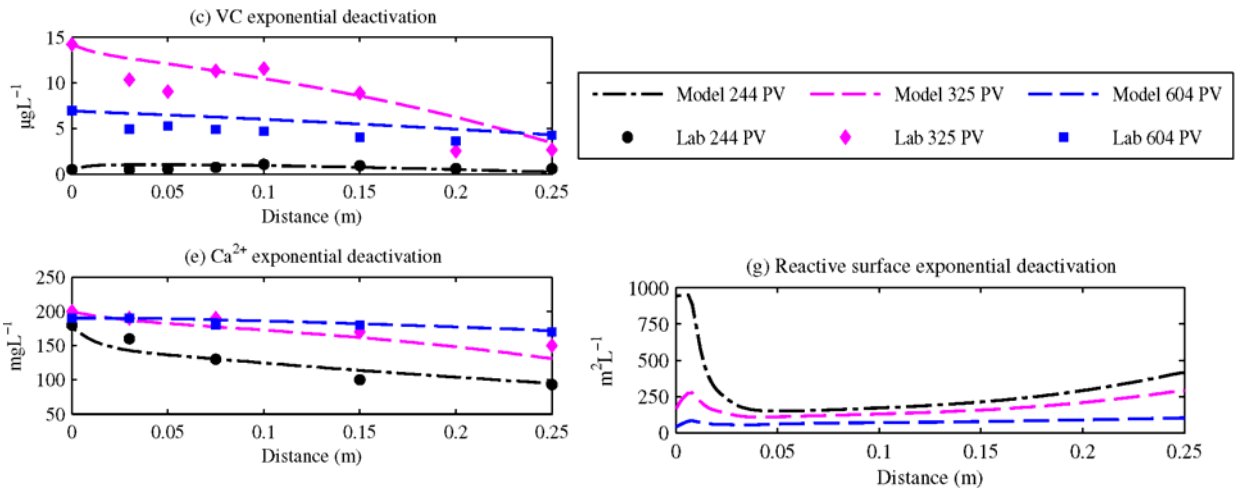


Figure 4: Lab-scale model validation results for estimating the longevity of a zerovalent Fe permeable reactive barrier. Symbols are measurements. Lines are model predictions.

Reactive transport models

The wetland model in FeFlow was evaluated/calibrated based on the following field data:

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

For example, Figure 5 shows two possible scenarios: (1) using only lab-derived parameters based on a zonation with four rates (with high rates in the peat layer and very low rate in the sand) and (2) calibrating the denitrification rate in the sand. Scenario 2 matches best the observations with a disappearance of nitrate between two set of wells. In the simulations, the denitrification rates only needed to be so high as to remove nitrate 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.

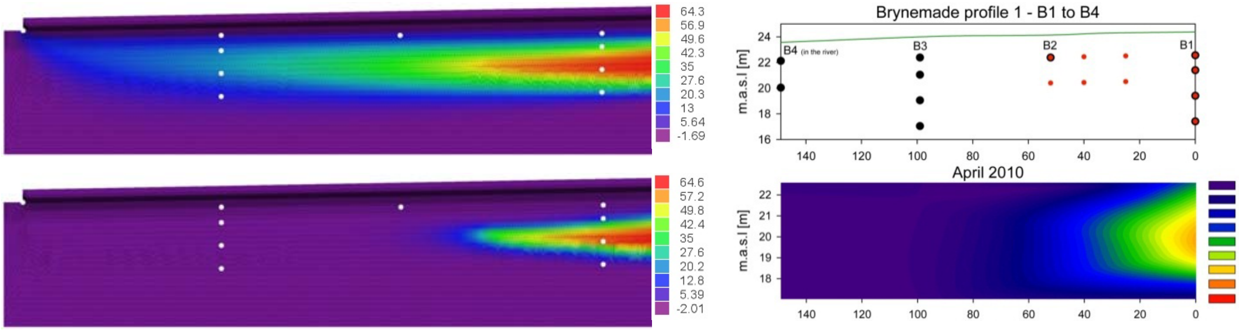


Figure 5: Feflow modelled scenario 1 (left top) and 2 (left bottom). The figure is with 3x vertical exaggeration. White circles are well screens. Measured nitrate profiles at Brynemade. Profile 1 – B1 to B4 (right top), measured nitrate April 2010 in existing piezometers (black dots) (right bottom). Nitrate is in mg/L.

Reduced reactive transport models for water management

A CAH polluted groundwater plume discharges in the Zenne river and 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 preliminary results presented below use constants that were derived in lab-scale experiments. The starting concentrations of *cis*-DCE and VC were set to 600 and 1560 μg/L, concentrations that were encountered at location SB-2 at the site. 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 are displayed in figure 6 for high flow rates (50 cm/d). The results show that the removal of DCE in the GRI is somewhat underestimated by the tanks-in-series model. 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.

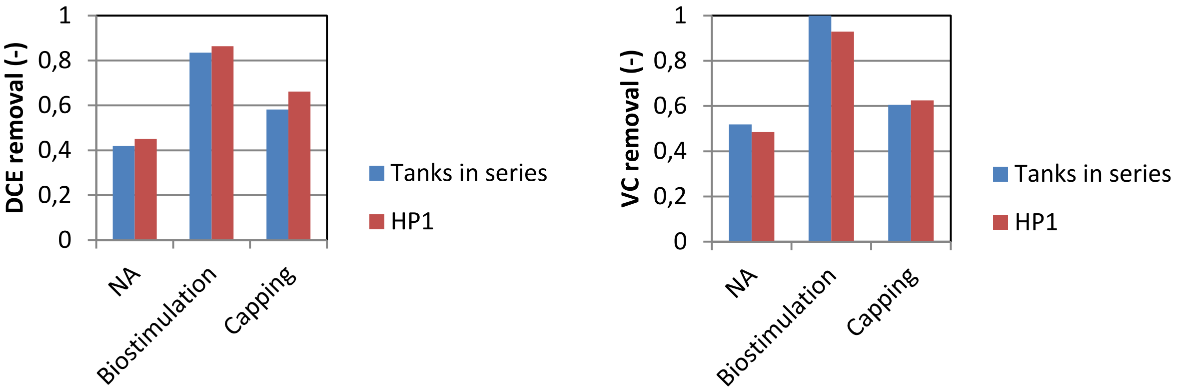


Figure 6: Calculated removal rates (fraction leaving GRI versus influent) using HP1 and the tanks-in-series model for three different scenarios of removal (NA = natural attenuation, aquifer biostimulation, and sediment capping) in the GRI.

CONCLUSIONS

The modeling work in the Aquarehab provided methods to design lab and field experiments for determining the performance of in situ groundwater remediation technologies. The following general conclusions can be drawn:

- a thorough schematisation of the subsurface is needed for site modeling, since the subsurface is heterogeneous in nature, which can affect performance of the technology and the model
- the determination of source zones and their history is crucial, since source term is important driver for observed concentrations in groundwater and design of the technology
- parameterisation of field models is an issue for the practical application of the models by consultants since a lot of parameters need to be estimated for technology performance assessment
- reasonable approximations are obtained with reduced models for performing first screening calculations of the performance for some in situ technologies, still the data availability may be an issue
- for uptake in decision support and water management groundwater body scale and river basin scale, field models cannot be used directly given the great level of detail in process description and amount of parameters needed, and simplified versions of the models need to be provided

ACKNOWLEDGEMENTS

This study was supported by the EU-project AQUAREHAB (Grant No. 226565)

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Extrapolation and transference of Remediation Technologies and generic approaches to new selected test locations - AQUAREHAB WP8

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8 SAPION, Belgium
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ABSTRACT: The last year of the AQUAREHAB project was foreseen to evaluate and test the generic character of some finding from the first three project years. More specifically, the aim was to apply generic rehabilitation guidelines, approaches and tools to other river basins/sites with other pollutant conditions and climates. With this goal in mind, four case studies have been selected and started focussing on: (1) The capacity of wetlands and soils in denitrification and elimination of pesticide; (2) Estimation of the long term performance of Zero Valent Iron (ZVI) Permeable Reactive Barriers to eliminate Chlorinated Aliphatic Hydrocarbons (CAHs) via a combination of improved lab scale tests and model tools; (3) The feasibility of micro scale ZVI injection into the subsurface to eliminate CAHs contaminants; and (4) The development of REACHER-local, a prototype management tool for groundwater management at a regional scale.

INTRODUCTION AND BACKGROUND

Within FP7 EU AQUAREHAB project, different innovative rehabilitation technologies for soil, groundwater and surface water have been studied and developed to cope with a number of priority contaminants (nitrates, pesticides, CAHs, BTEX and mixed pollutions) within heavily degraded water systems. Methods have been developed to determine the (long-term) impact of the innovative rehabilitation technologies on the reduction of the influx of these priority pollutants towards receptors like drinking water wells and surface water and links towards water management were made. WP8 of AQUAREHAB offered opportunities to extrapolate AQUAREHAB developments to other areas and sites, in order to test the robustness and generic character of the innovative rehabilitation technologies and the modelling tools developed during the project.

The subjects for extrapolation were determined 3 years after the start of the project, based on the results obtained. Different steps defined for WP8 were (1) preparing an inventory of potential extrapolation areas; (2) prepare, select and perform the extrapolation case and (3) prepare updated generic document based on the complementary acquired knowledge.

OVERVIEW OF EXTRAPOLATION CASES DEFINED WITHIN AQUAREHAB

In the first step 3 river (sub) basins were identified, as well as 3 sites contaminated with nitrate, 10 sites where chlorinated compounds were an issue, 3 sites where pesticides were measured and 2 sites with a mixed pollution. These account 21 cases of which 20 were described in some more detail in the project deliverable. Finally, 4 case studies for extrapolation were selected, which are summarized in Table 1.. Selected findings from the workpackages WP1, WP4, WP5, WP6 and WP7 were lifted to a next level. Finally, 15 out the 19 AQUAREHAB partners were involved in phase 2 of the project. In this table recent references of the technologies of phase 1 and first results of phase 2 of the project have been included

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)
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)

APPROACHES OF THE STUDIES AND RESULTS

Extrapolation case 1: Wetlands

The following phases have been performed for this extrapolation case study:

For nitrate studies the work comprised: (1) Monitoring of groundwater chemistry at 3 field sites ; (2) Selection of one field site based on groundwater chemistry for a more detailed investigation; (3)

Sampling of subsurface cores along a transect; (4) Determination of denitrification rates with the samples of the core (anoxic lab scale batch tests); (5) Monitoring the chemistry of groundwater in the field; (6) Modelling the validation; and (7) Improvements to the generic guideline.

The three field sites were located in the head water catchment of the Skjern River Basin in Mid-West Jutland, Denmark. They all belong to what is the Holtum sub-catchment, an approximately 126 km^2 large catchment. The river is here called the Holtum stream and is about 14 km long from the headwater to the outlet of the catchment. The Hyglid site was selected and two cores were sampled in May 2013. Denitrification tests have been finished and calculation of rates and modelling is on going. General results show a soil with less organic matter and denitrification potential than the previously studied site (Brynemade).

For pesticides studies, the following works were designed: (1) Survey of Moldova site; (2) Soil sampling campaign in Moldova; (3) Pesticide mineralization studies in wetland microcosm with Moldova soil; (4) Sampling campaign in Bernissem; (5) Pesticide mineralization studies in wetland microcosm with Bernissem wetland soil; and (6) Model validation; and (7) improvements to the generic guideline. The test with Bernissem soils have started and are ready to finish. Preliminary findings are shown in (Vandermeeren et al., 2013). The samples in Moldova have been obtained and studies have started.

Extrapolation case 2: ZVI-barrier

Activities envisioned for this case study are: (1) The collection and analyses of groundwater samples from 3 sites (Belgium, Spain & Italy) with the aim to select 1 site for further in detail study; (2) Sampling of larger volume of groundwater from selected site; (3) perform a column test according the updated feasibility test procedure with newly developed microscale ZVI; (4) derive kinetic parameter based on the collected data set; (5) Use of a numerical model and simplified model for longevity estimation, and comparison of the results; (6) Determination of the ZVI-barrier design parameters; (7) and improvements to the generic guideline.

From the three sites, the Belgian site was chosen and thus a large volume (120 L) of groundwater was sampled which was polluted with about 35 mg/L of TCE and about 10 mg/L of cDCE.. The column feasibility test was started in January 2013 at a flow corresponding to 25 cm/day. Once at least 5 concentration profiles were sampled and analysed, the column test was continued at a faster flow rate (corresponding with 200 cm/day). After more than 400 0.5 m pore volumes were pumped through the ZVI-column, the ZVI was still as reactive as fresh material. Kinetic parameters are being deduced and the longevity being estimated. During a workshop, non-modellers followed the modelling process with the aim to evaluate how accessible the developed numerical models are for non-modellers. It became immediately clear that a better elaborated user interface is at least needed, All finding will be used to update the generic guidelines.

Extrapolation case 3: injectable micro-scale ZVI (mZVI)

This extrapolation case comprises the following steps : (1) Selection of a suitable and accessible spot on the site based on additionally collected site information; (2) Pre-tests and calculations to prepare the design of the pilot tests; (3) Design of pilot test 1 where permeation of a mZVI dispersion via injection well is envisioned; (4) Design of pilot test 2 injection of an mZVI dispersion via high pressure direct push is envisioned; (5) Field work for 2 pilot injections – installation of wells and tools, injection; (6) Post injection soil core sampling to verify the fate of the inject mZVI; (7) Pre and post injection field monitoring to evaluate the impact on the pollutants (PCE) in the groundwater; (8) Improvements to the generic guideline.

An industrial site in Belgium, with a PCE groundwater contamination was selected as test site for this extrapolation case. A well accessible spot on the parking lot near the source of contaminants was selected based on samplings and chemical analyses.. Lab scale dose tests were performed to verify the reactivity of the different selected ZVI and the required dose of guar gum.

The field work comprised different aspects: Firstly, the injection well was installed by using a multilevel monitoring system (comprising iron-sensors, T-sensors and sampling points). As hydraulic tests revealed that the injection well was not suitable for the envisioned injection, it was decided to install a new well with an adapted design. Slug test results and water injections tests indicated that the second injection well was good. Secondly, two types of injections were performed: the injection of 50 kg of BASF iron (2µm) in 0.2% guar gum via the injection well, targeting permeation; and, the injection of 250 kg of Höganäs iron H26 (50 µm) in 0.45% guar gum via direct push technology, creating preferential flow paths and a radius of influence of 0.5 m.

Immediately after the injection, soil cores were taken for iron determinations via susceptibility and via hydrogen measurement after acid treatment. For the injection via the well, the iron seems to have reached a distance about 0.8 m far from the injection point. Significant amounts of iron were detected till mainly within 0.5 m from the direct push injection points, but occasionally also at a few meters distance. The long term monitoring is still taking place, but first results clearly indicate a conversion of PCE to lower chlorinated compounds and to ethane.

Extrapolation case 4: 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 work started with a Kick-off meeting in Berchem in June 2013 and inputs from other WPs were implemented.

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 & 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 (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.

CONCLUSIONS

Several studies have started in WP8 of Aquarehab project in selected sites to show the feasibility of extrapolation of results and modify generic guidelines obtained in the first part of the project. The updated guidelines will be made available via the Aquarehab web-site (**https://.aquarehab.vito.be**).

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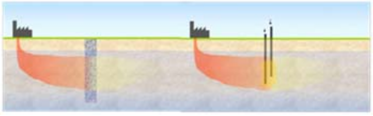

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