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Remediation Technologies and their Integration in Water Management

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Remediation Technologies and their Integration in Water Management

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Introduction

The quality of natural water resources 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/measures on different water-related aspects (point sources, groundwater, surface water, wastewater, prevention, ...), and coordination of these actions/measures. The Water Technology & Management Symposium aims at bringing together scientists, policy makers (local, country and European level), consultants, site owners, water managers and remediation companies who are working on or involved in water quality. The goal is to improve interaction between different disciplines as well as between people involved in different aspects of water management.

For the first edition of this symposium, barriers and potential approaches to come to the integration of groundwater and surface water in one water management, has been selected as important topic. 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 is a challenge for the near future. For this reason, lectures on both aspects have integrated in the programme.

Dealing with contaminated groundwater is an aspect of water management. Over the past 20 years, a variety of innovative remediation technologies have been developed as alternatives for dig & dump and pump & treat approaches. For instance in-situ technologies like Permeable Reactive Barriers (PRBs) and Reactive Zone (RZs) based on biotic as well as abiotic remediation processes have been studied and implemented to cope with different pollutants and pollutant mixtures in groundwater. An ongoing search for new materials, additives and concepts widens the application areas. The practical aspects of delivering reagents near the pollutants in the subsurface are being recognised more and more as crucial for the success of a remediation.

To include the impact of these remediation technologies in water management, knowledge on their sustainability, the associated costs, and their impact on the water quality in the wider environment and in time is required. Efforts in these directions have been made during recent years and will be presented and discussed during the symposium.

The Water Technology & Management Symposium aims at being a platform for different thematic symposia and different projects to disseminating their results. PRB/RZ-2012, and external conferences of the FP7 AQUAREHAB project and FP7 UPSOIL project are integrated in the event. The support of the SCARCE project and FP7 WATERDISS project is appreciated.

Wish you a pleasant and fruitful symposium.

Leen Bastiaens,
Conference chair

Session 1
Plenary session

Oral presentations

Importance of water remediation technologies and their integration in water management

Leen Bastiaens

Project manager & coordinator, Flemish Institute for Technological Research (VITO), Mol, Belgium

River basin management today and potential needs for the future: approach/challenges to deal with surface water as well as groundwater.

Lorenzo Galbiati

Water Manager ,Water management Catalan Water Agency, Barcelona, Spain – Invited speaker

Session 2
Reactive Iron Particles

Oral Presentations

Nanosized iron oxides in microbial BTEX oxidation: a novel concept for groundwater remediation

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Microbial reduction of ferric iron is a major biogeochemical process in groundwater ecosystems and often associated with the degradation of organic contaminants, as bacteria couple iron reduction to the oxidation of organic molecules like e.g. BTEX. Yet the high crystallinity and low solubility of iron oxides limits reduction rates. However, environmental nanosized iron(oxy)hydroxide minerals seem to have an unequally enhanced reactiveity potential compared to their bulk and highly crystalline parent materials of the same mineral.

Therefore, we examined the reactivity of nanosized, synthetic and environmental colloidal iron oxides in microbial iron reduction in static batch incubations and column experiments. Results Colloidial particles showed an enhancement of reaction rates of up to 2 orders of magnitude higher reaction rates than bulk phases, independent of the kind of mineral phase and or surface area. Furthermore, soil column experiments demonstrated the high persistence of nanosized iron oxides under simulated environmental conditions, opening the perspective for their technological application as electron acceptors in the remediation of BTEX and putatively PAH contaminated sites. First studies on the feasibility of this technology showed a 5x-fold enhancement of toluene oxidation after application of nanosized iron oxide particles to microbial incubations, as well as the possibility of custom-tailoring the subsurface mobility of these particles after injection into a contaminant plume.

Our results suggest that the injection of ferric iron nanoparticles as electron acceptors for microbial contaminant degradation in contaminated aquifers might develop into a novel bioremediation strategy creating in situ reactive barriers.

Remediation of CAHs with Guar Gum Stabilized Microscale Zerovalent Iron

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ABSTRACT: The present study focuses on the remediation of chlorinated aliphatic hydrocarbons (CAHs) by guar gum stabilized microscale zerovalent iron (mZVI) particles used in reactive zones. Results from previous lab-scale batch degradation experiments indicated that the presence of the guar gum had a positive impact on the mZVI stability, but significantly decreased chlorinated ethenes (PCE, TCE, cDCE) removal from artificially polluted groundwater by mZVI particles. The reactivity towards CAHs was only restored by intensive rinsing of the iron particles, simulating groundwater movement in the injection zone in the field, hereby removing the guar gum fragments from the particles. Here we report on similar tests performed with a different type of mZVI, who confirm the earlier conclusions. These findings are expected to have implication for field scale applications of the stabilized ZVI technology.

A column study has been performed under in situ conditions to evaluate to which extend the inactivation of the ZVI by the guar gum also occurs under continuous flow conditions. Five aquifer containing columns were set-up under different conditions. Based on the first data from the column experiments, the results from the lab-scale batch experiment are confirmed. A reduced activity of the ZVI has been observed in the column with guar gum stabilised iron. An even more reduced reactivity in the poisoned column containing stabilized guar gum, confirms that soil microorganism can degrade guar gum and that subsequent removal of the oligosaccharides by the groundwater flow (flushing effect) can reactivate the ZVI.

INTRODUCTION

Chlorinated aliphatic hydrocarbons (CAHs) such as perchloroethylene (PCE), trichloroethylene (TCE), and 1,1,1 trichloroethane (1,1,1-TCA) represent the frequently detected groundwater contaminants in industrialized countries. To remediate such sites, the use of zerovalent iron (ZVI) as a nontoxic material has been shown to be a promising remediation technique for in situ degradation of CAHs via abiotic reductive dehalogenation. Initially, granular ZVI particles were used to construct reactive barriers in the subsurface by digging and refilling a trench (Gillham and O'Hannesin, 1992). Recently, there has been growing interest in finer ZVI particles (micro- and nanoscale) because of their higher reactivity and the fact that they can potentially be injected in the subsurface as a slurry. The injection of solid particles in the subsurface, however, is much more challenging than initially expected, due to (1) aggregation of especially nano-sized ZVI particles, and (2) sedimentation of especially mZVI in the slurry reservoir, tubing and injection wells prior and during injection (Elimelech, 1995). In comparison with nanoscale (nZVI), microscale zerovalent iron particles are less expensive, do have a longer lifetime and pose less risk for human health. On the other hand, mZVI particles are less reactive than well suspended nZVIs. To enhance the mobility and prevent sedimentation of mZVIs during the injection process, the use of stabilizing agents such as guar gum is necessary.

The impact of guar gum as a low cost stabilizer on the CAHs-removal capacity of microscale zerovalent iron particles in a closed batch system has been previously reported (Velimirovic et al., submitted) where temporary reduced degradation of chlorinated aliphatic hydrocarbons by guar gum stabilized microscale zerovalent iron particles was observed. As the results of batch experiments might not be directly transferable to the field scale and other situations, further investigation was found necessary. Batch degradation experiment with other ZVI types were performed as well as a column experiment. The objective of this column study was to investigate the impact of guar gum on the ZVI reactivity in the presence of aquifer material under continuous flow conditions.

MATERIALS AND METHODS

Materials

The reactive micrometer-sized zerovalent iron particles used in this study were obtained from Höganäs (Sweden) with particle size distribution (D_{50}) less than 44 µm (batch experiments) and 58 µm (column experiments). For mZVI stabilization guar gum (Rantec Corporation, USA) was used.

Batch dechlorination experiments

Artificial groundwater for batch tests consisted of MiliQ water containing 0,5 mM $CaCl_2.2H_2O$ and 0,5 mM $MgCl_2.6H_2O$. After deoxygenating by flushing with nitrogen gas, 0,5 mM $NaHCO_3$ and 0,5 mM $KHCO_3$ were added. Under anaerobic conditions the pH was set at 7.0 and the artificial groundwater was spiked with approximately 5 mg/l of PCE, 5 mg/l of TCE, 5 mg/l of cDCE (cis-dichloroethene) and 5 mg/l of 1,1,1-TCA.

Batch tests were prepared in a 160 ml glass vials with butyl/PFTE grey septum containing 5 g of microscale iron and/or 0.6 g guar gum (Rantec Corporation, USA) and 100 ml of anaerobic artificially polluted groundwater, leaving a 60 ml headspace. Control conditions were set up following the same procedure but in the absence of mZVI particles and guar gum. The experiments were set up under anaerobic conditions and in quadruplicate, and were incubated (shaking) at groundwater temperature (12°C). Remaining concentrations of CAHs, ethene, ethane and acetylene were measured at the start (only blank) and after 7, 14, 21, 35 and 42 days. After 42 days, two vials from each quadruplicate were sacrificed for adding soil microorganisms and sampling was continued. After 70 days from the beginning of experiment dissolved sugars were flushed from bottles where microorganisms were added simulating groundwater flow. At each time point mass balances were made on molar basis (PCE + TCE + cDCE + VC (vinyl chloride) + 1,1,1-TCA + 1,1 DCA (1,1-dichloroethane) + acethylene + ethane + ethane) to determine whether sorption occurred.

Lab scale column dechlorination experiments

A column test was performed under anaerobic conditions to investigate inactivation of the mZVI by the guar gum. The lab scale column test was set up with representative groundwater and aquifer material from a Belgian site. Five flow through plexiglas columns were set up at controlled flow and temperature conditions (12°C). The first column system was completely filled with a mixture of aquifer material and filter sand. The second system contained the same filling material amended with 25 g/kg of mZVI, while the third was amended with 25 g/kg of mZVI as well as 2 g/kg of guar gum. Two dead control (DC) columns were included. One filled with only aquifer/filer sand material and the other contained in addition ZVI (25g/kg) stabilized by the guar gum (2g/kg).

The column systems were fed with real groundwater mainly polluted by 1,1-DCA (~ 5.5 ppm), TCE (~ 0.5 ppm), cDCE (~ 0.7 ppm) and 1,1-DCE (~ 0.4 ppm). Dead controls were additionally supplied with formaldehyde. Groundwater was applied to the columns at a flow rate of 17 mL/day using a Watson Marlov 205s peristaltic pump corresponding to hydraulic retention times of 17.2 (Blank - DC), 13.2 (Blank), 8.4 (mZVI), 12.5 (mZVI+GG) and 17.2 (mZVI+GG – DC) days. In time, influent and effluent samples were regularly taken for contaminant analysis. After 110 days, 5ml samples were collected in 12ml vials (previously capped and flushed with nitrogen) at sampling port located at every 10 cm along the column.

The experimental set-up is shown in Figure 1. Characteristics of the columns used for groundwater remediation are presented in Table 1.

Figure 1: Column experiment set-up.

Table 1: Characteristics of the columns used for CAHs remediation.

Characteristic	Blank (DC)	Blank	mZVI	mZVI + GG	mZVI + GG (DC)
Solid weight (g)	1034	1121	1051	862	871
Iron concentration(g/kg)	-	-	25	25	25
Guar gum concentration (g/kg)	-	-	-	2	2
Pore volume (mL)	292	224	143	213	203

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 each sampling point the redox potential (ORP) and pH were measured using a redox/pH meter (Radiometer).

RESULTS

Batch experiments

Lab scale reactivity experiments were performed to determine the impact of guar gum on the reactivity of another mZVIs type than previously tested. The presence of guar gum had a positive impact on the mZVIs stability, but test results confirmed the drastically reduced reactivity (increased half life times) of stabilized particles towards CAHs mixture (Figure 2). For the chlorinated ethenes (PCE, TCE, cDCE) only a very slow or no degradation was observed with guar stabilized mZVI. Subsequent addition of soil-microorganisms resulted in the cleavage of the polysaccharide guar gum into lower molecular fragments, but not in a restored reactivity. Guar gum is a potential energy source for soil microorganisms and can enhance the existing biodegradation of chlorinated solvents (Phillips et al., 2003; Liu and Lowry, 2006). Still, adding soil microorganism inoculums for guar gum breakdown has been found negligible for CAHs degradation in this specific test case, probably due to a lack of CAH-degrading microorganisms in the aquifer material used. The reactivity towards CAHs was only restored by intensive rinsing the iron particles, simulating groundwater movement in the injection zone in the field, hereby removing the guar gum degradation fragments from the particles. For 1,1,1-TCA, the situation is different. After stabilization, the degradation rate of 1,1,1-TCA was reduced but good removal was still observed. All these results confirm earlier findings (Velimirovic et al, submitted).

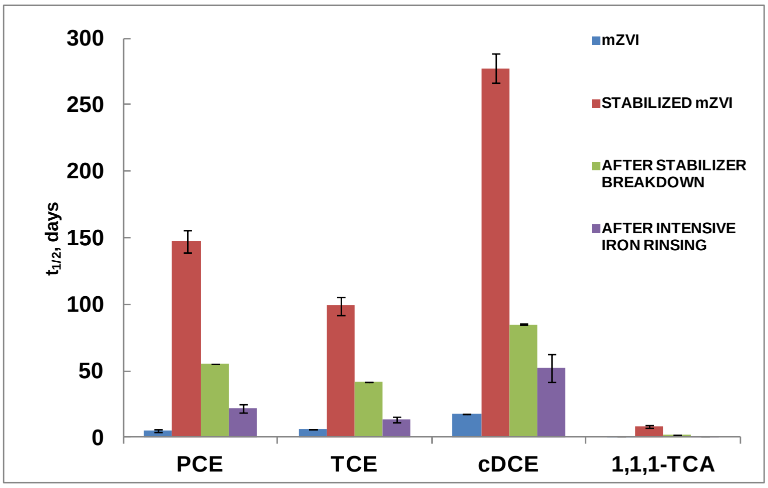

Figure 2: The half-lives of PCE, TCE, cDCE and 1,1,1-TCA degraded by mZVI stabilized by guar gum for different conditions in batch systems.

COLUMN EXPERIMENTS

Column experiments have been started to simulate in situ dynamic conditions and estimate the stabilized iron reactivity after injection. Concentration profiles of 1,1-DCA, TCE, cDCE and 1,1-DCE along the different test columns as determined after 110 days of operation are presented in Figure 1. In the presence of mZVI, TCE was rapidly degraded in absence and presence of guar gum. For cDCE and 1,1-DCA a partial removal was also observed under both conditions. The results measured here in the effluent are unexpected and need further investigation. Degradation of 1,1-DCE was observed in absence and presence of guar gum, but the degradation rate was clearly negatively influenced by the guar gum. The final degradation products were mainly ethane and ethane. Significant concentrations of VC and CA have not been observed.

In the dead controls with guar gum, a clearly reduced reactivity of mZVI was observed (results not shown). These findings indicate that soil microorganisms do have a function in degrading guar gum and that subsequent removal of the oligosaccharides by the groundwater flow (flushing effect) can reactivate the mZVI. This hypothesis is supported by the guar gum concentrations analysed at the effluent of the columns. Until 35 days of continuous operation, guar gum was measured in the effluent of the test column with stabilized mZVI. Afterwards no guar gum was detected in the effluent, while the effluent of the corresponding dead control still contained guar gum. Guar gum was probably used by soil microorganism as a carbon source.

Figure 2 shows the ORP and pH values measured in the effluent after 110 days. As expected, the presence of mZVI in the columns resulted in more reducing conditions (decreased ORP values) and slightly increased pH values. The changes are less pronounced than observed in the batch degradation experiments, explicable by the buffering properties of the aquifer material and the continuous operation mode.

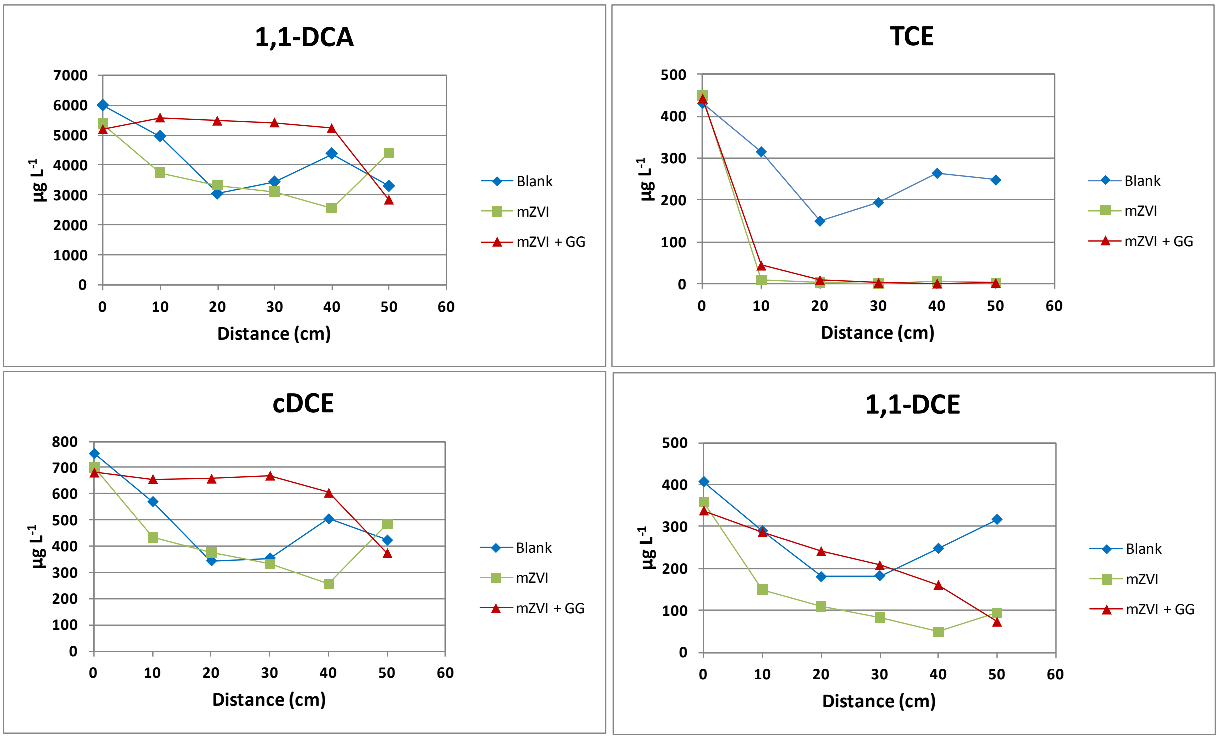

Figure 1: ***1,1-DCA, TCE, cDCE and 1,1-DCE reduction breakthrough curves after 110 days.***

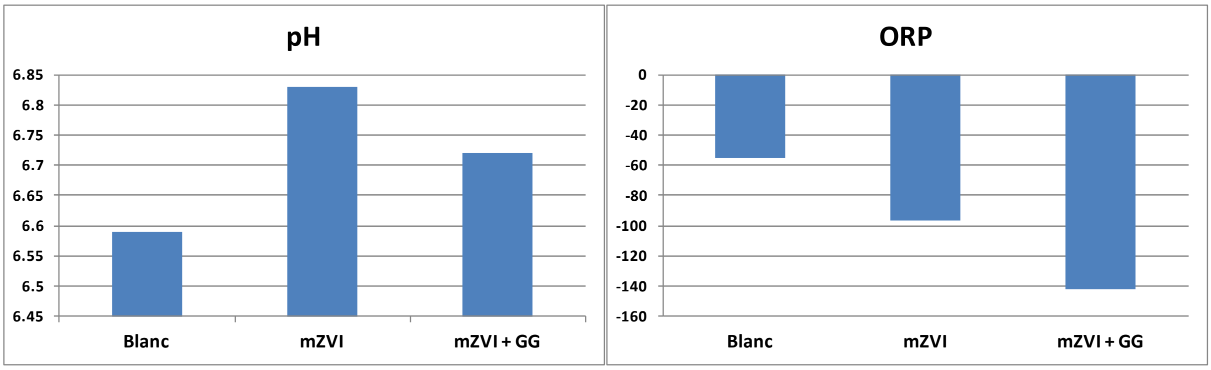

Figure 2: pH and ORP effluent values measured after 110 days.

CONCLUSIONS

The present study was designed to investigate the inactivation of the mZVI by the guar gum with different iron types and/or under different test conditions than previously studied. The batch degradation experiment confirmed earlier test results obtained with other mZVI types, being that the reactivity of mZVI is negatively influenced by the presence of guar gum as suspension stabilizer. This inactivation is temporal and the effectiveness of the mZVI for CAHs removal is restored by guar gum degradation followed by intensive rinsing.

Preliminary results of a column study demonstrated that, under conditions more closely to the real field conditions, guar gum can have a negative impact on the reactivity, but much less pronounced than was observed in batch degradation experiments. As such, guar gum used to stabilize mZVI particles, creating viscous slurry prior to the injection, can be considered as an interesting approach for in situ treatment of CAHs. The guar gum may have potential to serve as an electron donor for a potentially present CAH-degrading microorganisms, and stimulate as such CAH-biodegradation.

Experiments are still ongoing to deduce the effect of guar gum stabilized iron on the bacterial community in soil.

Finally, a pilot test in the field has been performed. Approximately 100 kg of guar gum stabilized zerovalent iron particles were injected into a test zone mainly polluted by TCE and 1,1,1-TCA.

ACKNOWLEDGEMENTS

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Injection of micro- and nano-scale zerovalent iron for source zone treatment: Laboratory and field evaluation

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The current study describes in-situ remediation activities with injectable zerovalent iron (Fe^0) that have been demonstrated on a laboratory- and field-scale level in the framework of the European CityChlor project. The objective was to compare the efficiency and feasibility of two types of injectable Fe^0, i.e. nano-scale and micro-scale iron, for in-situ remediation of soil and groundwater in a source zone contaminated with chlorinated aliphatic hydrocarbons (CAHs).

Laboratory-scale batch and column tests were performed to compare the reactivity and mobility of both iron types. Nano-iron exhibited a 4,5 times higher reactivity than micro-iron and a superior migration through porous media, as expected. However, the migration of micro-iron could be improved by preparing the iron slurry in a ~40% v/v glycerol solution. The primary function of glycerol was to increase the viscosity of the slurry, thereby lowering the settling velocity of the micro-iron particles. Without glycerol, rapid settling of the iron particles would inhibit an efficient injection. In addition, glycerol is expected to function as a substrate (electron donor), thereby stimulating biodegradation of the CAHs (electron acceptor).

Field injections were performed in March 2012 on an abandoned site contaminated with tetrachloroethylene (PCE), with groundwater concentrations up to 70.000 µg/L. The iron slurries were prepared and mixed under anaerobic conditions in a specially designed mixing vessel, to minimize iron oxidation. In total, 1 m^3 of a diluted nano-iron slurry (1 g Fe^0/L) was injected in three injection points from 2 to 8 m below ground surface (25 L per 0,5 m depth). Subsequently, micro-iron was injected as a diluted slurry (5 g Fe^0/ L) in three other injection points. For both iron types, the desired slurry volumes could be successfully injected without substantial short-circuiting (break-out) to the ground surface.

After injection, groundwater monitoring wells were installed at two depths in the middle of both injection triangles. During the drilling works, liners were collected at three different depths to verify the presence of the injected iron. Monitoring results will be presented on the symposium.

Rapid Reduction of Chlorinated Compounds using Triolein-Covered Nano Zero-valent Iron (nZVI)

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Nano zero-valent irons (nZVIs) are known to reduce the chlorinated compounds with high reactivity derived from their high specific surface area. However, nZVIs have a drawback of agglomeration or aggregation in practical application which can cause a diminution of specific surface area, and thus coating the particles with organic layer has been proposed as the effective method for stabilizing nZVIs. In this study, we focused on the sorption capacity of organic layer around nZVIs for the hydrophobic contaminants. Triolein was selected as the functional organic layer which could facilitate the mass transfer of hydrophobic contaminants to nZVIs by accumulation the contaminants in the solution as well as stabilize nZVIs and protect those from rapid oxidation in air or water. Morphology of triolein-covered nZVIs was observed using transmission electron microsocopy (TEM). Batch experiments were conducted to evaluate the removal mechanism of triolein-covered nZVIs for chlorophenol and its removal efficiency was compared with raw nZVIs and previous sorbents like activated carbons.

Zero-valent Iron Permeable Reactive Barrier for the containment of an hexachlorocyclohexane plume from the leaching of an Italian heavily contaminated soil.

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Hexachlorocyclohexane (HCH) is an highly chlorinated compound, mainly composed of four isomers (α, β, γ, and δ). It is classified as a priority organic pollutant due to its persistence and adverse effects on ecosystem and human beings. HCH has been heavily used as an organochlorine insecticide since 1940s, being commercially available in two formulations: technical HCH and lindane. HCH low aqueous solubility, relative high stability, lipophilicity and chlorinated nature contribute to its environmental persistence and resistance to degradation.

In this work, the degradation of dissolved HCH from a real heavily Italian contaminated soils with zero valent iron (ZVI) has been investigated through experiments conducted in batch and continuous mode.

Firstly, batch tests carried out on biphasic system, water and contaminated soil with and without ZVI, have clearly shown that ZVI was not able to directly degrade sorbed HCH in contaminated soil, which appeared as a slow-releasing contamination source. On the other hand, batch tests carried out on a leachate obtained from the contact of water with the real contaminated soil, showed the high ZVI degradation efficiency of HCH in the liquid phase.

Furthermore, in order to simulate leaching condition from soil to water, and consequently the contaminated eluate flow to an hypothetic permeable reactive barrier (PRB), a continuous experimental system was designed and build up, consisting of two connected columns containing respectively contaminated soil and a ZVI filling. The results showed that a PRB with ZVI can be applied as a containment wall and in the case of HCH contaminated plume.

Poster Presentations

Chemical reduction of PCE by zero valent iron colloids – Batch and column experiments

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In order to remove contaminants from the groundwater, a relatively new and promising method is the injection of nano-sized zero valent iron (nZVI) as suspensions directly into a source zone. In this way the reactant is brought in close contact to the contaminant phase and chemically reduces the dissolved chlorinated solvent before the solution is being transported with the flow of the groundwater. The reaction close to the pure phase strongly reduces the contaminant concentration in water and increases the rate of dissolution and hence the remediation time.

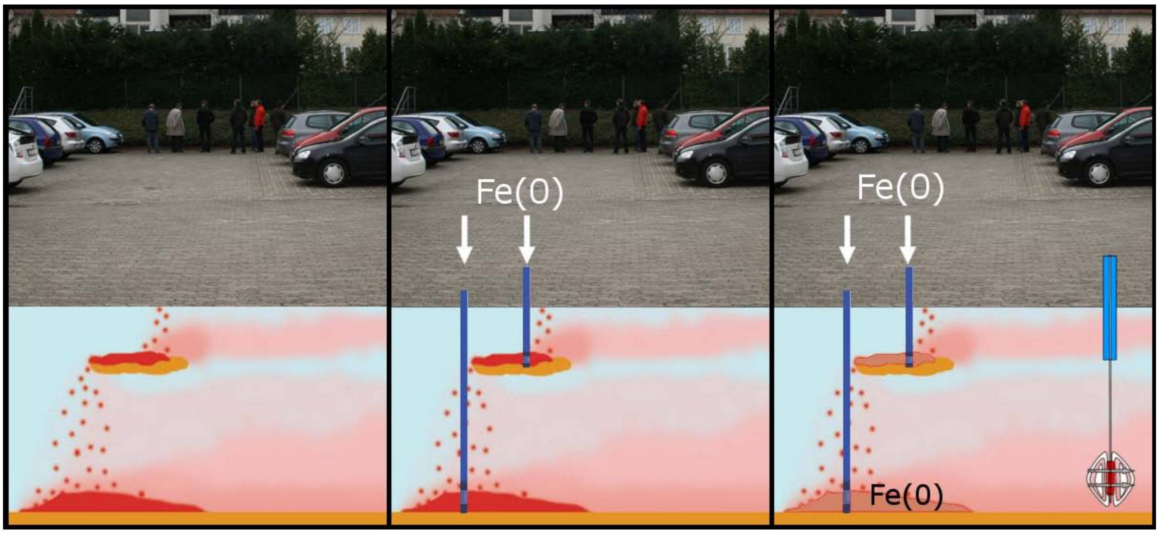

Figure 1: Principle of an application of nZVI for a source-zone remediation. The right image shows the measurement equipment to detect the distribution of nZVI in the subsurface.

In order to determine degradation performance and longevity of different iron particles, batch experiments have been conducted. However, the results are not directly transferable to the field scale since in batch experiments the contact between iron colloids and the chlorinated solvent is optimized by shaking or rotating the vial. But it is relatively simple to control the experimental conditions, and, therefore, it is possible to compare different nZVI suspensions to each other.

In porous media flow, the distribution of the chlorinated solvent is diffusion controlled resulting in a decrease in the availability of contaminants for the chemical reduction. In addition, the corrosion, which is self-inhibiting due to the production of OH- (increasing pH) in batch experiments, is not suppressed in column experiments, where the flow of “fresh” water keeps the pH more stable. Therefore, in batch the anaerobic corrosion is different to flowing systems as in column experiments or in the field.

This anaerobic corrosion shortens the longevity and, moreover, hydrogen as a by-product of these processes will be produced. If this happens in larger amounts, this hydrogen becomes a separate (gas-) phase and clogs the porous medium.

Figure 2: Columns during longterm experiments. 1 = Reduction of anaerobic corrosion due to addition of Ca(OH)2. 2 = Clogging of the porous media due to the production of hydrogen gas during the anaerobic corrosion (without Ca(OH)2).

Thus, column experiments have been performed as well and more elaborate column experiments are currently being set up. Preliminary experiments showed that the production of hydrogen gas could be reduced by adding burned lime (Ca(OH)2) to the nZVI suspension. Other experiments are currently performed to show, if the injection of Ca(OH)2 in the porous media as a pH increasing preconditioning of the aquifer is suitable. Also, the effect of Ca(OH)2 on the longevity and reactivity will be studied.

Several long term experiments have been planed for the column scale within the BMBFfunded project NAPASAN. Among these are investigations on the longevity of zero valent iron particles in porous media, either with pure phase present or in contact with dissolved contaminants.

Reactivity of nanoscale zerovalent iron towards chlorinated ethylenes: effect of silica coating

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ABSTRACT: This lab-scale study presents the effect of a silica coating on the reactivity of nanoscale zerovalent iron (nZVI) particles with respect to chlorinated ethylenes. Batch experiments were carried out to study degradation rates of chlorinated ethlenes from artificially polluted groundwater. Non-coated and silica coated nZVI particles were tested for their degradation potential towards selected chlorinated ethylenes: perchlorethylene (PCE), trichloroethylene (TCE) and cis-dichloroethylene (cDCE). Microscale zerovalent iron (mZVI) was included in the study as a control.

The commercial nanoscale zerovalent particles (NANOFER 25) were stabilized by environmental friendly silica using modified sodium water glass method. All reactive materials were characterized by ZVI measurement and N_2-BET analysis.

Batch degradation test results show that the silica coated nZVI particles were more reactive than the non-coated nanoscale iron. In the case of cDCE and TCE, the degradation rates are higher by one order of magnitude for silica coated nZVI than for non coated nZVI. The consumption of cDCE, the most problematic degradable contaminant, was described by rate constant related per equivalent mass of zerovalent iron 0.257 g/(Ld). Surprisingly, a fast reaction of silica coated nZVI was achieved despite the high pH≈(pH 11), which was given by character of the water glass. Both non-coated and silica coated nZVIs showed faster degradation rate up to two order of magnitude than mZVI even the dose of the mZVI was 10 times higher. Results suggest that the silica coated nZVI is effective for the degradation of chlorinated ethylenes and has a great potential to intensify remediation of contaminated sites.

INTRODUCTION

Application of nanoscale zerovalent iron particles (nZVI) supports remediation technologies for treatment of chlorinated aliphatic compounds such as chlorinated ethylenes from contaminated groundwater. The highly reactive nZVI particles lead to faster and more effective reductive dehalogenation of the chlorinated ethylenes than microscale powder. Their high reactivity and associated fast consumption make nZVI especially interesting for 'boosting' effects within a short time period. Moreover, nZVI particles can be directly injected in the subsurface. Because of the great surface energy of and magnetic attractive forces, the nZVI particles tend to form agglomerates, adhere to the ambient subsurface and react with reducible compounds in groundwater. The agglomeration causes problems with the transport of nZVI, and reduces its reactivity, which can reach level of the reactivity of microscale powders (Quinn at al, 2009).

Stabilizing coatings are applied to nZVI particles to improve colloidal stability and enhance a remediation effect of the technology. Nevertheless, some of these surface coatings change their reactivity towards contaminants. A convenient coating improves stability but does not decrease reactivity of particles (Phenrat at al., 2009). Nowadays, surface coatings based on silica are investigated to provide environmentally friendly and cost-effective stabilization agents which are also able to stabilize iron nanoparticles (nZVI, iron oxides). The principle of permeable silica shell formation on nZVI surface is that the molecules of mono-, oligo- and polymeric silica are adsorbed to the hydrated iron oxides of the nZVI particles in several layers at random cross linkage (Bergna et al., 2006). Depending on the conditions (pH solution, temperature, silicite concentration), the deposited silica on nZVI particles can inhibit or support the corrosion process of metal iron. Therefore the silica can slow or accelerate the redox reactions with contaminants which can affect degradation rate (Kohn T. at al, 2006; Powel at. al, 1997).

In this study we focused on the effect of silica coating on reactivity of nZVI particles to remove mixture of selected chlorinated ethylenes from an aqueous solution. The silica coating was prepared by the sol gel method of silica deposition on nZVI particles. The reactivity of silica coated nanoscale zerovalent iron (Si-nZVI) particles was also compared to the reactivity of microscale zerovalent iron (mZVI).

EXPERIMENTAL PART

Media

Artificial groundwater consisted of anaerobic autoclaved MilliQ water (Milipore, Symplicity® UV System) supplemented with $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $NaHCO_3$ and $KHCO_3$ to a final concentration of 0.5 mM each. Under anaerobic conditions, the pH was adjusted to 7.0. The artificial groundwater was spiked by pure phases of PCE, TCE and cis-DCE. The initial concentration of each contaminant was 5.5 ± 1 mg.L^{-1}. The chemicals cis-dichlorethylene (cis-DCE), trichloroethylene (TCE), tetrachlorethylene (PCE, 99+ %, extra pure, stabilized) were supplied by Acros Organics.

Zerovalent iron particles

The commercial available suspension of nanoscale zerovalent iron particles NANOFER 25 (NANOIRON Ltd.), the suspension of Si-nZVI particles and the dry mZVI particles BASF HQ micro-scale iron particles were used for a degradation experiment. The coating of nZVI was performed using the sodium silicate water glass method. Sodium silicate was hydrolysed by adding strong ion exchange resin to form silica resulting in a solution with moderately alkaline pH (≈ 8.5 - 9.5). The silica solution was introduced to the nZVI suspension and condensation of silica species on nZVI followed from oversaturated silica solution during several hours. For experiment we obtained the Si-nZVI mixture in gel form, which was directly used for degradation experiment.

Specific surface area (SSA) of the lyophilizated particles was measured using N_2-BET. The amount of Fe^0 was determined from the volume of hydrogen after the acidify mineralization of the particles in 1M HCl.

Degradation experiment

Batch experiments were performed to study degradation of chlorinated ethylenes by silica coated nZVI particles. The selected chlorinated ethylenes (PCE, TCE, cis-DCE) in an aqueous solution were degraded in 160 mL serum bottles. The bottles were filled by the nZVI suspension containing 0.245 ± 0.033 mg.L-1 of Fe^0 or dry mZVI particles (2.5 g) containing 2.21 g Fe^0. Anaerobic artificially contaminated groundwater (100 mL) was added to the vials under anaerobic conditions (nitrogen), leaving a 60 ml headspace and capped by Teflon lined aluminium crimp caps. The bottles were intensively shaken (110 rpm) at 12 ± 1°C in darkness. Control bottles without the nZVI particles demonstrated max 15 % loses of the contaminants within 6 weeks, which were mainly due to sampling. The average of triplicate measurements was used to determine each concentration point.

Chemical analyses

Once per week, chlorinated ethylenes were analysed via headspace measurements using a Varian GC-FID (CP-3800) (Varian CP_3800 with CTC-autosampler) equipped with RT-U-PLOT/DB-1 GC/RT-X-502.2 capillary columns. Hydrogen evolved from Fe^0 dissolution was quantified using a Trace GC MPT-10286 equipped with packed columns Heyesep Q and Carbosphere and TCD detector. At each sampling point the redox potential (ORP) and pH of the suspensions were measured using a redox/pH meter (Radiometer).

Determination of chlorinated ethylenes degradation rates

Experimental data were evaluated by the fitting of the pseudo-first-order kinetics equation in the program ERA 3.0. The pseudo-first-order kinetic constants Kobs were normalized to the mass concentration of Fe^0 in particles to obtain constants Km_{Fe0}. We decided to evaluate Km_{Fe0} because the amount of silica in the Si-nZVI suspension was influenced the weight of a material after drying.

RESULTS

Characterisation of zerovalent iron particles

According to the N_2-BET measurements, the specific surface area for the non coated nZVI particles was 18.50 m^2.g^{-1}. The silica coating of nZVI significantly enlarged specific surface area to 132.29 m^2.g^{-1}. Silica coating might also change pores distribution which could contribute to the increasing surface area. Specific surface area 0.95 m^2.g^{-1} was determined for mZVI particles. The storage nZVI and Si-nZVI suspension of contained 22.6 % and 20.4 % of dry iron particles/solid reagent. In the case of the nZVI suspension, the dry weigh contained approximately 84.8 % of metallic iron. In the case of Si-nZVI, the particles had 54.5 % of the metallic iron. Slow oxidation of the powdered mZVI particles during a long time period of handling resulted in 87.7 % of the metallic iron. Maintaining approximately the same amount of Fe^0 (2.45 g.L^{-1}) both nZVI systems, 2.5 g.L^{-1} of nZVI particles and 5.1 g.L^{-1} of solid reagent of Si-nZVI particles was used because of different percentage amount of Fe^0 determined in each nZVI's.

Effect of silica coating on nZVI reactivity

The main idea of batch experiments was to investigate the effect of silica coating on nZVI reactivity. Sı-nZVI particles were applied to degrade PCE, TCE and cis-DCE in an aqueous mixture (data not shown). The degradation potential of Si-nZVI was compared to the measured trends of the contaminants for non coated nZVI and mZVI particles. In the degradation system of the nZVI particles, TCE and cis-DCE were completely degraded after four weeks, while almost 14 % of PCE still left in the solution. On the other hand, in the presence of the Si-nZVI particles TCE and cis-DCE were completely removed after two weeks, while PCE was removed with full efficiency after four weeks. Finally, in the mZVI system (22.1 g.L^{-1} of Fe^0), 20 %, 95 % and 85 % of PCE, TCE and cis-DCE remained after 3 weeks.

All measured concentration trends were exponential which is typical for the reaction of pseudo-first-order. Evaluated kinetic constants Km$_{Fe0}$ normalized per Fe^0 mass are shown in Figure 1. Presented results show that the Si-nZVI degradation system degraded TCE and cis-DCE with the higher rate by one order of magnitude than the system with the nZVI particles. The degradation of the most problematic degradable cis-DCE was described by the reaction rate constant 0.257 d^{-1}.g^{-1}.L. Using the Si-nZVI particles, the degradation rate of PCE was 40 % faster than in the degradation system of the nZVI particles. Our result shows that silica coating significantly supports degradation of less chlorinated ethylenes which is favourable for contaminated sites containing intermediates after natural attenuation. It seems that the enlarged surface area and bigger amount of the solid reagent regarding to same mass of Fe^0 as nZVI could enhance the degradation potential of the Si-nZVI particles. Because silica can be corrosion active (Powel at. al, 1997), we suppose also the effect of the silica on the reaction rate of chlorinated ethylenes. As shown in Figure 1, the removal rate of all three contaminants by the mZVI particles was to two orders of magnitude slower than in the both nZVI systems. The removal rate of TCE and cis-DCE was slower up to three orders of magnitude than Si-nZVI. This effect was probably caused by a big difference in the specific surface area of the mZVI and Si-nZVI particles.

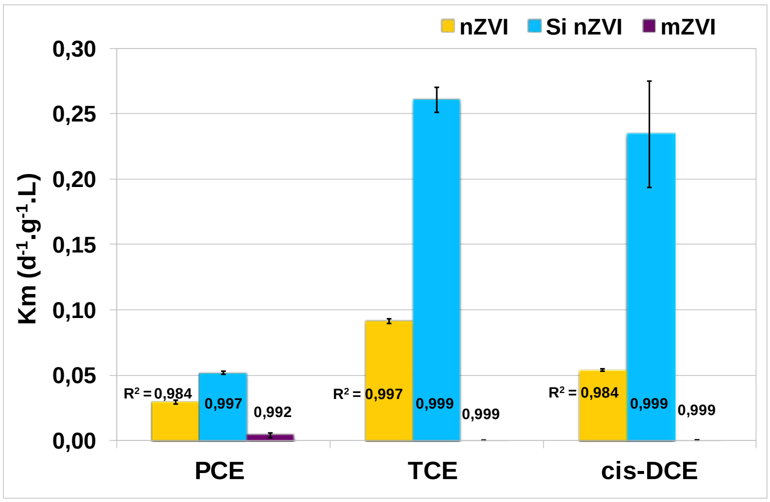

Figure 1: Comparison of rate constants (normalized per g.L-1 Fe0) for chlorinated ethylenes in studied degradation systems. Error bars are standard deviations.

In Figure 2 A and B, the reactivity of the Si-nZVI, nZVI and mZVI particles is confirmed by the nonselective reaction with water, which is showed by the increase in pH and decrease in ORP in aqueous solution within experimental period. In the case of Si-nZVI, final pH ≈ 11 was caused by the alkaline character of the silica coating. Even in such alkaline conditions, the degradation of the chlorinated ethylenes was finished. Probably bigger amount of the Si-nZVI solid reagent caused more intensive decrease in ORP than in the case of the nZVI particles. pH in the nZVI and mZVI degradation systems remained in value around pH ≈ 8.9, which is usual for an equilibrium of iron hydroxide in water. The alkaline pH was convenient to keep the stability of the silica coated Si-nZVI particles.

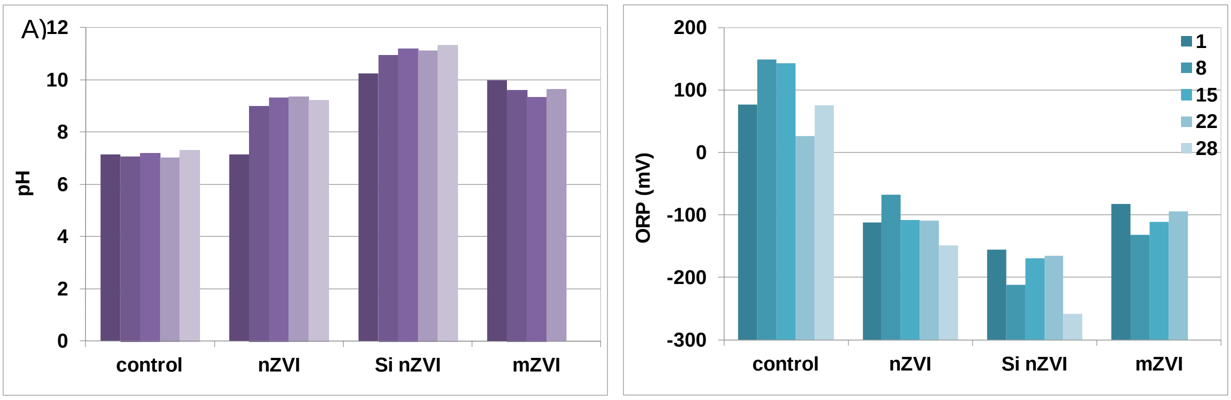

Figure 2: Changes of pH (A) and ORP (B) in studied degradation systems recorded in sampling days.

CONCLUSIONS

Based on the results of our batch experiments, silica coated zerovalent nanoiron particles (Si-nZVI) improved the degradation rate of tested chlorinated ethylenes (PCE, TCE, cis-DCE) in comparison with a non coated nZVI (NANOFER 25). Our results suggest that the amount of solid reagent, large surface area and corrosion effect of silica coating can contribute to the improved degradation over a longer time period. The advantage of Si-nZVI is that it degraded the chlorinated ethylenes according to pseudo-first-order kinetics. Results shows that Si-nZVI has large potential for the effective degradation of chlorinated ethylenes in contaminated subsurface.

ACKNOWLEDGEMENTS

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Estimation of Zerovalent Iron Particles Lifetimes via Direct Hydrogen Measurements

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Subsurface injection of nanoscale zerovalent iron (nZVI) as well as microscale zerovalent iron particles (mZVI) has been used for the in situ remediation of chlorinated solvents. In our previous batch degradation study, we reported the efficiency of different zerovalent iron particles (ZVI), particularly mZVIs in remediating chlorinated ethenes and ethanes (PRB/RZ-2010). It is shown that microscale zerovalent iron particles effectively degrade different chlorinated aliphatic hydrocarbons.

Further, one of the fundamental parameters for a successful application of mZVIs besides reactivity and mobility, is the lifetime of the particles for long-term impact assessment.

In this study the aging behavior of 26 different types of microscale zerovalent irons was investigated by measuring the amount of hydrogen produced as a consequence of anaerobic corrosion during the batch degradation experiments. Granular iron and nanoscale irons were included in the study as controls. The direct H_2 measurements were used to calculate corrosion rates and subsequently the lifetime of the iron particles. This approach was found more reliable than the estimation of the life-time via pressure measurements like described by Liu and Lowry (2006). In addition, the correlation between the corrosion rate and reaction rate constants of PCE, TCE, cDCE and 1,1,1-TCA was evaluated.

The first results show that the degradation rate constants are positively correlated with iron corrosion rate, but there are exceptions. This implies that the most reactive particles will have the lowest lifetime and they will be consumed faster after the injection in the field.

To confirm the data obtained during batch degradation experiments in liquid aquifer free conditions, hydrogen evolution was monitored during the batch tests in the presence of aquifer material and real ground water containing TCE and 1,1,1-TCA. Efforts were made to compose a model describing the corrosion behavior and lifetime of the particles, which may be useful to predict the impact of the inorganic composition of the groundwater on the lifetime/inactivation of the iron particles.

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

Emulsified nano- and micro-scale iron particles for in-situ Remediation of Chlorinated Ethenes in Groundwater

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Nano- and microsize metallic iron particles (ZVI) can be injected in groundwater to achieve in-situ reductive dechlorination of chlorinated solvents (CAH). They tend to aggregate and they may not only react with target pollutants, but also with reducible soil matter. Attempts were made to enhance the specificity and effectiveness of the particles by incorporating them in emulsified vegetable oil (EZVI). CAH present as NAPL may be taken up in iron containing vegetable oil micelles for a more targeted reaction of ZVI with the pollutants. We have evaluated various forms of emulsified reactive metal particles for in-situ reductive dehalogenation. These included nano-size ZVI, two types of micro-scale ZVI and micro-scale iron sulphide (FeS).

At first we have evaluated different recipes for emulsifying the reactive metal particles. Three types of vegetable oil, three non-ionic surfactants and water in varying ratio's were tested. With some of them the emulsions did not incorporate the metal particles inside the oil micelles, while we did achieve incorporation with a new recipe. Dilution of the emulsions led to the observation of metal incorporation in the micelles. The stability of the emulsions varied for different recipes.

We have investigated the reactivity of different formulations of EZVI by batch experiments for reductive dechlorination of TCE. Emulsified metal particles where less reactive than their non-emulsified counterparts. Nano-scale EZVI was more reactive then microscale EZVI. Significant degradation of TCE could still be achieved by some of the emulsified particles of nano-ZVI and micro-FeS. Formulations for which the metal particles where not incorporated in micelles showed higher activity than their counterparts which had ZVI incorporated in micelles.

Column tests were done to investigate the mobility in soil and effectiveness for reductive dechlorination of the best recipees of emulsified nano-iron. A first test series with columns filled with glass beads (500 µm diameter) included control columns with emulsified oil only, columns with EnZVI, columns with straight nZVI and a control with water only elution. Emulsified nZVI exhibited a much improved mobility compared to the straight nZVI. Straight nZVI resulted in faster degradation of CAH, but the EnZVI also achieved enhanced removal of TCE when compared to the control with only emulsified oil. A second column test was done with real soil for two recipes of EnZVI which were injected as 1/10 dilutions. One recipe showed improved mobility of EnZVI, the other type of EnZVI did not migrate through the soil. Effluents of columns fed with unamended nZVI had similar quantities of alkane reaction products than those with EZVI.

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Session 3

Wetlands & Riparian zones

Oral presentations

Mitigation systems to attenuate diffuse agricultural pollution: location and design choice

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ABSTRACT: In agricultural watersheds affected by diffuse pollution, limitation of fertilizer and pesticide application may not be sufficient to achieve good river water quality. After waterworks had to be closed in Brittany due to elevated nitrate concentrations in the river Ic (> 50 mg-NO_3 L^{-1}), the project *Aquisafe* has been initiated. The objective of *Aquisafe* is to reduce pollutant loads (nitrate and pesticides) from agricultural fields by implementation of near-natural mitigation zones at diffuse pollution hotspots at the head of watersheds. Simple and small solutions have to be designed in order to more efficiently reduce nitrate and pesticide concentrations in receiving rivers. In addition, a planning tool has to be developed to determine optimal locations to construct these systems. Finally, a tool to assess the effectiveness of these reactive zones on watershed water quality will be implemented.

In order to reach the first objective, design features are tested on three scales: 1) laboratory scale, 2) technical scale and 3) field scale. 1) In the laboratory, column experiments were conducted with different organic substrates at short hydraulic residence times (HRT). The efficiency for parallel reduction of nitrate and two common herbicides in Europe, Bentazon and Isoproturon, was explored (Krause Camilo, 2012). 2) In technical scale, two parallel swales were filled with the most suitable material determined in (1) for a one year test. The influence of HRT and temperature was investigated. For nitrate, high reduction could be achieved at short HRT; results for herbicides still have to be confirmed. 3) One infiltration ditch and two simple wetlands were constructed in Brittany (France), taking into account experiences from other scales. These systems are now monitored to investigate the effects of up-scaling.

Site locations were chosen based on a validated and repeatable GIS-based overlay method that prioritises zones of potential contribution to nitrate pollution (Orlikowski et al, 2011). Additionally, a new wetland module is being developed for the Soil and Water Assessment Tool (SWAT). It allows to predict impacts of wetland constructions on nitrate concentrations in receiving rivers; the module is now implemented but still has to be calibrated with in situ monitoring results.

The presentation will focus on results of the up-scaling approach, and will show how the tools of *Aquisafe* can be used for supporting the development of strategies at catchment scale.

INTRODUCTION

Diffuse nitrate (NO_3^-) and pesticide pollution from intense agriculture adversely impacts freshwater ecosystems, but can also pose a risk to human health if the water is used for drinking water production. A strategy often adapted to decrease nitrate and pesticide pollution is to limit fertilization and pesticide application. However, this is often not sufficient to reach the objectives given by the European water framework directive (WFD) or drinking water directive (DWD). Further countermeasures such as the implementation of mitigation zones can efficiently support pollution reduction if 1) they focus on critical source areas (CSA), 2) many of these zones can be implemented and 3) they are properly designed. Within the KWB project *Aquisafe 2*, different tools are developed to support an efficient implementation of mitigation zones: a simple GIS-approach for CSA localization for application in rural catchments with low data availability, and a wetland module for SWAT to predict the impact of wetland construction on nitrate concentrations in impacted rivers. Furthermore, work is carried out on mitigation zone design. Tests are conducted in different scales, laboratory, technical and field scale (in situ) in order to develop recommendations for efficient designs that result in the attenuation of nutrients and also selected pesticides. All these tools are tested in the Ic catchment, located in the northern part of the department Côtes d'Armor in Brittany, France. It covers an area of 92 km², land use is clearly dominated by agricultural use with 64% of cropland. Due to the intensive crop production and livestock farming, NO_3^- concentrations in the river exceed 50 mg L^{-1} almost year-round. Since the area has no major aquifers, river water was used for drinking water production until the beginning of 2009, when waterworks had to be closed as a result of high nitrate levels.

GIS METHOD TO LOCALIZE CRITICAL SOURCE AREAS OF DIFFUSE NITRATE POLLUTION

The aim of this part of the project was to assemble a universal GIS-approach for critical source area (CSA) localization for application in rural catchments with low data availability. Although methodologies for identification of CSAs are already available, they are generally difficult to apply. Numerical models (e.g SKOP & SØRENSEN 1998, KUDERNA et al. 2000) can be used but require many input data. Some Geographic Information Systems (GIS) (e.g., SOYEUX et al. 1993, JORDAN 1994, MUNAFO et al. 2005) require less data but are mostly site specific and therefore not transferable to other catchments.

In order to keep the GIS-approach as simple as possible and maximize transferability, existing concepts of catchment analysis and CSA identification (MUNLV 2005; KUDERNA et al. 2000; TREPEL & PALMERI 2002) were broken down to the most basic and available parameters. The idea of the method is to provide a ranking of areas within a catchment regarding their potential as NO_3^- sources for surface water, but not to predict actual NO_3^- concentrations or loads in surface waters.

This approach focuses on small to medium size catchments with fairly homogeneous climate conditions. The following five parameters are taken into account: land use, soil, slope, riparian buffer strips, and distance to surface waters. All parameters are classified into three classes of low (1), medium (2) or high risk (3) (Figure 1). For transferability, risk classes are defined by relating them to the full range of possible values for each parameter, independent of the range of values found in a given catchment. Technically the overlay is performed by averaging raster cells of the GIS layers. The resolution depends on the raster size of available input data. More details concerning this method can be found in Orlikowski et al. (2011). This method was tested at the Ic catchment and validated by comparing results with average NO_3^- loads at seven monitoring stations in the catchment (ten years of monthly NO_3^- and discharge measurements).

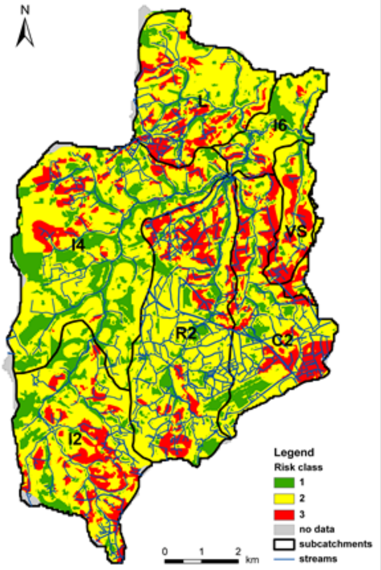

Figure 1: Overlay of five parameters for Ic catchment (from Orlikowski et al. 2011)

This GIS approach is of interest, given its relatively simple application, its high flexibility to varying data availability and resolution, as well as its high transparency of how final results were achieved. However, it has to be clear that GIS-based CSA identification can only be a first step, which has to be followed by validation in the field. Local information (soil type, topography, cooperation of land-owner, etc.) needs to be collected and cannot be replaced by a GIS-based approach alone.

SWAT WETLAND MODULE FOR PREDICTION OF WETLAND CONSTRUCTION IMPACT

The Soil and Water Assessment Tool SWAT is a long-term, continuous watershed simulation model. This model simulates land cover impacts using weather, soil, topography, and vegetation data as input parameters. Within *Aquisafe 2*, an additional wetland module was implemented in SWAT to support decision makers in developing catchment strategies including wetlands. With this module it can e.g. be evaluated, if potential wetlands may have a sufficient effect in protecting a river from diffuse nitrate pollution.

The module takes into account the nitrogen (N) turnover processes that were identified as critical in wetlands: mineralisation, nitrification, volatilisation and denitrification (Julich et al., 2010). Four different species of N (also computed by SWAT) are considered: organic N (ON), ammonium N (NH_4-N), nitrite N (NO_2-N) and nitrate N (NO_3-N). The considered N transformation processes are summarised in Figure 2.

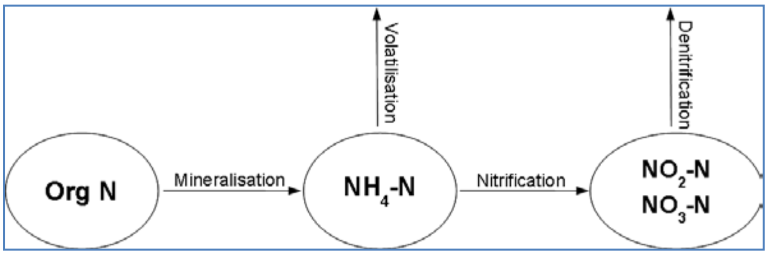

Figure 2: Turnover processes considered in the new wetland module (from Exbrayat et al. 2011)

The first application of the wetland module to the Ic catchment is realised in a very conceptual way. A large wetland is simulated at the outlet of the catchment ‘Ic Amont’, a 14.5 km² upstream sub-catchment of the Ic catchment. Its surface area is set to correspond to the total surface area which may be converted to wetlands over the next years in the Ic Amont catchment, i.e. 1% of the agriculturally used area, corresponding to 12 ha. This simulation gives an overview of the cumulative effect of the different wetlands to be implemented. The module is fed with the output of the SWAT model calibrated over a four year period from 1/1/2006 to 31/12/2009.

In general the reliability of a model is guaranteed if there is a good agreement between model predictions and observed data. The wetland module relies on some free parameters regarding the turnover processes in the wetland. With the lack of observation data, these free parameter values are difficult to estimate. In order to get an idea of the expected wetland denitrifying potential, a Monte-Carlo based sensitivity and uncertainty analysis simulation was performed.

The range of simulated global nitrate retention rates is shown in Figure 3, in which the red curve represents the daily nitrate-N inflow into the wetland as predicted by SWAT (Exbrayat et al. 2011). The daily nitrate-N outflow predicted for each of the different 10,000 wetland model runs are merged into the shaded area which represents the predictive uncertainty associated with the module parameters. Modelled nitrate retention rates reach up to 813 mg N $m^{-2}d^{-1}$, which is in good agreement with published results that range between -123 and 2493 mg N $m^{-2}d^{-1}$ (Périllon and Matzinger, 2010).

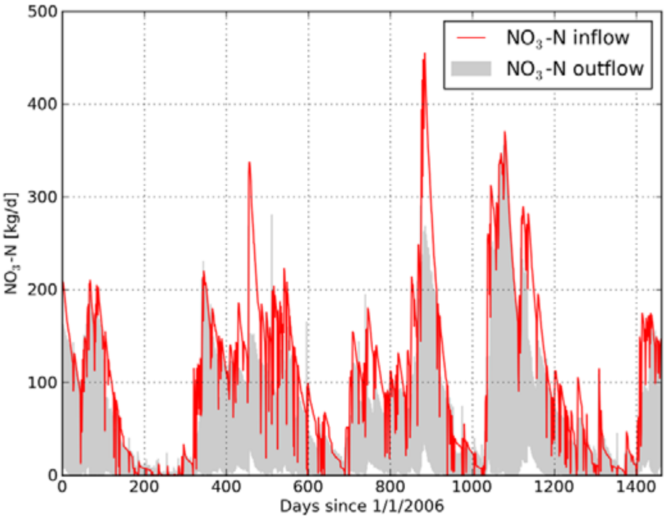

Figure 3: Nitrate-N balance in hypothetical wetland at the outlet of the Ic Amont sub-catchment

The wetland module always predicted denitrifying conditions with any of the randomly chosen parameter sets. This confirms that the wetland module is well designed and behaves like a natural wetland with mostly denitrifying conditions. However, the first application of the wetland model is still very conceptual and cannot be considered as a definitive statement about the effect of mitigation zones in this region. Hydro-chemical data that will become available in the near future will be used for model testing and verification. This data will further allow to calibrate the relevant wetland module parameters and quantify the effect of the pilot sites on the in-stream N balance.

IDENTIFICATION OF EFFICIENT MITIGATION ZONE DESIGNS FOR THE RETENTION OF RELEVANT HERBICIDES AND NUTRIENTS

Simple and small solutions have to be designed in order to reduce nitrate and herbicide loads more efficiently. In a first step, a report focusing on systems able to reduce pollutant loads in surface and tile drainage from agricultural fields (with particular focus on nitrate) has been compiled (Périllon and Matzinger, 2010). This review showed that a number of feasible options exist that have the potential to mitigate NO_3^- pollution from drained agricultural land. The most promising approaches with high removal potential were found to be controlled drainage, bioreactors at tile level, reactive swales, constructed wetlands and river-diversion wetlands. Most practical experience exists for constructed wetlands with surface flow (globally) and for controlled drainage (mainly in the USA), whereas the other systems are currently at an experimental state. In terms of absolute nitrate removal, wood chip walls parallel to tile drains and constructed wetlands with straw as carbon source were found to be most effective. However, for both systems only little experience exists, so further testing is necessary. Regarding cost efficiency, constructed surface flow wetlands with low construction cost (dam) and controlled drainage are most efficient. Whereas constructed surface flow wetlands can be implemented independently, drainage control structures need to be managed by farmers, which require their active cooperation and proper training. Regarding other contaminants such as pesticides or veterinary products, no recommendations can be made given the low number of existing studies. This is probably due to the large variety of possible pollutants and the high cost of chemical analysis.

Based on this review, adapted design features were selected for testing. Laboratory and technical scale experiments were carried out at the German Federal Environmental Agency (UBA). In laboratory scale (Fig. 4 (left)), column experiments with different promising organic filter materials (straw and bark mulch) were conducted at short hydraulic residence times (HRT). The substrate efficiency for parallel retention of nitrate (100 mg L^{-1}) and two common herbicides in Europe, Bentazon (50 µg L^{-1}) and Isoproturon (30 µg L^{-1}), was explored under high flow conditions, which are most critical for the effect of mitigation zones. The pollutants were constantly dosed to the inflow to simulate nutrient-rich drainage water with realistic average herbicide concentrations after application. The tests were conducted over a 12 month period to observe the impacts of substrate ageing on its potential as organic carbon sources and adsorbents. Based on the results obtained during laboratory column tests, technical scale tests (Fig. 4 (middle)) were designed. For technical scale experiments, two parallel swales were filled with the most suitable material for a one year test, and the influence of HRT and temperature was investigated. At HRT of few hours nitrate reduction ranged between 60 and 90% during summer, but decreased to 20 to 30% during winter months due to temperature decrease. At HRT of a few days nitrate reduction did not sink below 90% throughout the entire range of observed temperatures. The experiments show that with the tested design good nitrate retention can be achieved under high flow conditions, even at low temperatures. Comparable to results of column experiments, temperature-independent decrease of denitrification performance was observed over time due to ageing of the substrates. Herbicide results still have to be confirmed.

Figure 4: Up-scaling from laboratory- (left) to technical site- (middle) to field conditions (right)

In order to demonstrate the efficiency of simple designed wetlands in reality, field scale tests were designed and constructed in the Ic catchment (Brittany, France) consisting of one infiltration ditch (vertical flow filter in a constructed channel, Fig. 4 (right) and Fig. 5), and two simple wetlands (infiltration basin and surface basin, run in parallel). These systems are still monitored to test the effects of up-scaling. These tests focus on nitrate removal, as information on pesticide uses within the catchment is poor. The sites are monitored for nutrient concentrations (N and P species), water flows and general water quality parameters (temperature, conductivity, redox potential, O_2 and COD) at the inlet, outlet and within the systems to improve understanding of the processes involved in nutrient retention within the wetlands. Unfortunately, 2011 and 2012 were exceptionally dry years and only few data could be gathered. Nevertheless, until now 30% nitrate retention could be achieved, which corresponds to technical scale results obtained by UBA for temperatures <10°C. All observations have to be confirmed with further monitoring under normal precipitation conditions.

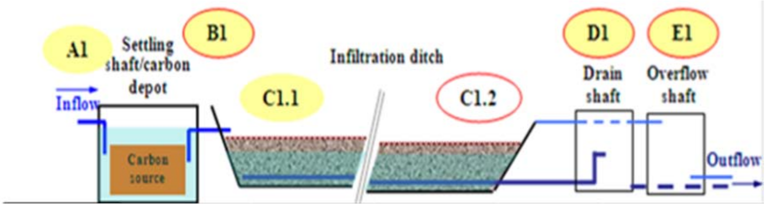

Figure 5: Longitudinal section of infiltration ditch with sampling points

CONCLUSIONS

Within *Aquisafe 2*, a simple GIS-approach for determination of critical source areas of diffuse nitrate pollution was developed, which is transferable to other catchments. In addition, a wetland module was implemented for the more complex Soil and Water Assessment Tool (SWAT). With these tools, new nitrate mitigation strategies at catchment scale can be developed and tested. Furthermore, recommendations for simple wetland design will be given based on experimental field tests. Designed systems should be able to remove nitrate but also chosen herbicides. All these steps can then be used to support decision makers for developing strategies for pollution control at catchment scale.

ACKNOWLEDGEMENTS

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The effect of seasonal disturbances on microbial degradation of pesticides in restored riparian wetlands

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Pesticides have been used intensively since the second half of the 20th century to control weeds and pests of all kind in agriculture. Diffuse pollution of surface waters by pesticides is a difficult problem to tackle. However, the recent trend to restore riparian wetlands may fulfill an important need for the improvement of surface water quality, including amongst others the mitigation of pesticides. Soil microbial communities that have been exposed to xenobiotics (like pesticides) may have adapted in such a way that they can metabolize these compounds. The goal of this project was to investigate a wetland in Sint-Truiden (Belgium) for its potential of breaking down mobile pesticides (MCPA and isoproturon) using radiolabelled tracers. Both were degraded by soil microbial organisms, but we hypothesized that seasonal disturbances such as freezing and drying may negatively influence the kinetics and extent of the mineralization. Soil samples ($n = 30$) were taken from the wetland in August and December 2011 and in January, February and March 2012 and were incubated in the lab at 20 °C. The wetland was flooded at all sampling dates except in January and a 10 days freezing period (-10 °C) preceded the sampling campaign of February. Whilst mineralization of MCPA was fast and efficient in all samples, the mineralization of isoproturon was much more heterogenous within the wetland. The abundance of the respective degraders and the nature of their metabolic pathways most likely are of major importance regarding these observations. Overall, a significant difference in mineralization of MCPA and isoproturon was found between the 5 sampling points, interposed by February's freezing period. The negative influence of a freezing period, as well as a period of drought, on the mineralization of the former pesticides was already observed in microcosm experiments in the lab, in which mineralization of MCPA and isoproturon was studied under flooded conditions. We noticed an even larger effect of drying on the mineralization of these compounds in the microcosm setup. No substantial drought period occurred thus far, which in the future may allow us to investigate the effect of drying on the mineralization of MCPA and isoproturon *in situ*.

Development of a dynamic MODFLOW model to assess the nitrate removal processes in the riparian aquifer of the North German lowland river Kielstau

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ABSTRACT

The Kielstau catchment in northern Germany, federal state of Schleswig-Holstein is situated in a lowland area and thus is characterized by flat topography, shallow groundwater, low hydraulic gradient and flow velociteis, high interaction between groundwaster and surface water, and high capacity of water retention in peatland and lakes. Kielstau is a rural catchment with prevailing land use arable land (56%), meadows and pasture (26%), only scarcely forested. The fraction of drained agricultural area in the catchment is estimated to be 38%.

To investigate the nutrient transport and transformation processes in a riparian zone, several monitoring campaigns have been set up along a transect. In order to support the interpretation of these data, a 3D MODFLOW model is developed for the riparian zone on the basis of piezometric measurements, river stage observations, and detailed DEM observations. The MODFLOW model allows to quantify the flux of the water as well as to assess the residence time. This information is fundamental to understand the transport and denitrification processes in the riverine aquifer. This paper describes preliminary modeling results.

INTRODUCTION

Surface-groundwater interaction is a critical component of the hydrology of riparian zones. The riparian corridors separating a terrestrial ecosystem from a riverine ecosystem are areas of major surface water-groundwater interactions. Due to their strategic locations they generally exert significant controls on water quality and quantity. Riparian zones intercept surface as well as subsurface flows and thus function as buffers for the river system. For instance, riparian zones significantly reduce nitrogen loads entering streams, by removing nitrate from the groundwater via many processes such as denitrification (Rassam et al., 2008).

In the riparian zone, surface water interacts with groundwater mainly in two ways: When the groundwater level is higher than the water level in the stream, groundwater flows are directed towards the stream resulting effluent flow. During flood events stream water levels rise in response to runoff and results water flow from the stream to the neighboring aquifer or floodplain. When the stream water level drops the infiltrated water slowly released back to the stream.

Dynamics of surface water groundwater exchange processes and associated ecosystem in river corridors clearly relate to hydrologic variability. The residence time of the water within the riparian zone determine the extent to which the riparian zone interacts with slope runoff which, in turn depends on the dominant flow paths operating in the area. If the residence time in the riparian zone is small there is a little opportunity for buffer zone processes to operate. Therefore, knowledge of the flow system in the riparian zone is essential for evaluating the role of the riparian zone processes on the water quality.
The main objective of this study is to develop a flow model that enables better understanding of surface and groundwater interaction and flow processes in a drained riparian wetland in northern Germany. It should be noted that surface water-groundwater interactions and the velocity distribution in the aquifer as determined by the flow model is by far the most important factor in controlling solute transport and leads to better understanding of solute removal processes in the riparian zone. Therefore this study will help to establish the connection between groundwater; nitrate and land use and contribute to better understanding of nitrate removal and transport in the riparian zone and to infer future changes.

METHODOLOGY

STUDY AREA

The study site is situated in the lowland catchment area “Kielstau” in the north of Schleswig-Holstein.

The studied riparian wetland area is about 0.15 km^{2} (appox. 750 x 230 m) and is drained by ditches (Figure 1). As shown in Figure 1, there are 11 ditches in the study area located perpendicular to the Kielsatu River that drains the riparian zone. In this study, because of lack of data we only consider three of the major ditches. As described in Schmalz et al. (2008), these ditches are of different ages, type and length. Ditch one (between well 1 and 3), constructed in 1999 has a length of 250 m and an average depth and width of 0.65 and 1.36 m respectively. Ditch four, (between well 4 and 6), constructed in 1990 has a length of 230 m and an average depth and width of 0.80 and 5 m respectively. Similarly, ditch eight (between well 7 and 8), constructed and partly redirected in 1996/1990 has a length of 130 m and average depth and width of 0.67 and 1.19 m respectively. Detail description about the study area can be found in Schmalz et al. (2008).

Field monitoring and data collection

During two days of field monitoring campaign (May 28-29, 2012) electrical resistivity survey along transect was carried out, temperature at different depths in the river bed and ditches were measured using T-stick temperature sensor and isotope samples were collected from the river, ditches and aquifer at monitoring wells.

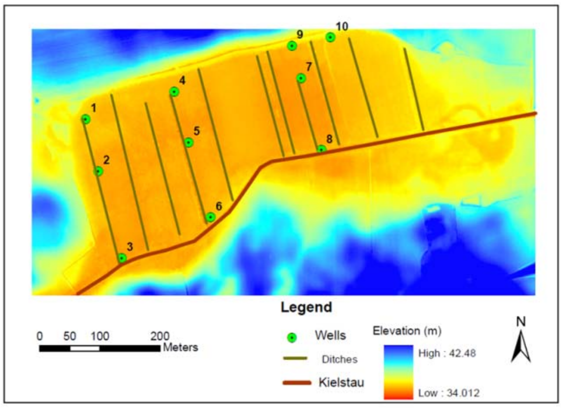


Figure 1: Investigated riparian wetland in the kielstau catchment

GROUNDWATER FLOW MODEL

Model description and design

The groundwater flow system was modeled using the MODFLOW code in Processing MODFLOW modeling environment. The model domain covers an area of 0.15 km^{2}. The finite-difference mesh consists of 111 rows and 209 columns with a uniform grid size of 4 m x4 m. In the vertical directions, the model consists of one layer with constant layer thickness. The thickness of the aquifer is 7 m. The 1m x 1 m DEM was resampled in to 4 m x4 m.

Boundary conditions

As there are no well-defined geologic and hydrogeologic features or physical boundary conditions along the western side, a specified head boundary conditions were used based on the observed water level data. Three wells namely well-1, well-9 and well-10 were used to define the western side boundary. In the eastern side kielstau River water level was used as boundary. In the north and south boundary a no flow boundary was assumed. In the vertical direction, the model is bounded by a recharge flux at the top and by impermeable layer at the bottom. The recharge fluxes were computed with the observed water levels in the wells as described in the next section. Figure 2a shows the conceptual model and the associated boundary conditions.

River

The Zenne River is represented in the model with river package. The river package needs river bed elevation, river stage and conductance of the river bed material. River bed elevations are available along the reach on some points. These points are linearly interpolated along the entire reach to get the river bed elevation for every grid cell. Weekly measured river stage was obtained from stage measured close to the end of ditch one.

The river package allows the river cell or node to be a sink if flow is toward the river (gaining stream) or a source if flow is out of the river (lossing stream). River fluxes are calculated by the model using a riverbed conductance term and the driving difference in head between the river stage and the calculated groundwater elevation in the cell. However, if the groundwater elevation drops sufficiently below the riverbed, the conductance term becomes limiting and further drops in the calculated groundwater elevation do not influence the flux. The riverbed bottom elevation was taken as one meter below the actual riverbed elevation. The river bed conductance term is a function of the riverbed vertical hydraulic conductivity and the riverbed geometry within the cell.

Drainage

The MODFLOW drain package was used to simulate the effect of the drainage ditches on the groundwater flow regime. MODFLOW drain package was developed to simulate agricultural tiles that removes water from an aquifer at a rate proportional to the difference in water level(head) between the aquifer and some fixed drain elevation, as long as the head in the aquifer is above that elevation (Harbaugh, 2005; McDonald and Harbaugh, 1984). If the head in the aquifer falls below that of the drain, no additional water removal occurs. In other words, the drainage level is assumed to be equal to the highest level groundwater will reach before it is discharged.

In this study, drain elevations were fixed based on the measured water level at the two ends of the drainage ditches and the drain elevations in between these points were linearly interpolated.

In addition to a drain elevation, the drain package needs the drain conductance to be specified. This lumped parameter incorporates information on characteristics of the drain and its immediate surroundings, as well as the head loss between the drain and the aquifer (Harbaugh, 2005; McDonald and Harbaugh, 1984).

Starting values for drain conductance were used from literature and adjusted during calibration.

Aquifer Parameters

The various aquifer parameters, such as hydraulic conductivity, and specific yield/ specific storage, were estimated and assigned into the model. Hydraulic conductivity is one of the highly variable parameter in space. In most of the cases our knowledge regarding the values of hydraulic conductivity parameter is limited to randomly located point measurements. In this study we used two zones of hydraulic conductivity (Figure 2a) to represent the spatial variation in hydraulic conductivity field.

In addition to hydraulic conductivity, transient flow simulation requires data on specific yield for unconfined aquifers. While specific yield is the volume of water that an unconfined aquifer releases from storage per unit surface area of aquifer per unit decline of the water table, specific storage is the volume of water that a confined aquifer release from storage under a unit decline in head.

Recharge

Groundwater recharge estimation is one of the key components in any model of groundwater flow and contaminant transport model. Various methods for recharge estimation exist in literature, the subject of choosing appropriate techniques for quantifying groundwater recharge is addressed by Scanlon et al.(2002). In this study groundwater recharge is estimated using water-table fluctuation method and compared with recharge estimated using existing SWAT model (Figure 2b) and the later one was used.

Water-Table Fluctuation Method

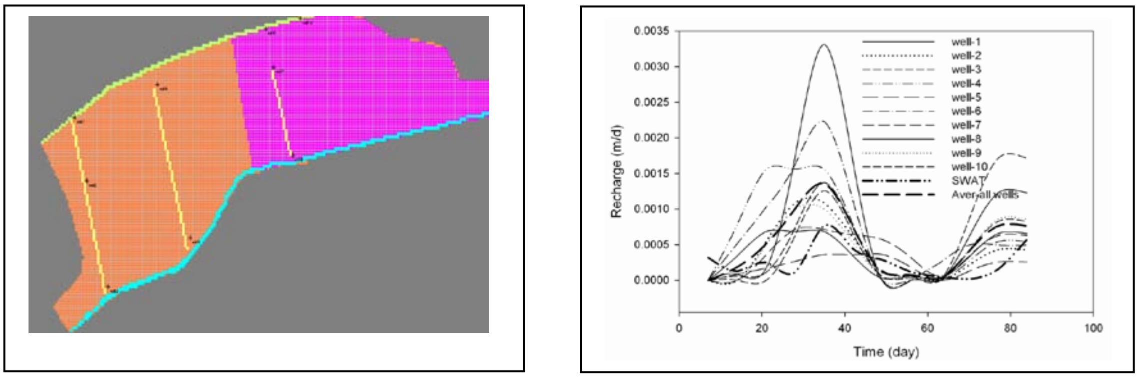
The water fluctuation method is based on the hypothesis that a rise in groundwater levels in the unconfined aquifers is due to recharge water arriving at the water table. Recharge is calculated as (Healy and Cook, 2002).

— —-------------------------- (1)

Where Sy is specific yield, h is water-table height, and t is time.

is equal to the difference between the peak of the rise and low point of the extrapolated antecedent recession curve at the time of the peak.

According to Healy and Cook (2002) the WTF method is best applied for short-term water-level rises that occur in response to individual storms. These conditions usually occur in regions with shallow depths to the water table.



(a) (b)

Figure 2: Model boundary and zonal array of hydraulic conductivity (a) and recharge estimated using WTF method and existing SWAT model (b)

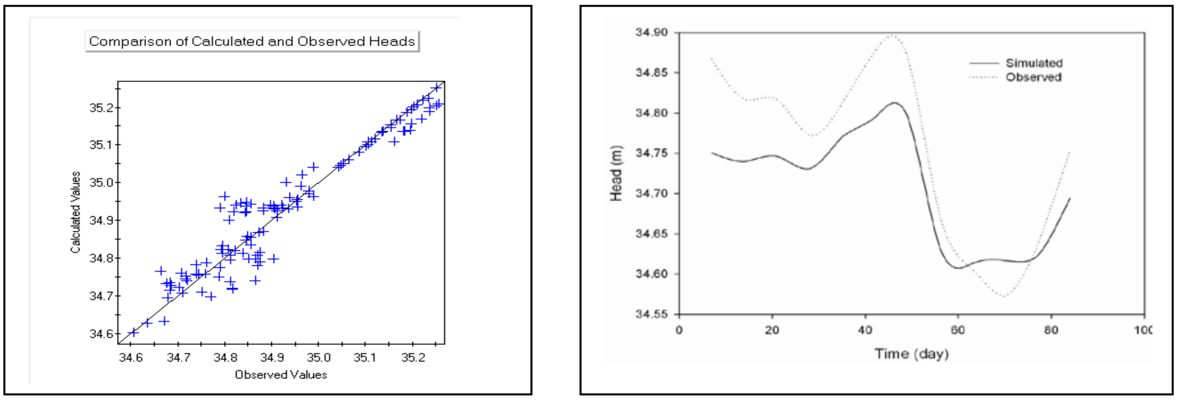
RESULT AND DISCUSSIONS

Model calibration

The groundwater flow model was calibrated using observed heads from seven monitoring wells measured from January 2006 till February 2006. The calibration was performed using the automated parameter estimation code PEST (Doherty et al., 2000). Steady state model was first calibrated so as to create steady state head solutions for initial conditions for transient model calibration. Use of model-generated head values ensures that the initial head data and the model hydrologic inputs and parameters are consistent.

The transient model was set up with a weekly stress period. The transient model was calibrated by adjusting the specific yield and using hydraulic conductivities of the steady state model. The calibration was carried out based on 84 groundwater heads measured in seven observation wells. The hydraulic conductivity values found during model calibration for the two distinct zones ranged between 1 m/d (zone 2) - 2.85 m/d (zone 1). A specific yield of 0.14 measured in the laboratory was applied uniformly to the entire model. The drain conductance found in the calibration were 25, 150 and 70 m^2/d for ditch one, four and seven respectively.

Figure 3a shows the comparison of the measured and observed groundwater heads. It shows a good agreement between the observed and simulated groundwater heads with a root mean square error of 0.06 m and a mean absolute error of 0.048 m. The observed and simulated heads are uniformly scattered around the mean of the observation indicating that there is no systematic bias. The narrower the area of scatter around 45^0 line, the better is the match between observed and calculated values. For transient model, observed values were superimposed on calculated hydrograph to illustrate any temporal trend in the match between observed and simulated values. Figure 3b shows the observed and simulated head during the simulation period for observation well 3, which is located around end of ditch one. Result shows that the model was able to capture the temporal fluctuation of the observations.



(a) (b)

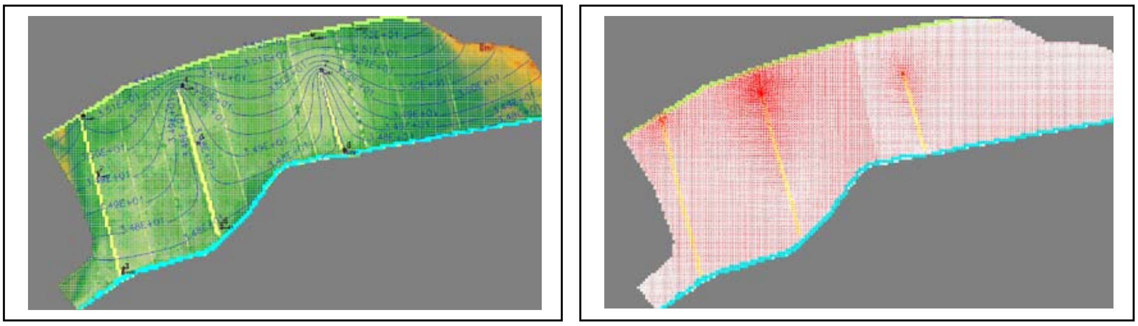
Figure 3: observed vs simulated heads for all simulation times (a) and head time curve at well 3 close to the end of ditch one (b)

Flow paths and residence time

Residence time is the main factor that control nutrient dynamics in the riparian zone. We therefore, require a better three-dimensional (3D) physically based modeling of flow paths within the riparian zone and improved field survey techniques to support the modeling.

The groundwater model simulates hydraulic head in three dimensions, and allows analysis of groundwater flow direction and groundwater budgets anywhere in the model area. Groundwater in the Kielsatu area flows generally from North West to South east following the slope of the riparian wetland, but drainage ditches alter these flow paths. Figure 4a shows simulated water table contours for the first stress period.

After the flow model was calibrated, path line and travel time analysis was undertaken. Figure 4b shows the path lines calculated using MODPATH (Pollock, 1994). As it can be seen in figure 4b at the beginning of the drainage ditches, many flow lines converge showing that the groundwater flow paths from the specified head boundary entering the ditches.



(a) (b)

Figure 4: Simulated hydraulic head during first stress period (a) and Groundwater flow direction using PMPATH

Water Balance

In addition to water levels, MODFLOW prints a water budget for the entire aquifer system. The zonal budget package calculates sub-regional water budget using the results from the MODFLOW simulation. The budget lists inflow to and outflow from the aquifer system for all hydrologic features that add or remove water.

The water balance of the model for January 2006 to March 2006 is as follows: The total recharge to the riparian wetland is 88 m^3/d. The total inflow from the constant head is 38 m^3/d and the total outflow through river leakage and drains is 12 and 36 m^3/d respectively. The subsurface outflow to storage holds the major share and it accounts about 78 m^3/d.

Figure 5 shows the river aquifer exchange at closest cell to river stage measuring point, at the downstream end of ditch one.

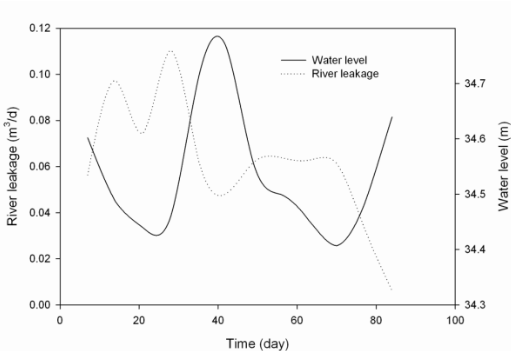


Figure 5: River-aquifer exchanges at the cell end of ditch one and water level of Kilesatu River at the same location

CONCLUSIONS

Detailed 3D groundwater model was constructed for the Kielsatu riparian zone for the period of three months (January - March) year 2006 using temporally distributed recharge as a main constraint. The distributed recharge together with a variable river stage helps to fully capture the transient nature of the groundwater system and to quantify the exchange fluxes between the river and the groundwater system. Hence, a transient groundwater flow model would capture better many of the dynamics of the drivers that ultimately dictate the transport of nitrate in groundwater.
The exchange fluxes are highly governed by the recharge in the area, the precipitation in the catchment and the river stage.

As additional data become available, particularly at a finer temporal scale, the stream-aquifer interaction will be explored in more detail.

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Aerobic and anaerobic mineralisation of pesticides in sediment from a reconstructed wetland

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Reestablishment of wetlands has been used in many countries as a restoration technology to reduce the load of nitrate to rivers and lakes. Little is known however, about the potential of such re-established wetlands to remove pesticides transported through the wetlands into surface waters. The aim of our research was to study mineralisation of pesticides at the redox conditions prevailing in the wetlands at the border between an agricultural area (Christmas tree plantation) and a reconstructed wetland, along the Odense River, Denmark. The Odense River has been brought back to its original meandering track, and the river bed was raised resulting in frequent flooding of the adjacent wetlands. The redox conditions of the wetland was characterised by measuring O_2, NO_3^-, SO_4^{2+}, Fe^{2+}, Mn^{3+} and other redox sensitive parameters in water samples from 50 established monitoring wells. Sediments were collected as cores extending from the surface down to 6 meter depth. The potential for mineralisation of ^{14}C labelled benzoic acid, MCPA, isoproturon and bromoxyniloctanoate in the sediments was determined using sealed deep-well micro plates combined with digital autoradiography, a new technology allowing the analysis of 492 small (0.5 g) subsamples simultaneously.

Both aerobic and anaerobic conditions were found at the border between the wetland and the agricultural area, while anaerobic conditions dominated in the wetland itself. Aerobically, MCPA, isoproturon and bromoxyniloctanoate were all mineralised in the topsoil and MCPA to a certain extent also in deeper sediments. MCPA was also mineralised at denitrifying-, but not at iron-reducing conditions. At iron reducing conditions only bromoxyniloctanoate was mineralised and only in one sample from a depth of 1.2 m. No mineralisation of isoproturon was seen either at denitrifying or iron-reducing conditions. Benzoic acid, used for measurement of the general metabolic activity, was mineralised in all samples at all redox conditions.

To conclude, the most efficient mineralisation was seen at aerobic conditions for all compounds. However, at least some pesticides were also mineralised at denitrifying and iron-reducing conditions indicating an hitherto unknown potential in wetlands for anaerobic natural attenuation of pesticides.

Poster Presentations

Study of groundwater denitrification in riparian zones by using soils from a wetland in the Ebro river basin

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Riparian zones have been used as natural systems to decrease nitrates present in groundwater that discharge to rivers by enhancing anoxic conditions. In order to perform denitrification, batch experiments using wetland soils with high content of organic matter and microorganisms, and high quality Dissolved Organic Carbon (DOC) usually show a fast capacity of denitrification. At field scale, low vertical hydraulic conductivity in the vadose zone of the soils is also needed in order to increase the contact time between the infiltration water and the soils and increase DOC that finally reaches the groundwater.

In previous works [1], the assessment at laboratory scale of the denitrification capacity of a wetland soil in which Phragmites have been present during years placed in the Sebes Natural Reservation of Flix, (Tarragona, Spain) was performed. The results pointed out that batch denitrification under anoxic conditions using these soils was possible, but a continuous setup were a thin layer (5 cm) of this soil irrigated with water was unable to perform denitrification.

The objective of the present work is to study the feasibility to increase residence time of irrigated water in order to obtain higher concentrations of dissolved organic matter and obtain better anoxic conditions for denitrification. Four types of soils S-01 (decomposed soil with submerged *Phragmites* in long contact time with water), S-02 and S-03 (wet superficial soil with vegetal material at two depths (0-50 and more than 50 cm) and S-04 (dry soil and dry reed zone) were studied for activation of riparian zones. S-02 soils showed the best capacity for denitrification (18.6 to 30.8% of nitrate elimination) and high levels of DOC, with consumptions similar to glucose during denitrification. Furthermore hydraulic conductivity values obtained for soil S-02 were 7.04 m/d and for soil S-03 $1.1 \cdot 10^{-2}$ m/d, indicating a high conductivity for the denitrifying soil that could be balanced with S-03.

A continuous flow system using 17 cm soil type S-02 in top layer and 3 cm of S-03 (peat soil) in a secondary layer was used to decrease the vertical hydraulic conductivity of the vadose zone and mimic the activation of a riparian zone.

Denitrification experiments were performed in the described setup. In a first period, a solution that consisted in 25 mg/l of NO_3^-, 50 mg/l of SO_4^{2-} and 50 mg/l Cl^- was used. Episodes of vertical infiltration of water were mimicked by showering 2.5 liters of deionised water during 30 minutes. Irrigated water was retained 2 hours before reaching the saturated zone. Solution was pumped through the system at 3 ml/min the first 314 hours and after this period was changed to 1 ml/min.

Excess of DOC was leached from the soil in a pulse from 100 to 150 h that allow removal of 9 mg/l of NO_3^- (36%) of initial nitrate. After this pulse DOC and denitrification decreased, probably due to the lack of organic matter. Reduction of flow to 1 ml/min allowed a more continuous level of DOC but denitrification was more oscillating with peak values close to 50% and valley values around 20%. As a conclusion, similar denitrification results that in batch systems were obtained. Denitrification was incomplete, probably due to the poor quality of vegetal organic matter.

The present research work has been co-funded by the EU-project AQUAREHAB (FP7 - Grant Agreement Nr. 226565)” and project ATTENUATION (CGL2011-29975-C04-03, Natural and Induced Attenuation of groundwater pollution from agricultural and industrial sources) funded by Spanish Ministry of Science and Innovation.

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Arsenic retention in subsurface flow constructed wetlands

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The presence of high arsenic concentrations in drinking water has been declared as a major risk to human health in many parts of the world. A suitable treatment of water supplies must face up the arsenic issue. The best available technologies candidates for drinking water treatment are basically based on physical and chemical processes: filtration, coagulation, ion exchange and reverse osmosis. Their efficiencies in terms of reducing arsenic concentrations from water are high, but the most important drawback is that their costs are sometimes prohibitive. An economically viable and alternative option of treatment is the constructed wetland (CW) technology. CWs have been used for the treatment of a wide set of water. Although their application in arsenic removal from drinking water is relatively new, Rahman (2009) showed that CW systems were highly efficient in removing arsenic. Much has been elucidated in the last few decades about arsenic speciation and the important parameters and processes that affect the speciation and mobility of arsenic under different conditions. However, there still exist some lacks of knowledge about the performance of these systems treating high arsenic waters, basically due to the arsenic retention in these systems involves a large number of physical, chemical and biological processes that take place simultaneously.

Modelling, especially mechanistic mathematical models, has become a powerful tool to better understand the performance of water treatment systems such as CWs.

The aim of the present contribution is: 1) to present the results of some experimentations carried out at a prototype level in the lab (in order to select the proper arsenic-tolerant species for the success of rhizofiltration as a water cleanup strategy); and, 2) to present the results of the finite element code RetrasoCodeBright (RCB) adaptation (RCB-ARSENIC) for the simulation of the most significant arsenic retention processes that take place within horizontal subsurface flow CWs (HSSF CWs). At this moment the first step implementation of one of these processes (aqueous complexation and arsenic precipitation) is ended and more work is going on to the next step implementation (sorption processes).

Session 4

Impact of chemical treatments on biological processes & soil matrix

Oral presentations

Impact of chemical oxidants & reductants on CAH-biodegradation

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Chemical remediation techniques are a way for removing the bulk of a contamination in soil, and may be combined with less aggressive techniques like bioremediation for removing the remaining contamination (smart coupling of remediation techniques). Within the FP7 EU-projects UPSOIL, GOODWATER, and AQUAREHAB, the impact of different chemical oxidants and reductants on post chemical bioremediation was investigated. Specific research questions were: Which are suitable methods to monitor this impact?, To which extend is stimulated biodegradation possible after a chemical treatment?

Firstly, experiments with chlorinated aliphatic hydrocarbon (CAH) degrading mixed cultures were performed where the impact of different concentrations of chemicals was studied. The impact was evaluated via measurements of bacterial activity (pollutant degrading activity, total ATP, flow cytometry) and quantification of biomarkers (molecular analyses at DNA & RNA level). As micro-organisms are not protected by the aquifer material in these tests, the test results are considered as worst case impacts. Determination of CAH concentrations, total ATP as well as molecular analyses (but only at RNA level) were found as the good monitoring methods to study the effect of the chemical compounds on the CAH degrading population. Chemical oxidants influenced the microbial activity in a negative way, and are more pronounced with increasing oxidant doses. The microbial activity could not always be regained by applying bioaugmentation since especially the higher permanganate concentrations influenced the microbial activity in an irreversible way. In respect to chemical reductants, the CAH-degradation population was negatively influenced by nanoscale zerovalent iron (nZVI) at doses as low as 0.05 g/L. With micro-scale iron (mZVI) stimulation of bacterial activities was observed, which was less pronounced with higher doses. Doses of 15-30 g/L of mZVI showed a negative effect on the microbial community.

In a next step, lab scale experiments were performed where a homogenized contaminated aquifer slurry from a Flemish site was subjected to three reducing (nano, micro- and granular zerovalent iron) and 3 oxidizing agents (permanganate, cold and activated persulphate), each in three different concentrations (5, 10 and 20 g/kg wet aquifer). After three months of incubation (when chemical oxidants were no longer active) lactate was added to evaluate the remaining biodegradation potential of soils after chemical treatments. The originally present anaerobic biodegradation potential was impacted by the chemical treatments, mostly by chemical oxidants. While in the test conditions with the lowest oxidant concentration biodegradation activity was regained after a lag phase, no activity was seen in the test conditions where higher doses were applied. The highest negative impact was observed with permanganate. The redox potential seems to be a crucial parameter. In the presence of chemical reductants, elevated concentrations of vinyl chloride suggest simultaneous occurrence of biodegradation and chemical reduction. At different time points, samples have been taken for a more detailed study of the active microbial population via molecular analyses at DNA and RNA level. In the presence of aquifer material, the results were found less conclusive in comparison with the experiments performed without aquifer, explicable by (1) interference of the soil matrix with the DNA/RNA analyses and (2) protection of the bacteria against the chemicals by the aquifer.

Some general considerations will be provided that can be helpful to decide between chemical oxidation and chemical reduction to be used at a site.

Pilot study on treatment of mineral oil contaminated site with combined chemical and biological methods

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ABSTRACT
Diesel oil contamination concerns especially railway sites, fueling stations, fuel depots and reloading sites, refineries, postindustrial and post military areas. in-situ methods. One of the innovative approaches to remediation of those sites are in-situ methods which are the subject of the 7th European Union Framework Program UPSOIL "Sustainable Soil Upgrading by Developing Cost effective, Biogeochemical Remediation Approaches UPSOIL". The project aims at the effective coupling of chemical and biological in-situ methods of soil and groundwater remediation. Laboratory and field studies are carried out in the project to investigate solutions for application of cost efficient in-situ remediation. A field study is performed at a railway site contaminated with diesel oil in Poland. Based on the results of the laboratory analyses and taking into account the soil matrix characterisation (anthropogenic fill on top of natural peat layer), persulfate is selected as oxidant for this pilot. The field test is aimed at determining the impact of oxidation on physical and chemical properties of soil and groundwater relevant for sustaining further biological treatment. Monitoring of the oxidation process thus focused on changes in soil structure, contaminant degradation, nutrient availability and microbial growth potential. Results of the test should aid in improving designs for the remediation of oil contaminated sites using combined in-situ solutions.

INTRODUCTION

Diesel oil contamination concerns especially railway sites, fueling stations, fuel depots and reloading sites, refineries, postindustrial and post military areas. These sites are frequently characterised with soil, and groundwater contamination. Although, in most cases removal of the free product and/or removal of the contaminated ground for ex-situ remediation is performed it is not always feasible or reasonable. In such situation it is interesting to use in-situ methods. This issue is the subject of the 7th European Union Framework Program UPSOIL "Sustainable Soil Upgrading by Developing Cost effective, Biogeochemical Remediation Approaches UPSOIL". The project aims at the effective coupling of chemical and biological in-situ methods of soil and groundwater remediation. Laboratory and field studies are carried out to investigate solutions for application of cost efficient in-situ remediation. A field study is performed at a railway site contaminated with diesel oil in Poland. Based on the results of the laboratory analyses and taking into account the soil matrix characterisation (anthropogenic fill on top of natural peat layer), persulfate is selected as oxidant for this pilot. The testing field, with injection and monitoring wells, is without free phase present but located close to source area with high concentrations of mineral oil. The field test is aimed at determining the impact of oxidation on physical and chemical properties of soil and groundwater relevant for sustaining further biological treatment. Monitoring of the oxidation process focuses on changes in soil structure, contaminant degradation, nutrient availability and microbial growth potential. A number of basic physical parameters are measured by automated loggers. Results of the test should aid in improved designs for the remediation of oil contaminated sites using combined in-situ solutions. The use of chemical methods predominantly as stimulation for biological degradation is viewed as a potentially cost efficient solution.

KEY CHALENGES

Research and experiences shows that the most effective in-situ approach of remediating sites contaminated with petroleum hydrocarbons is bioremediation. The most important factors of its effectiveness are concentration of the hydrocarbons in soil, accumulation of bacteria degrading the hydrocarbons and biodegradation potential (Siegrist, 2006, Sperry, Cookson, 2002). Efficiency of this method is also limited by processes of soil degradation caused by the presence of contamination, which prevents development of bacteria leading to impaired exchange of gases and lowering water sorption capacity. Applying of chemical oxidation can also improve the soil condition for biodegradation (Wijn at all, 2010). The UPSOIL project research gives an opportunity to improve and determine the rules (chemical, biochemical, hydrogeological and hydrogeochemical) of coupling in-situ chemical and biological methods, based on new technical knowledge of new materials and tools. Two phase approach is applied:

Phase I – active remediation with chemical removal of contaminants

The aim is to initiate simple chemical reactions (oxidative or reductive) to degrade contaminants to the highest possible degree and at the level securing natural biodegradation potential in the further phase. Effectiveness of In Situ Chemical Oxidation (ISCO) approach is determined by the time of contact of the oxidant with the contaminant, oxidation potential of the added agent, local specifics of the soil and groundwater conditions (soil type, hydrogeological conditions), susceptibility of the contaminants to degradation and time of degradation. Those parameters are decisive for determining the amount of applied oxidant and distribution of the injection wells.

Phase II – natural biodegradation

In this phase soil biological potential should be sufficient to initiate natural biodegradation processes which can be stable for a longer period leading to gradual improvement of the soil conditions and functions. The effectiveness depends on the availability of substrates and soil conditions. One of the factors is potential raise in toxicity caused by releases of heavy metals.

PILOT TEST OF BIOGEOCHEMICAL METHODS

A pilot test of ISCO procedure in Węgliniec (Poland) was planned and executed to test various aspects of chemical and biological methods in the view of coupling chemical and biological methods. Results of laboratory tests performed for soil samples taken at the site were analysed and interpreted in the context of the field test design. The testing field 5x5m area (Figure 1) is located in the up stream part of the site contamination in the source zones.

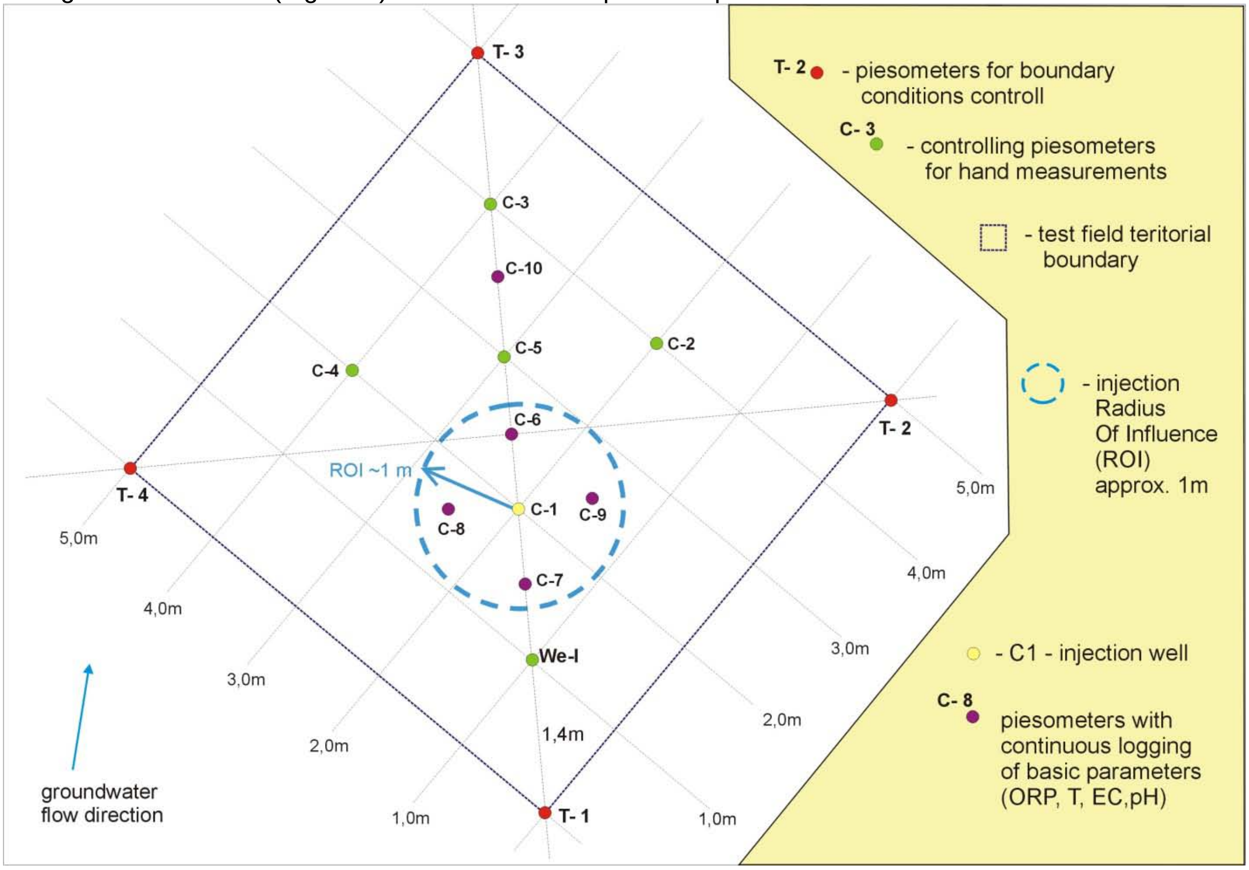

Figure 1: Scheme of the pilot test area in Węgliniec site

Detailed characterisation of the site and the testing field was performed with additional extensive investigation and preparatory work carried out. Soil samples were taken during installation of 4 monitoring wells (C1, C2, C3, C4 see

Figure 1) in August 2011. Another 5 wells were installed for the purposes of fitting in the automatic loggers (C6, C7, C8, C9, C10 see Figure 1). Based on the data obtained hydrogeological profiles were prepared for the wells and soil cross sections. Water table level and physicochemical parameters were measured on monthly basis in all wells during the 2011 and 2012. Heterogeneity of the site was confirmed with a variety of anthropogenic layers (Figure 2). These data were a good basis for characterisation of the site conditions including the hydro geologic conditions. Injection well (C1) was specially prepared according to the design securing even distribution of injected solution around the filter volume. Loggers were prepared to allow for automatic readings of physical parameters including ORP, temperature, electric conductivity, pH.

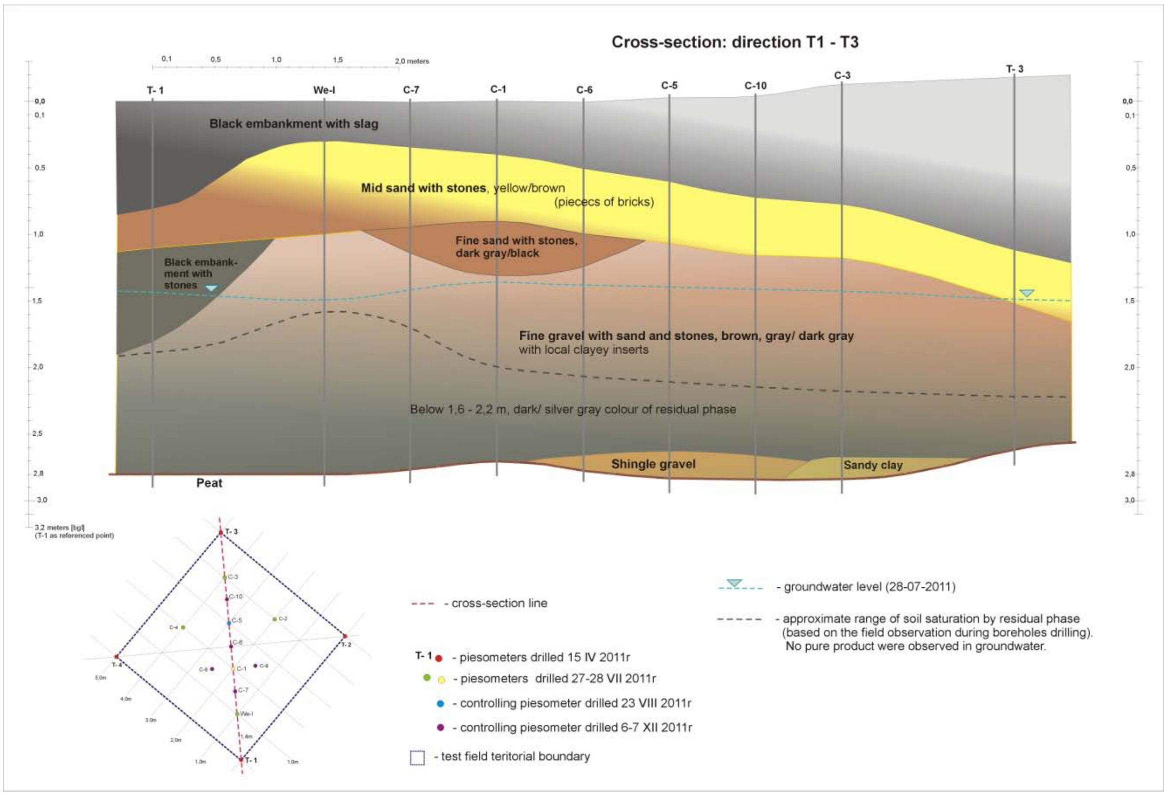

Figure 2: Hydrogeological profile of in the test field area

The field test was performed in the period May – September 2012. It comprised:

- first injection of sodium persulfate: 8% solution 550 l which was performed on the 8 th of May 2012
- second injection of sodium persulfate: 8% solution, 1100 l injected volume, performed on the 18th of June
- third injection with nutrients for bacteria stimulation performed on the 9th of August 2012
- constant monitoring of physical and chemical parameters.

Third injection was performed with nutrients intended for bacteria growth stimulation. The amount of 846 g of commercial fertiliser were injected in a volume of 150 l of solution with the content of 115 g of nitrogen and 40 g of phosphorous. All injections were gravitational with the injection rates in the range of 2 – 2,5 l per minute and performed in the well C1 located centrally in the testing field.

23 monitoring campaigns were carried out to gather data for evaluation of the test performance. They included:

- Groundwater sampling with on-field samples preparation for chemical and biological analyses. The scope of sampling and frequency differed in the period, with high frequency in the days following the injections,
- Manual measurements of physico-chemical parameters with three independent instruments including ORP, temperature, electric conductivity, pH, total dissolved solids,
- Registering and characterising general environmental conditions (weather, rainfall).

Groundwater samples were analysed in the laboratory for inorganic and organic parameters. The inorganic parameters were analysed for the following: alkalinity SO4, HCO_3, Ca, Na, K, Mg, Mn, Fe, Cl, Total Organic Carbon, Dissolved Organic Carbon and Total Oxigen Demand. The following parameters were analysed for hydrocarbons: total petroleum hydrocarbons, BTEX, mineral oil, benzenes, and hydrocarbons profiles.

Various aspects of chemical and biological treatment were analysed in the study. It included:

- Improvement of inferred physical soil properties impairing chemical and biological processes
- Efficiency and time of chemical treatment,
- ISCO application in heterogeneous soil conditions (mixed anthropogenic fill)
- Risk related side effects of ISCO application (release of metals and organic contaminants),
- Changes of soil properties in the view of biological treatment,
- Reliability of the treatment process monitoring

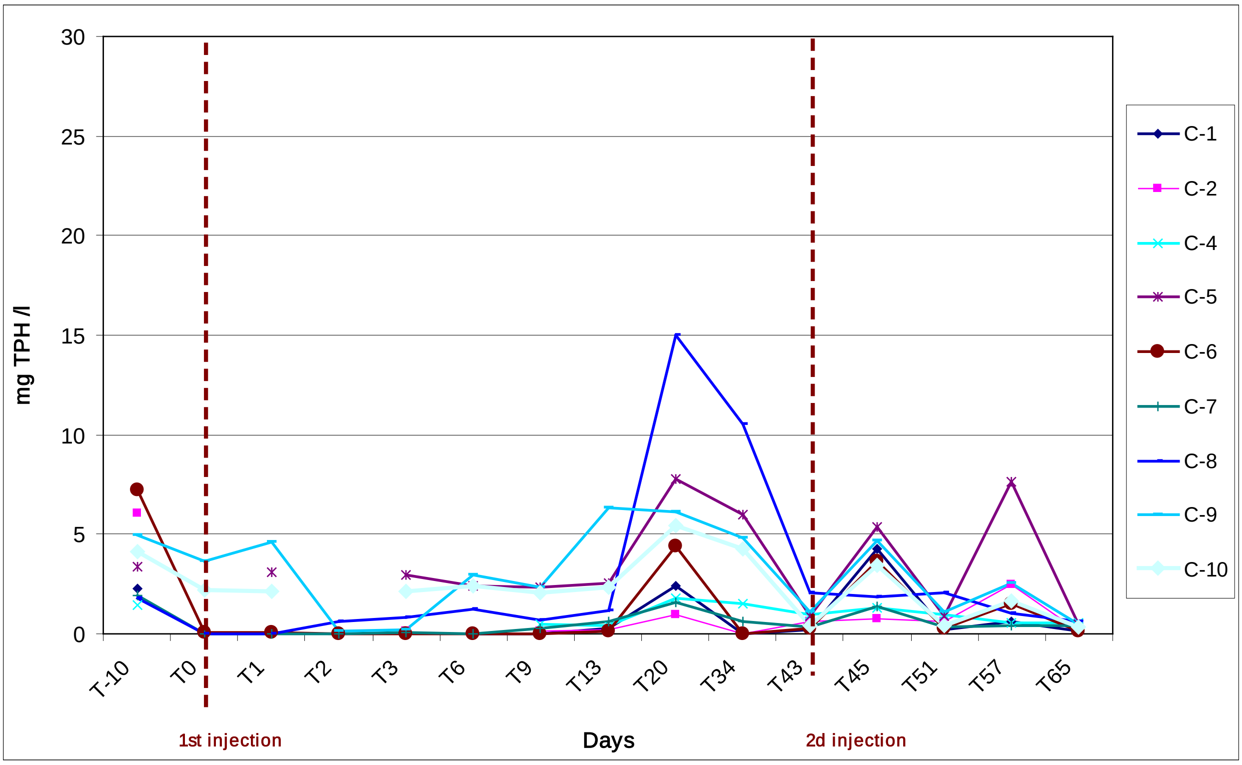

Figure 3: Concentration of total petroleum hydrocarbons during the 70 days of two injections

The chemical injections changed distinctly the environmental conditions which were observed through physical and chemical parameters measurements. Lowering pH and raise of ORP values were the indicators of oxidant presence (Figure 2). High oxidative conditions were observed in 30 days after the first injection and 50 days after second condition. After 90 days the drop of ORP and raising pH values from 4 up to 6 was indication to perform third injection of nutrients as stimulation of bacteria growth. High degradation of hydrocarbons was observed immediately after the injections with rebound effects visible after 10 days periods. Low concentrations were observed especially in the injector well and the wells being in the radius of influence (Figure 3). The rebound effect was observed in some wells (in the radius of influence: C8) with high concentrations indicating free phase presence – higher than 5 mg/l which is assumed as the maximum solubility for TPH in water (Keijzer at all, 2010). After first injection soil samples were taken from a new drilled profile located in the area directly impacted by the injection close to C1 profile and analysed. The results showed lower values of TPH in comparison with preinjection data. Although it is not a direct indicator of efficiency of the ISCO procedure as it does not relate to the preinjection sampling points although it shows a general potential of cleaning the soil matrix absorbed mineral oil fractions.

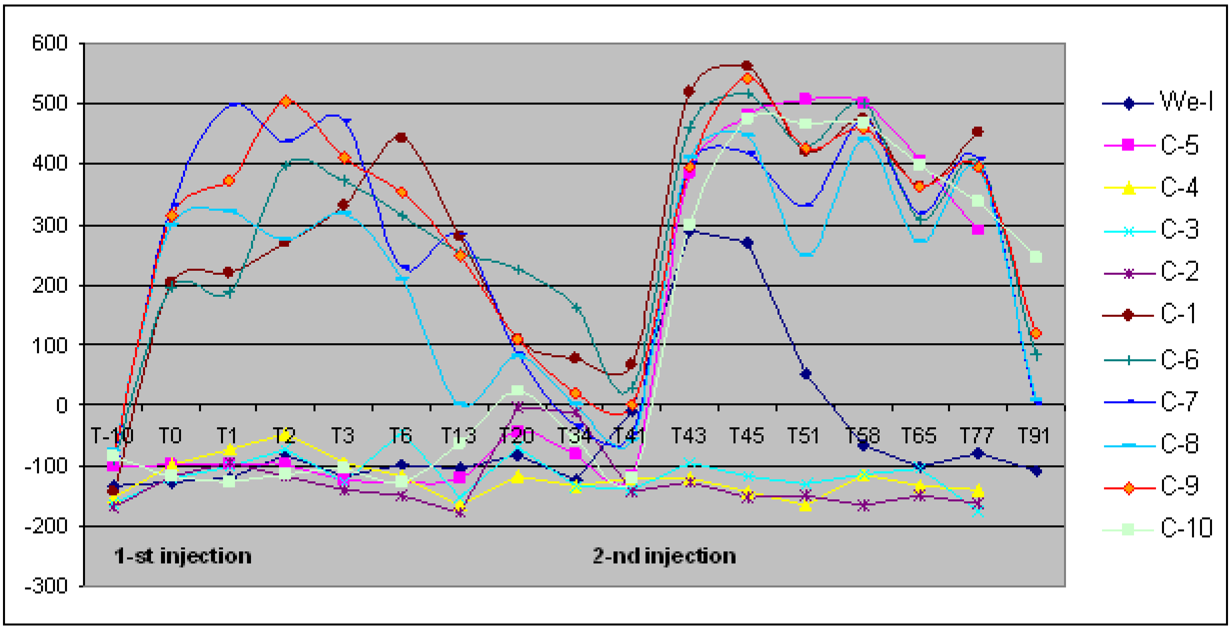

Figure 4: ORP manual reading during the 100 days period of two chemical injections

CONCLUSIONS

The approaches applied in the project UPSOIL relates to two important aspects of sustainable remediation: short time of the degrade site release for redevelopment (investor and socio-economic perspectives), and long term rehabilitation of soil functions (ecological aspects). It provides opportunity to link redevelopment of degraded sites in the best business practices and to fulfill the society expectations for sustainable developments. The results of the test carried out in Węgliniec can be useful in planning sites remediation with application of coupled in-situ chemical and biological methods. They can be used in planning and conducting remediation at sites, where soil and groundwater is contaminated with mineral oils such as railway areas, fuel stations and depots, reloding point, refineries, postindustrial and post military areas. Test results can be used in practical applications of ISCO method and as a basis for administrative decisions in the scope of contaminated land remediation

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Effect of temperature on the chemical oxidation of organic matter and PCE

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In situ chemical oxidation (ISCO) is a soil remediation technique, using an oxidant like potassium permanganate ($KMnO_4$), sodiumpersulphate (NaS_2O_8) or Fenton's reagent to oxidize organic pollutants such as petroleum hydrocarbons and chlorinated hydrocarbons. When applying this technique in practice, not only the pollutants can be oxidized, but also other soil components like organic matter (OM). ISCO becomes more sustainable and cost effective if more pollutant and less soil material are oxidized. One of the factors that might influence this balance in a positive way is the temperature of the oxidant solution. Therefore, the effect of temperature on the oxidant consumption of both natural organic matter and DNAPL PCE was investigated.

Various types of OM, like reed, cellulose, anthracite and oak wood, were oxidized with $KMnO_4$ and activated NaS_2O_8 with 100 mg/l Fe^{2+}. The oxidant and OM were present in an oxidant:OM ratio of 1:1 and 1:2, based on stoichiometric calculations using the amount of C, O, H, N and S present in each type of OM. DNAPL PCE was oxidized with $KMnO_4$ and activated NaS_2O_8 in a stoichiometric oxidant: PCE ratio of 1: 0.25, 1:0.5 and 1:1. The bottles with OM or PCE and oxidant contained 65 ml liquid and were incubated horizontally shaken at 5ºC and 15ºC Permanganate was measured in time by UV-spectrophotometry at a wavelength of 525 nm, and NaS_2O_8 was measured with a modified iodometric titration method and UV-spectrometry at a wavelength of 352 nm.

Permanganate was consumed by all OM-types except anthracite, indicating oxidation of the OM, whereas NaS_2O_8 was hardly consumed, indicating no oxidation. The oxidation rate between the types of OM and $KMnO_4$ differed, with the fastest oxidation observed for reed. Thereby, the oxidation of all types of organic matter was slower at 5ºC as compared to 15ºC. In contrast, the rate of oxidant consumption with $KMnO_4$ and PCE did not differ between temperatures.. In literature, experiments are reported that show faster oxidation at higher temperatures of dissolved PCE. However, in the presence of (residual) DNAPL, as in our case, the dissolution of the PCE plays an important role and it turns out that temperature has less effect on this, resulting in a comparable overall oxidation rate.

Hence, using a lower temperature of the oxidant solution during chemical oxidation can result in less oxidation of the organic matter, with a comparable amount of DNAPL oxidized, thereby increasing the sustainability and cost effectiveness of the treatment.

Poster Presentations

Effect of chemical oxidant stress on microbial dechlorination activity and re-activation possibilities

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In this study, the potential effects of the oxidants potassium permanganate (PM) and sodium persulfate (PS), on the quantity and activity of the microorganisms, and subsequently on the re-activation potential of the system were investigated. Forty µM of trichloroethene (TCE) and 5.6 mM of lactate were added to the test systems having enrichment culture. The oxidants were applied within the range of 0.005 to 2 g/L for permanganate and 0.01 to 4.52 g/L for persulfate. TCE concentrations, copies of genes and transcripts, and total ATP concentrations were measured in function of time. *tceA*, *vcrA* and 16S rRNA genes of *Dehalococcoides* species were expressed with an average value of 10^4, 10^5, and 10^8 transcripts/mL, respectively, in the test systems having concentrations of 0.005 to 0.01 g/L PM and 0.01 to 0.02 g/L PS. However, gene expressions were below detection limit between concentrations of 0.5 to 2 g/L PM and 1.13 to 4.52 g/L PS. Similarly, total ATP concentrations were also not detectable under these conditions. The results revealed that these oxidants inhibited the microbial activity at concentrations above 0.5 g/L PM and 1 g/L PS. Dilution of the reaction medium and bioaugmentation did not promote the resuscitation and/or dechlorination in any of the test systems when the redox potential was still above -100 mV. On the other hand, when the redox potential was decreased till -300 mV and the reactors were bioaugmented for a second time, dechlorination took place successfully, but only in the reactors having persulfate concentrations of 1.13 and 2.26 g/L.

Soil matrix reactivity and buffering potential in the selection of coupled *in situ* remediation technologies

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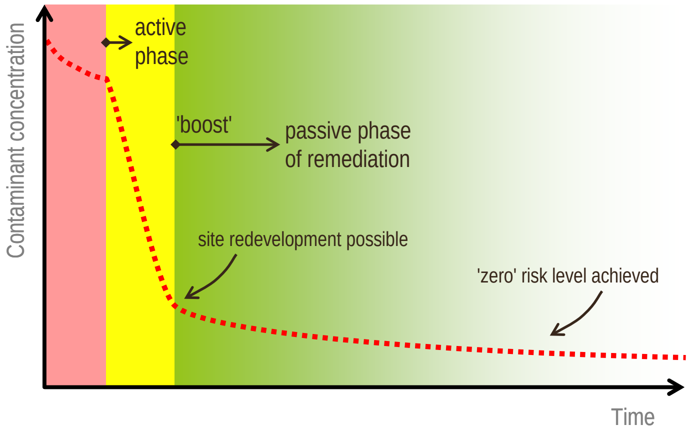
Chemical remediation techniques are aimed at the degradation of contaminants in the subsurface, but in most cases a considerable part of the reagents is also consumed by the soil matrix. This leads to inefficient use of the reagent and undesired changes in the soil/aquifer matrix. Also in the case of enhanced bioremediation, the buffering capacity of the soil matrix may impede realisation of the oxidation-reduction potential (ORP) that is necessary for the bacterial degradation process envisaged. Within the FP7 EU-project UPSOIL (GA 226956), one of the research lines is dedicated to the development of more cost-effective and sustainable remediation approaches, through a balanced use of existing technologies that considers contaminant conditions, soil system characteristics, and soil functioning in an integrated way. The general approach is to couple an active treatment phase, to significantly reduce the concentration of contaminants, to a passive phase in which residual contaminants are typically biologically degraded over a longer period of time (see Figure). In a joint effort of several Upsoil consortium partners, chemical oxidation batch experiments and biological microcosm experiments were performed with samples from contaminated sites in Poland (petroleum hydrocarbons) and Austria (chlorinated hydrocarbons). Sample characterisation in the experiments focussed on contaminant concentration, composition and bioavailability, and natural organic matter content and pH. The effects of treatments towards the contaminants, soil matrix, and suitability of post-treatment conditions for sustained biodegradation were investigated. Results were generalised and presented in the form of decision flow charts and selection matrices.



Possibilities for increased efficiency of chemical in-situ remediation via specific targeting

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ABSTRACT: Chemical remediation techniques, and especially chemical oxidation, do destroy pollutants in the subsurface, but part of the reagents is also consumed by the soil matrix. This leads to inefficient use of the reagent and undesired changes of the soil/aquifer matrix. Within the FP7 EU-project UPSOIL (GA 226956), one of the research lines is dedicated to the development of improved oxidants/reductants, which could lead to a more selective oxidation/reduction of the pollutants in the subsurface. More specifically research was performed to realise

- Less interaction between the reagent and the soil matrix (1) for not loosing expensive reagents (COST-EFFICIENCY) and (2) for not effecting the soil matrix (SUSTAINABILITY)
- Reactants that can be ‘attracted’ to the NAPL, meaning preferential reaction with the pollutants

Different approaches to increase the efficiency of chemical treatments via more targeting of the reagents were considered and tested. It concerns (1) protection of the soil, (2) hydrophilic coated-packed reagents, (3) hydrophobic coated/packed reagents and (4) micelles. Lab scale experiments were performed by different project partners to evaluate the possibilities and limitations. The reagents considered are permanganate (PM), persulphate (PS), percarbonate (PC), zerovalent iron (ZVI) and ironsulfides (FeS). Tests have been performed with oil as well a chlorinated compounds as model pollutants.

In general, it can be concluded that the development of new more selective reagents is a challenging task. However, the results indicate that possibilities do exist which are worth to be elaborated further technically and economically.

INTRODUCTION

Effective in-situ remediation requires efficient migration of the injected reactants through the soil and contact between the reagent and the pollutants. Retention and consumption of the reagent by the soil matrix is not desired. The aim of the presented research is to modify existing injectable reactants and to convert them into a mode which allows specific targeting of pollutants such as DNAPL and LNAPL compounds. Chemical degradation of these pollutants can require the use of oxidants as well as reductants. The most commonly used oxidants include permanganate (MnO_4^-), hydrogen peroxide (H_2O_2) optionally with iron (Fe), persulfate ($S_2O_8^{2-}$), and ozone (O_3). Suitable reductants include zerovalent iron (Fe^0), sodium dithionite ($Na_2S_2O_4$), and reactive iron minerals (e.g. iron sulfides, carbonate green rust, magnetite). Reactants can be injected in the subsurface as an aqueous mixture, slurry or suspension.

Within the UPSOIL project, four concepts were selected and investigated to promote degradation of the target pollutants and to minimize reactions with other substances present in the soil matrix (e.g. organic matter, minerals, soil microbial population):

Concept 1 aims at targeting via protection of the soil matrix against the reactants
Concept 2 focuses on particles ‘packed’ with a hydrophilic coating that migrate well in the groundwater, but that can have a ‘chemical lock’ to interaction with NAPL/pollutants and to be active near water-NAPL interphase.
Concept 3 are hydrophobic transportable particles that can enter in NAPLs.
Concept 4 is related to micelle-like particles

The reagents considered in the UPSOIL study comprise: permanganate (PM), persulphate (PS), percarbonate (PC), zerovalent iron (ZVI) and ironsulfides (FeS). The research approach followed is depicture in figure 1 and consists of 5 levels. This document gives an overview of the UPSOIL research for the first 3 levels.

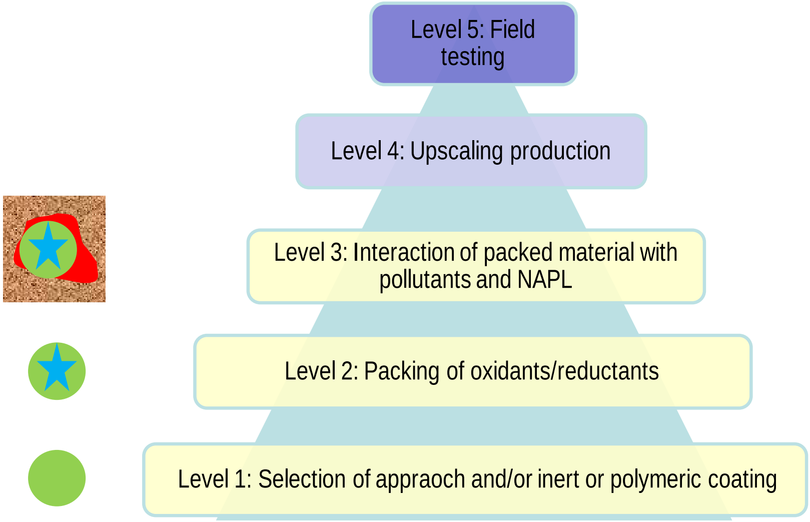

Figure 1: Schematic overview of the test site.

CONCEPTS FOR SPECIFIC TARGETTING

Protection of the soil (Concept 1)

The basic idea of this concept is protection of the soil against the reactants by using ‘something’ that reduces/prevents reaction with organic matter and minerals in the soil, and as such, realise a more specific pollutant destruction. In this concept, the following approaches were selected for study:

<u>Targeting via Temperature</u> (applicable for oxidants): Decreasing temperature is expected to lower degradation rates of the soil organic matter more than degradation rates of pollutants. As such, lowering of temperature can lead to more selective reaction of the oxidant.
The approach was tested for permanganate and persulphate, both with PCE and toluene as pollutants. Different organic matters were used as references for the soil matrix. For treatment of PCE with permanganate, results indicate that there can be an added value of temperature decreases during treatment, as the degradation rate of some organic materials by permanganate decreases more than the degradation rates of PCE. For the other combinations this could not be shown. More detailed results are described by De Weert et al. (2012).

<u>Use of Phosphates</u> (applicable for reductants): Phosphate is known to adsorb well to iron oxide mineral surfaces, and can as such potentially protect oxides form reductive dissolution.
The test performed seemed to be proof of principle, since on average reductive dissolution of the iron minerals was reduced by the phosphate coating. However, results were not considered sufficiently promising to proceed along this research path.

Hydrophilic (coated) particles (Concept 2)

Particles ‘packed’ with a hydrophylic coating are expected to migrate well in the groundwater. For interaction with NAPL/pollutants and to be active near water-NAPL interphase, a ‘chemical lock’ is necessary. The following hydrophilic coating materials were selected and were evaluated for targeting reducing iron particles:

<u>Cyclodextrines</u>: Cyclodextrines are large molecules that possess a cavity that can host more hydrophobic molecules like reduced iron particles, which are in that case expected to have a reduced tendency to aggregate and an improved transport in the groundwater.
Some encouraging results were obtained towards reactivity. However, further development and optimisation is needed as the reactive molecules obtained, did not stay in suspension. More detailed results are described by Gemoets & Simons (2012).

Dithiotreitol: A complex of ferrous iron with DiThioThreitol (DTT) was prepared. The latter is a small molecule that has two sulphur atoms that can form a catalytic complex with iron, while it also has two hydroxyl groups that are expected to provide a polar surrounding to the complex which may facilitate its transport in groundwater;
Some reactivity by the soluble particles was observed. However, further optimisation of the particle is needed because of the incomplete nature of the dechlorination, the lack of observation of important quantities of harmless daughter products and the persistence of precipitates that were formed. Also complexes of ferrous iron with thioglycolate (TGA) have been studied. More details are described by Gemoets & Simons (2012).

Polymers: Polycaprolactone (PCL) is a synthetic aliphatic polyester which is sold as a biodegradable polymer. PCL has a low melting-point, low viscosity and it is easy to process. Two approaches were used to prepare packed ZVI-particles: (1) via a caprolactone coating and (2) using a copolymer-caprolactone coating. More detailed results are described by Ocejo and E. Goiti. (2012).

Hydrophobic coated particles (Concept 3)

Concept 3 aims at developing hydrophobic transportable particles that can enter in NAPLs. A large number of polymeric coatings were listed and evaluated theoretically. Next, a number of coatings, soluble in NAPL, were experimentally tested in the lab.

Paraffin wax was shown to have interesting properties as coating material for oxidants (figure 2). With paraffin wax coated oxidants (1) only minor release of the oxidant in the water phase was observed, (2) the coating dissolved in NAPL, leading to release of the oxidant near the NAPL phase, and (3) the released oxidant was found reactive. The type of paraffin wax and the particle size were found to influence significantly the properties of the particles.

Others: Other waxes and different ways of coatings have been evaluated and are described by Stefanescu et al (2012).

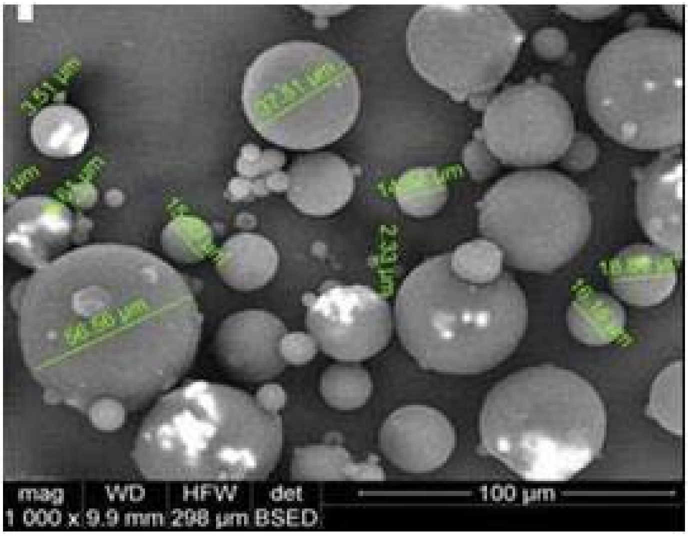

Figure 2: Hydrophobic packed permanganate.

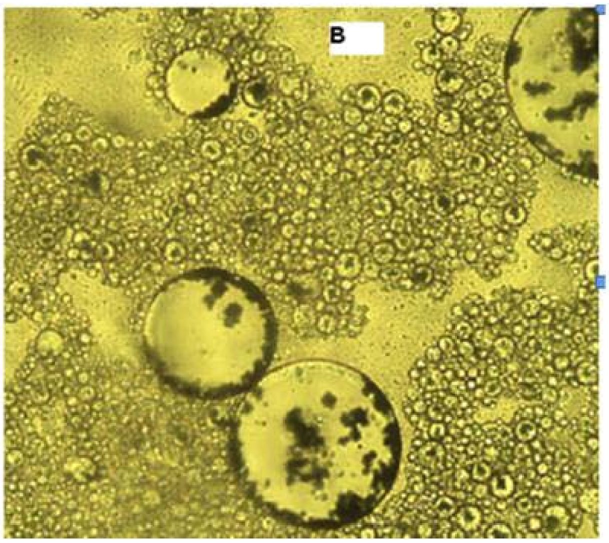

Figure 3: Emulsified ZVI.

Micelle-like particles (Concept 4)

For concept 4, micelle-like particles, oil was selected as coating for production of emulsified reductants. CAH present as NAPL in source areas may be taken up in iron containing vegetable oil micelles, allowing for a more targeted reaction of ZVI with the pollutants. Different recipes for preparing emulsified ZVI (figure 3) were tested and compared with the recipes described in literature. Reactivity as well as mobility were evaluated via labscale testings. More details of the preformed tested and obtained results are described by Gemoets et al.(2012).

GENERAL CONCLUSIONS

In general, it can be concluded that the development of new more selective reagents is a challenging task. Treatments to make particle more mobile and more selective, result often in larger reagent particle. This larger particles size negatively influences the mobility of the particles in the fine pores in the subsurface. To come to a commercial product, a number of parameters need to be taken into account, such as the production methods, the production cost, storage conditions, stability of the products, safety issues.

No particles readily available for market introduction were obtained. However, the results indicate that possibilities do exist which are worth to be elaborated further technically and economically.

ACKNOWLEDGEMENTS

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Assessing the potential for long-term in situ bioremediation following in situ chemical oxidation

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With the rising prevalence of in situ remediation technologies, current interest focuses on further optimizing such treatment. Within the FP7 European project Upsoil, we investigate the smart-coupling of in situ techniques in terms of cost-effectiveness, time, and sustainability. One manner of improving especially cost-effectiveness and sustainability is by better utilizing natural biodegradation potential. Through initiating bioremediation following a more active chemical oxidation treatment, costs and time are saved in a sustainable manner. Within this framework, we investigate the potential for long-term bioremediation specifically following chemical oxidation with the goal of optimizing the overall treatment.

While chemical oxidation can be temporarily detrimental to the microbial population, it has been shown that biological potential rebounds over the long term. Here, we investigated the conditions present following a chemical treatment with the goal of understanding their impact on a subsequent biological phase. Research specifically focused on understanding changes in contaminant concentrations and bioavailability, heavy metal mobility, reduction in the microbial population, and changes in the soil structure which directly impact further bioremediation.

In order to ensure long-term bioremediation, conditions must be created which are conducive to extended biodegradation. Here, research attempted to identify factors that limit long term bioremediation. Through varying both the chemical oxidant used as well as the post-treatment amendment, successful as well as ineffective combinations were identified.

Finally, when coupling chemical oxidation to a long-term bioremediation phase, it is important to be able to assess conditions at the end-point to the treatment. An estimate of the residual contaminant concentrations, eco-toxicological risk level, and additional geochemical conditions is essential to determining if the overall treatment is feasible at the location in question. Through performing laboratory experiments in which long-term remediation is simulated, these end points, as well as the inputs required to achieve them, can be estimated.

With the goal of creating more efficient and effective treatments, the results presented here give both practical guidelines as well as specific results identifying the potential to couple chemical oxidation with long-term bioremediation. This research furthers the optimization of these techniques into a smart-coupling treatment for improved in situ remediation.

Micelle-coated zero valent iron nanoparticles for in-situ remediation

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One of the research lines of the FP7 EU-project UPSOIL (GA 226956), is dedicated to the development of improved oxidant/reductant reagents, which could lead to a more selective and efficient oxidation/reduction of the contaminants during the in-situ remediation. **Zero valent iron nanoparticles** (nZVI) represent a promising technology as in-situ remediation technique for contaminated groundwater and/or soils. During recent years it has become very attractive, due to the exceptional properties of these nanoparticles. Nanoscale size iron particles show higher surface area than microparticles or iron powder, and therefore nZVI present enhanced reactivity towards a wide range of contaminants, making it a promising technology in terms of sustainability and cost-effectiveness.

However, high reactivity is not only sufficient to make nZVI a good in situ remediation reagent. Iron nanoparticles must also be readily dispersible in water such that they can migrate through water-saturated porous media along the contaminated area. Therefore, colloidal stability of aqueous nZVI dispersion is a critical property to yield efficient in-situ remediation processes[1].

Herein we present the development of new nZVI-based aqueous dispersions. The general approach we have followed is the preparation of polymeric micelles in such a way that the iron nanoparticles are embedded within the core part of these structures. Two different synthetic routes have been used: i) pre-stabilization, the nZVI are fabricated within the core of the micelles and ii) post-stabilization, the nanoparticles are first prepared and then they are “encapsulated” within the micelles. The particles obtained by these two routes have been compared in terms of stability and reactivity with TCE in aqueous solutions.

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Chemical treatment of a contaminated aquifer: Impact of different oxidants and reductants on CAHs and post-chemical biodegradation

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ABSTRACT: Here we report on a lab scale experiment where a homogenized contaminated aquifer slurry from a Flemish site was subjected to three reducing (nano, micro- and granular zerovalent iron) and 3 oxidizing agents (permanganate, cold and activated persulphate), each in three different concentrations. Over time the evolution of the contaminants and breakdown products (PCE, TCE, cDCE, Vinyl chloride, Dichloromethane, 1,2-dichloroethane, toluene, ethylbenzene, ethene, ethane, acetylene) was followed, and samples for characterization of the soil matrix have been taken. The results showed that, for the tested aquifer, chemical reduction had a much higher impact on the chlorinated contaminant concentration than chemical oxidants. Even repeated applications of the chemical oxidants did not lead to a total removal of the pollution, while a single application of zerovalent iron did remove most of the chlorinated contaminants. The very high matrix demand that was observed may be part of the explanation here. This emphasizes the importance of considering the redox state of the aquifer during the selection of the chemical reagent. BTEX-compounds were not degraded by chemical reduction as expected. After three months of incubation, when the chemical oxidants were no longer reactive, lactate was added to evaluate the remaining biodegradation potential of soils after chemical treatments. In the original aquifer material, without chemical treatment, an anaerobic biodegradation potential for a number of the chlorinated compounds was observed. The chemical treatments, however, did impact the biodegradation in most of the chemical oxidation cases. While in the test conditions with the lowest oxidant concentration biodegradation activity was observed after a lag phase, no activity was seen in the test conditions where higher doses were applied. The highest negative impact was observed with permanganate. The redox potential seems to be a crucial parameter. In the presence of chemical reductants, elevated concentrations of vinyl chloride (only a major degradation product of biodegradation and not of chemical reduction) suggests simultaneous occurrence of biodegradation and chemical reduction.

INTRODUCTION

Chemical remediation techniques can be a suitable way of removing the major part of a contamination from soil and groundwater. These are, however, rather aggressive techniques as not only the pollutants but also the soil matrix is altered. It may be a sustainable approach to combine chemical remediation technologies subsequently with less aggressive techniques like bioremediation for removing the remaining contamination. Within the FP7 EU-project UPSOIL, this smart coupling of remediation techniques is being studied to (1) realize by chemical in-situ remediation a fast reduction of the pollutant concentrations till a level acceptable for a certain land-use, and (2) to reduce the remaining concentration further to levels required for less restricted land use by bioremediation during a longer phase. In addition, this active phases may be followed by even longer passive phase where the aim is to reduce the concentrations even more during the next decade(s). The impact of different chemical oxidants and reductants on pollutant removal, soil organic matter and the soil microbial population (e.a. CAH-degraders) are a point of attention. More specifically, one of the research questions addressed in this publication is: To which extend is stimulated biodegradation possible after a chemical treatment, and under which conditions?

Here were report the results of a lab scale experiment where a homogenized contaminated aquifer slurry from a Flemish site was subjected to three reducing (nano, micro- and granular zerovalent iron (ZVI)) and 3 oxidizing agents (permanganate, cold and activated persulphate), each in three different concentration. The impact of the treatments (1) on the pollutant concentrations was followed, as well as (2) the impact on the soil micro-organisms, more specifically on the biodegradation potential in the aquifer. In the study, chlorinated Aliphatic compounds (CAHs) were used as model pollutants.

MATERIALS AND METHODS

Aquifer material and groundwater used in this study originates from a contaminated site in Belgium. Undisturbed core samples were taken at three closely located spots at the site, and were dismantled and homogenized under anaerobic condition. The pollutant concentration measured in the aquifer, as well as in two different groundwater's that were used for the test, are summarized in table 1.

Table 1: Pollutant measured in the groundwater's and aquifer material.

	Groundwater 1	Groundwater 2	Aquifer
	µg/l	µg/l	µg/kg DS
Dichloromethane (DCM)	600000	< DL	67
Tetrachloroethylene (PCE)	850	< DL	< DL
Trichloroethylene (TCE)	< DL	< DL	< DL
Cis-DIchloroethylene (cDCE)	18000	2227	49
Vinylchloride (VC)	< DL	329	134
Chloorethaan (C)	< DL	< DL	858
Toluene (T)	832	131	10
Ethylbenzene (EB)	1800	1744	404

The degradation experiment was set-up in 160 glass bottles sealed with Teflon-lined caps. Each bottle contained initially 40 g of wet aquifer material (30g dry aquifer) and 70 ml of liquid consisting of groundwater 1 and additives. The additives added were function of the test condition and comprise oxidans, reductant and/or lactate. In total 21 different test conditions were set-up in 3- to 6-fold. Three reducing (nano, micro- and granular zerovalent iron) and 3 oxidizing agents (permanganate, cold and activated persulphate), each in three different concentrations (5, 10 and 20 g/kg wet aquifer for the oxidants, 5, 25 and 50 g/ kg dry matter for nano-iron (nFe), 25, 50 and 100 g/ kg dry aquifer for microscale ZVI (µFe) and 50, 100 and 200 g ZVI/ kg dry aquifer for granular iron (gFe)). Further, an abiotic control, a natural attenuation and a condition with lactate (without CR & CO) for biostimulation were included. In function of time, the following parameters were followed: concentration of chlorinated compounds, BTEX-compounds, pH, ORP, gases (ethane, ethane, acetylene, methane), TOC, remaining concentrations of oxidants.

After about 48 days of incubation, additional oxidants were dosed to the test conditions which already contained oxidants at concentration identical to the first addition for each condition. After 100 days, the groundwater in the bottles was replaced with fresh groundwater 2 containing a lower concentration of pollutants (see table). This time point is considered to be the start of the biotic test period, implicating that for most test conditions in part of the flask lactate was added. Lactate was added to these flasks after 100, 156 and 191 days. After 226 days a bacterial culture, able to degrade chlorinates ethenes, was added to selected test bottles ,to see effect of bioaugmentation.

Concentrations of CAHs, BTEX, 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 acetylene or a split-splitless injector followed by a Rt-X column (Restek) and a DB-1 column (J&W Scientific) for analysis of CAHs.

RESULTS AND DISCUSSION

Comparison of pollutant removal by chemical oxidation and chemical reduction (Phase 1).

The evolution of pollutants in time in the test conditions with µFe, persulphate and permanganate, are given in figure 1. A general overview of removal percentages of the different pollutants under the tested conditions at the end of the chemical phase, is summarized in table 2.

For the examined aquifer, a very high matrix demand for chemical oxidation were observed. In case of PCE and TCE, the best results were obtained via chemical reduction, while cDCE was the most efficiently degraded by permanganate. As expected, toluene and ethylbenzene decreased in concentration only in the presence of chemical oxidants. For DCM, no good degradation was obtained.

Chemical oxidation only realized partial degradation of most pollutants, also after repeated additions of oxidants. Rebounds and the high matrix demand of the tested aquifer are possible explanations. On the other hand, chemical reduction did lead to a more complete degradation after a single addition. The observed degradation rates were the highest with nFe and the lowest with gFe. With permanganate a faster pollutant removal was observed in comparison with persulphate. On the other hand, persulphate was efficient to a larger pollutant range (for instance DCM) permanganate. Alkanine activated persulphate was less active than cold persulphate.

An important observation, with implications for the subsequent biological phase, is the impact on the ORP, especially after chemical oxidation. The ORP was shown to increase significantly with the number of oxidant additions.

The results showed that, for the tested aquifer, chemical reduction had a much higher impact on the chlorinated contaminant concentration than chemical oxidants. Even repeated applications of the chemical oxidants did not lead to a total removal of the pollution, while a single application of zerovalent iron did remove most of the chlorinated contaminants. The very high matrix demand that was observed may be part of the explanation here. This emphasizes the importance of considering the redox state of the aquifer during the selection of the chemical reagent. BTEX-compounds were not degraded by chemical reduction as expected.

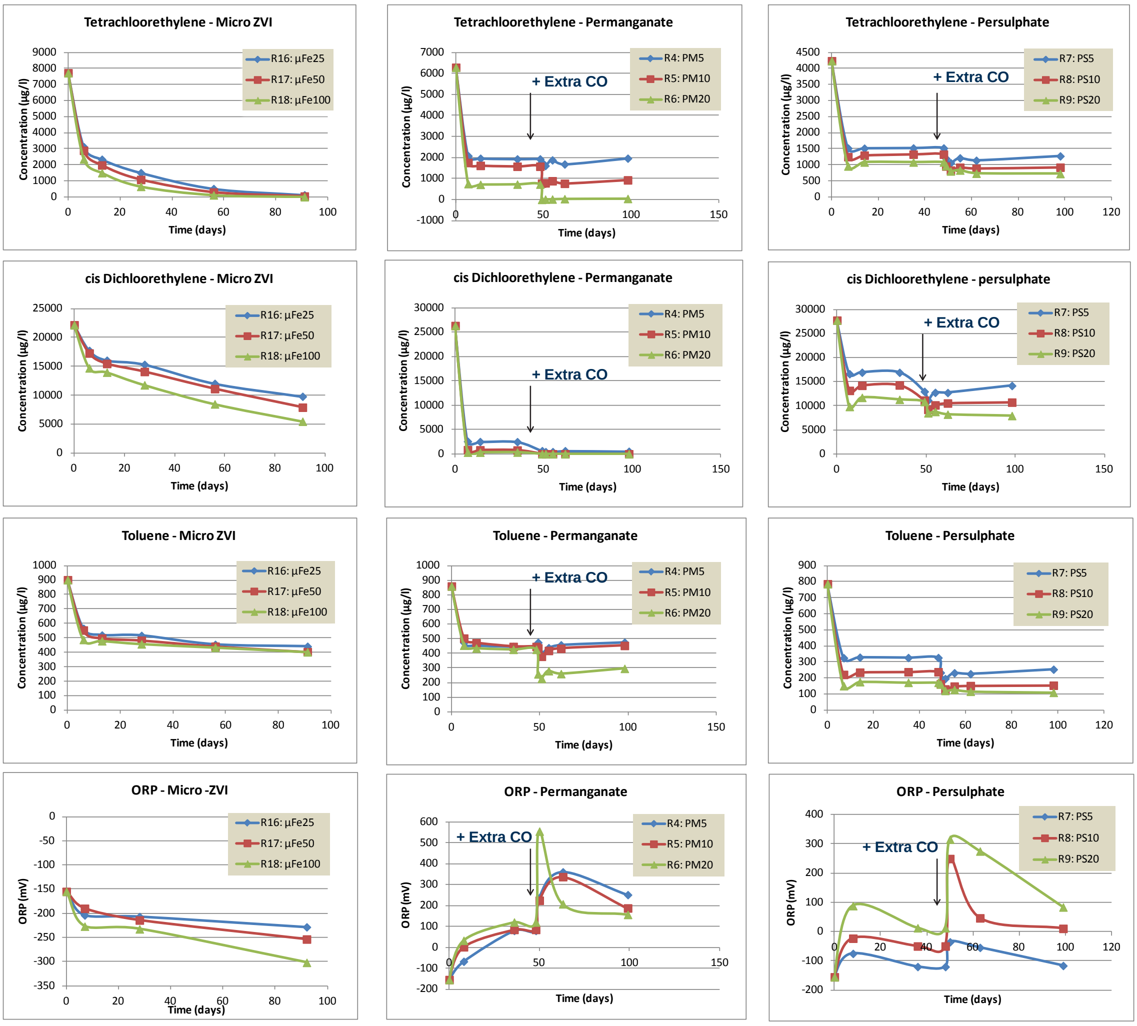

Figure 1: Impact of µFe, permanganate and persulphate on the PCE, cDCE, toluene concentrations and ORP (concentrations of the reactant are given in g/kg dry aquifer).

Table 2: Overview of pollutant removal percentages at the end of the chemical phase for all test conditions.

Test conditions	% removal at end of phase 1 (after 100 days)					
	DCM	PCE	TCE	cDCE	Toluene	Ethylbenzene
R1: poisoned	0%	12%	4%	0%	0%	9%
R2: natural attenuation	0%	25%	0%	0%	1%	0%
R3: stimulation	1%	21%	6%	1%	6%	0%
R4: PM 5 g/kg (2x)	1%	50%	91%	97%	20%	37%
R5: PM 10 g/kg (2x)	1%	76%	100%	100%	24%	51%
R6: PM 20 g/kg (2x)	5%	99%	100%	100%	50%	94%
R7: PS 5 g/kg (2x)	4%	52%	54%	32%	53%	60%
R8: PS 10 g/kg (2x)	19%	65%	75%	49%	72%	74%
R9: PS 20 g/kg (2x)	34%	73%	81%	62%	80%	81%
R7: PSA 5 g/kg (2x)	0%	42%	20%	5%	31%	40%
R8: PSA 10 g/kg (2x)	0%	43%	31%	8%	38%	44%
R9: PSA 20 g/kg (2x)	1%	51%	60%	33%	61%	62%
R13: nFe 5 g/kg	0%	81%	91%	22%	18%	10%
R14: nFe 25 g/kg	22%	100%	100%	94%	37%	34%
R15: nFe 50 g/kg	32%	100%	100%	100%	44%	45%
R16: µFe 25 g/kg	13%	98%	100%	41%	29%	35%
R17: µFe 50 g/kg	19%	99%	100%	53%	35%	50%
R18: µFe 100 g/kg	23%	100%	100%	67%	36%	52%
R19: gFe 50 g/kg	0%	48%	67%	0%	11%	7%
R20: gFe 100 g/kg	0%	57%	86%	0%	12%	13%
R21: gFe 200 g/kg	0%	68%	98%	5%	17%	19%
Startvalue	390-770 mg/l	2,3-4,8 mg/l	600 µg/l	16-21 mg/l	600 µg/l	5-9 mg/l

Biodegradation potential

After three months of incubation, when the chemical oxidants were no longer reactive, lactate was added to evaluate the remaining biodegradation potential of soils after chemical treatments. In the original aquifer material, without chemical treatment, an anaerobic biodegradation potential for a number of the chlorinated compounds was observed as shown in figure 2 for PCE. The CAH-biodegradation activity started in the biotic controls after a lag phase of 3 months (at the end of the first phase) in the presence of the highly polluted water. This was evidenced by an increase in the vinyl chloride concentration (figure 2). In the aquifer sufficient electron donor seems to be present. Addition of lactate in the second phase, even delayed the CAH-biodegradation.

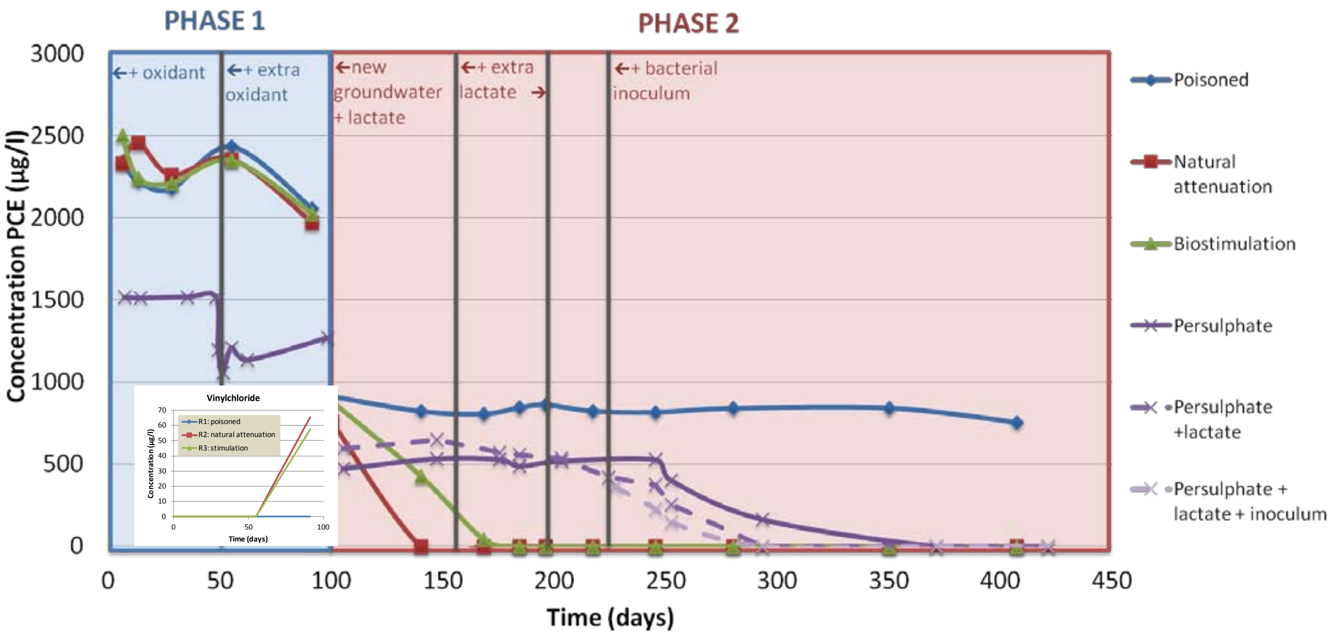

Figure 2: Evolution of PCE (VC) concentrations in the controls without chemical reagents and with persulphate (5 g/kg dry aquifer).

Biodegradation potential after chemical treatment (Phase 2).

The chemical treatments, however, did impact the biodegradation in most of the chemical oxidation cases. In the test condition with 5 g/kg permanganate (PM), no biodegradation was observed in the first part of the second phase, also not when lactate was added as electron donor at day 100. Only after several extra additions of lactate and when the ORP was lowered till -150 mV, the CAH-biodegradation revived. Addition of a bacterial CAH-degrading culture did not lead to an improved degradation. No activity was seen in the test conditions where higher doses of permanganate were applied. Persulphate (figure 2) seemed to have a slightly smaller negative impact on CAH-biodegradation, In this case, addition of lactate and inoculum shows a positive effect on de the biodegradation. Again, in test conditions treated with higher doses, no biodegradation was observed. The redox potential, significantly increased by the chemical oxidants, seems to be a crucial parameter. Lowering of the ORP by addition of an electron donor like lactate was found feasible, but requires time.

In the presence of chemical reductants, the redox potential was lowered. As during the second phase the zerovalent iron was still reactive, elevated concentrations of vinyl chloride (only a major degradation product of biodegradation and not of chemical reduction) were used as indicator for simultaneous occurrence of biodegradation and chemical reduction. ZVI concentration compatible with biodegradation were found to be > 5/kg of nFe and > 100 g/kg of µFe. At different time points, samples have been taken for a more detailed study of the active microbial population via molecular analyses on DNA and RNA level in a next step.

CONCLUSIONS

For the aquifer considered, chemical reduction was found more suitable than chemical oxidation to remove the chlorinated ethenes, but the latter did not cope with a number of co-pollution. Chemical oxidation, and especially permanganate, was found to have a negative impact in biodegradation. On the other hand, chemical reduction was found more compatible with subsequent and even simultaneous CAH-biodegradation.
The choice of chemical oxidation versus chemical reduction is site dependent**.** Generally, chemical oxidation preferred (1) for oxidized aquifers (high ORP), (2) when aerobic biodegradation envisioned in next phase, or (3) when no biodegradation envisioned, (5) for pollutants not degradable by reduction, and (6) when a fast removal & short activity period is required. On the other hand, generally, reduction preferred (2) for reduced aquifer (Low

ORP), (2) with high organic carbon content, (3) when anaerobic biodegradation envisioned in next phase, (4) when a relative fast degradation over potentially longer time period is envisioned.

ACKNOWLEDGMENTS

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Session 5

Numerical models to estimate impact of remediation technologies

Oral presentations

Groundwater-stream interactions in a seasonal flooded wetland: Field investigations and numerical modeling

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The effects of seasonal flooding of a wetland on groundwater-stream interactions and nitrate reduction have been investigated at a field site in Denmark. The wetland was reconstructed in 2003 bringing the river back to its meandering track and raising the river bed. The objectives of this study have been to investigate and quantify the capacity of reconstructed wetlands to rehabilitate polluted groundwater from diffuse sources, here agrochemicals such as nitrate and pesticides. The study is part of an EU integrated project AQUAREHAB (www.aquarehab.vito.be).

A conceptual model of the wetland is based on numerous hydrogeological and hydrogeophysical investigations. The wetland is a low-lying wetland with a width of ~200 m and is therefore flooded regularly over the year due to either prolonged or short bursts of rainfall. The groundwater residence time during periods with no flood is ~7-11 years. A redox zonation exists with oxygen and nitrate present in the first 20-40 m of the wetland (viewed from the edge of the wetland) followed by a zone with nitrate reduction. Generally nitrate is depleted before groundwater reaches the stream.

The exact mechanisms of nitrate attenuation may, however, not only be due to nitrate reduction alone, but rather a combination of flow dynamics (seasonal flooding) and nitrate reduction. We hypothesise that the sandy aquifer is low-reactive (no data yet) and the rate of nitrate reduction therefore low. Thus, during periods with no flooding, nitrate will move with groundwater to the stream with little attenuation. During periods with flooding (3-4 months per year) the stream-wetland system will act more like a groundwater-lake system with groundwater now discharging near the moving maximum flooding distance. This has the effect of; (1) forcing part of the groundwater and nitrate up through the organic-rich peat layer causing high nitrate reduction and, maybe more importantly, (2) trapping part of the groundwater and nitrate in the aquifer below the flooded area in a now stagnant zone allowing the (slow) nitrate reduction to be effective compared to transport.

The hypothesis has been tested by comparing field results and 2D cross-sectional flow and reactive transport simulations (Feflow). A dynamic upper boundary condition was built into Feflow allowing the boundary to switch from being flooded or not. The main results are; (1) in the model, the point of discharge follows the changing location of the flooding distance, which is corroborated by the observed hydraulic head distributions that show increased gradients between the edge of the wetland and the flooding distance and stagnant groundwater below the flooded part of the wetland, (2) a model sensitivity analysis shows how the periodic flooding controls the movement of nitrate in the wetland and how the groundwater residence time versus the time scale for nitrate reduction is important, and (3) an analysis of the hydroperiods shows that the average flooding distance correlates with the maximum intrusion of nitrate into the wetland.

The apparent success of this wetland in rehabilitating groundwater (little nitrate reaches the stream) therefore relies on how flooding change the pattern of groundwater-stream interaction.

Modelling biological, geochemical and isotopic processes during enhanced denitrification using two different sources of organic carbon in batch experiments

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Groundwater pollution by nitrate is an important environmental problem. Enhanced *in-situ* biodenitrification seems to be a clean and economical technology that allows remediating nitrate-polluted groundwater. Compound-specific isotope analysis (CSIA), on the other hand, is a powerful tool to determine the degree of nitrate degradation. Using the Rayleigh equation, it relates the change in the isotope ratio of the nitrate molecule ($\delta\ ^{15}N\text{-}NO_3^-$, $\delta\ ^{18}O\text{-}NO_3^-$) to the fraction of molecules remaining as a result of denitrification, via the kinetic isotope fractionation factor of the isotope pair and the degradation process. Nevertheless, it is known that its implementation to groundwater systems has high limitations due to the coexistence of other processes like dispersion, dilution or sorption as well as to the heterogeneity of hydrogeological media. An alternative approach for CSIA is the incorporation of isotope fractionation processes into numerical or analytical reactive transport models (RTMs). Usually, RTMs with isotope fractionation have focused on natural attenuation and barely on stimulated bioremediation. In this work, we model different batch experiments of enhanced heterotrophic denitrification that used two different external sources of organic carbon (ethanol and glucose) using the Phreeqc-2 code. The models involve microbiological processes (redox processes, biomass growth and decay), main geochemical equilibrium (precipitation-dissolution of calcite), and isotopic fractionation during denitrification ($\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$ and $\delta^{13}C$-TIC). Modeling results allow evaluating the interaction between biodenitrification, calcite equilibrium and isotopic fractionation of the above mentioned isotopes. We demonstrate that the source of organic carbon plays a specific role in calcite equilibrium (dissolution or precipitation). Moreover, the model shows the importance of biomass decay (endogenous respiration) in nitrate and inorganic carbon isotope fractionation.

Predictive assessment of groundwater remediation efficiency for a permeable reactive barrier site

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ABSTRACT: Fe^0 permeable reactive barriers (PRBs) are used to remediate groundwater pollution, especially in the case of VOCs (volatile organic compounds) contamination. These systems are installed in the subsurface where the naturally present hydraulic gradient makes the contaminated groundwater flow through the barrier. Inside the barrier the contaminants are removed by abiotic reactions, which are typically much faster than natural attenuation rates. Precipitation of carbonate minerals reduces the barrier reactivity and permeability, hampering its long term efficiency.

In this study, a three-dimensional reactive transport model of a field PRB site in Wilrijk (Belgium) was developed using data from a twelve year long monitoring campaign where the dissolved contaminant concentrations, inorganic ions and groundwater levels were measured with different frequencies in a total of 250 monitoring wells.

Laboratory batch and column experiments performed with groundwater and aquifer material from the field site were used to independently estimate contaminant biotic and abiotic degradation rates. The model was calibrated with the data collected at the site (groundwater levels and contaminant concentrations) using PEST software. After model calibration three scenarios were built to assess different remediation actions at the site.

In the first scenario, no remediation action is taken and the contaminants are degraded only by natural attenuation. In the second scenario, the contaminants are removed by natural attenuation and by the PRB. This scenario resembles actual field conditions and the simulation results were compared with available data. In the third scenario, natural attenuation and enhanced biodegradation downgradient of the PRB is modeled. This last scenario represents a hypothetical situation where organic matter (e.g. lactate) is used to enhance contaminant biodegradation downgradient of the PRB. Simulation results and measured data show an abrupt decrease of contaminant concentrations after the PRB installation in the downstream piezometers close to the barrier.

INTRODUCTION

The use of PRB for groundwater remediation is an active research field, which has grown tremendously during the last 15 years. Much research has focused on monitoring of pilot studies or actual field sites where PRBs were installed [1]. Much less research has been devoted to interpretation of field trials and rigorous modelling to enhance physical understanding and predict long-term efficiency of these systems. Multi-component reactive transport modelling of PRB systems has been reported by [2-5]. Their simulations illustrated that secondary mineral precipitation in the upgradient portion of the barrier may decrease the barrier porosity in the long term.

Mayer et al. [4] focused on a PRB at the Coast Guard Support Center near Elizabeth City, North Carolina. Reactive transport modelling was performed using the MIN3P model [6]. In a similar study, Yabusaki et al. [5] reported reactive transport simulation results using the OS3D model for a pilot-scale PRB installed at Moffett Field in Mountain View, California. They confirmed that secondary mineral precipitation in the barrier may impact long-term operation of the PRB. Using data from previous studies and a modelling approach based on MODFLOW [7] and RT3D [8], Li et al. [3] showed that porosity reductions in zero-valent iron PRBs are mostly due to precipitation of calcium and iron carbonates, and therefore are more extensive when groundwater contains high concentrations of bicarbonate and carbonate ions.

In this study, a three dimensional model of a contaminated PRB site in Wilrijk (Belgium) was build to assess barrier remediation efficiency at the site. The model was calibrated using groundwater levels and concentration measurements collected over a period of 12 years.

After model calibration three scenarios were simulated to assess different remediation actions at the site.

In the first scenario, no remediation action is taken and the contaminants are degraded only by natural attenuation. In the second scenario, the contaminants are removed by natural attenuation and by the PRB. This scenario resembles actual field conditions and the simulation results were compared with the available data. In the third scenario, natural attenuation and enhanced biodegradation downgradient of the PRB is modeled. This last scenario represents a hypothetical situation where organic matter (e.g. lactate) is used to enhance contaminant biodegradation.

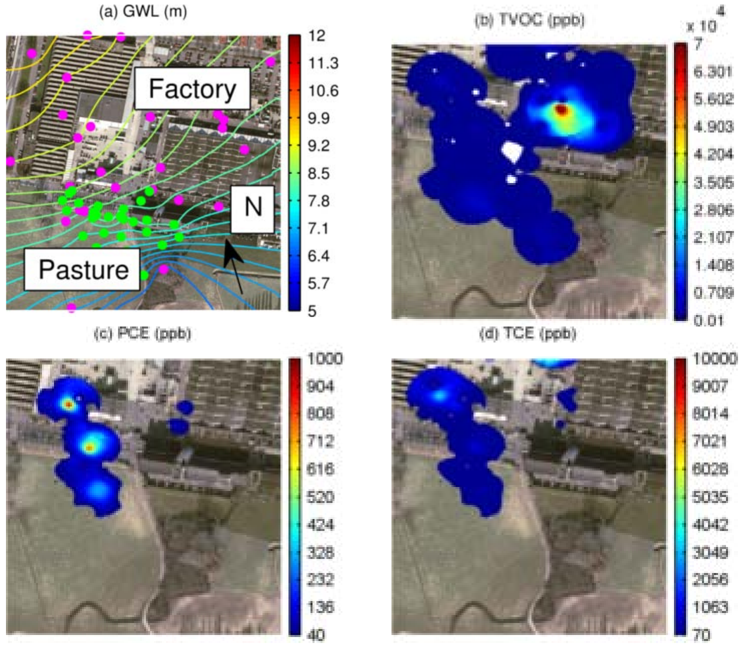
METHODS

Site description

The studied site is located in Wilrijk, Antwerp (Belgium). The contaminated phreatic aquifer consists of a sandy-clay soil overlying a fine clay formation (“Boom clay”) located at an average depth of 5 meters. The contamination originates from the use of Volatile Organic Compounds in the factory area (Figure 1) for painting/degreasing activities from 1957 to 1994. In the years 2000-2003 an extensive monitoring campaign using more than 250 piezometers was performed to better delineate the plume extent by measuring the concentrations of various contaminants (PCE, TCE, cis-DCE, VC, TCA and DCA). Most of the piezometers were screened over a depth of 1 meter above the clay layer.
As can be seen from Figure 1, multiple separate plumes have developed at the site. From the historical records the parent contaminants were PCE, TCE and TCA, while cis-DCE and VC were mostly generated by natural attenuation of parent contaminants.
To prevent contaminant migration from the factory to the pasture area (Fig. 1a), a PRB was installed in August 2005 (red line in figure 2). The barrier consists of a trench approximately 180 m long and 0.3 m wide, filled with a mixture of fine iron and sand (20% and 80% in weight respectively). After installation, the monitoring effort was concentrated on 23 piezometers near the barrier (green piezometers in Figure 1a).

Site model

A flow and transport model based on MODFLOW-2000 [7] and RT3D [8] was constructed to simulate contaminant migration and degradation. The model is composed of 2 layers, 133 rows and 125 columns with a local grid refinement (2.5 by 2.5 m) in the PRB area (Figure 2). The bottom model layer coincides with the screened interval of the piezometers.



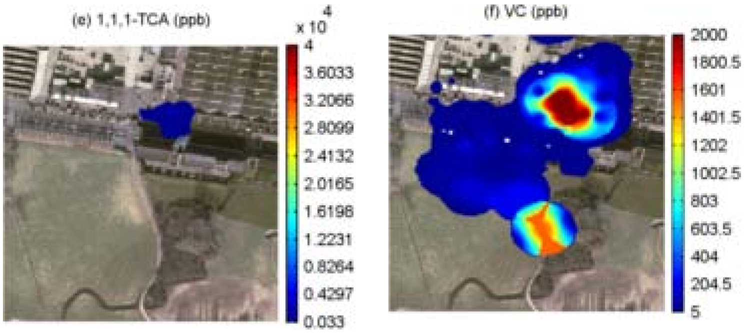


Figure 1: Measured groundwater levels contaminant concentrations (scale 1:8000). The top-left figure shows locations of the monitoring piezometers.

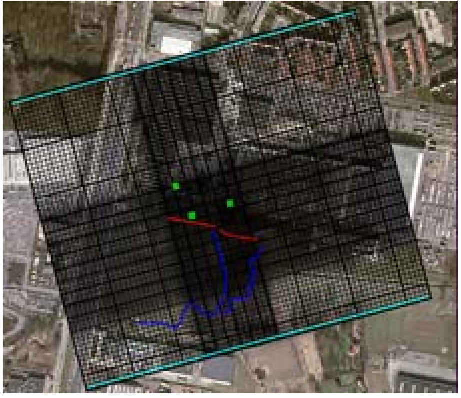


Figure 2: Model discretization and boundary conditions. Red line = PRB, green squares = contaminant sources, light blue lines = general head boundaries, dark blue lines = drains

Cauchy type boundaries (general head) were used at the north and south side of the model domain. No-flow boundary condition were specified for the west and east boundaries. Three drains are specified in the pasture area, as observed in the field. Evapotranspiration and recharge were included only in that part of the model that coincides with the pasture area (Fig. 1a)

Transport of contaminants was simulated in the central part of the model domain (refined area in figure 2), as this part of the site was relatively well characterized. Release of contaminants from the sources was simulated accordingly to the following mass transfer rate:

$$\frac{dC}{dt} = \max\left[KLA(C^{*} - C), 0\right]$$

where C is the dissolved contaminant concentration (mol L^{-1}), KLA is a mass transfer coefficient (d^{-1}) and C^{*} is the solubility of the parent contaminant in groundwater.

The barrier is not oriented perpendicularly to the main flow direction (as derived from the head measurements) and is represented in the model as a series of reactive connected cells, resulting in a stair-type representation of the barrier in the model grid.

The model simulates a period from 01/01/1966 to 30/05/2012 for a total of 16950 days. The first 12410 days (from 01/01/1966 to 01/01/2000) were simulated using one steady-state stress period. This allows the plume to fully develop downstream of the barrier, providing a starting picture of the contamination before the PRB installation. The following time period from 01/01/2000 to 30/05/2012 was discretized using 149 monthly stress periods, forcing the model with the evapotranspiration and precipitation fluxes measured in a weather station close to the site.

Natural attenuation of VOCs was modelled as a sequence of first-order degradation reactions (Figure 3).

Chemical degradation of contaminants (PCE, TCE, cis-DCE and VC) by zero-valent iron was assumed to mainly occur by β-elimination. The stoichiometric coefficients and the reaction network proposed by Arnold and Roberts [9] were used for the contaminant degradation by zero-valent iron. Individual VOCs degradation were described by a mixed-order rate law [10]:

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

where k_{VOC} is the rate coefficient per unit iron reactive surface area (mol m^{-2} s^{-1}), S is iron reactive surface area per unit water volume (m^2 L^{-1}), and $K_{1/2}$ is the half-saturation constant (mol L^{-1}). These constants were determined for each contaminant in a separate column experiment [11].

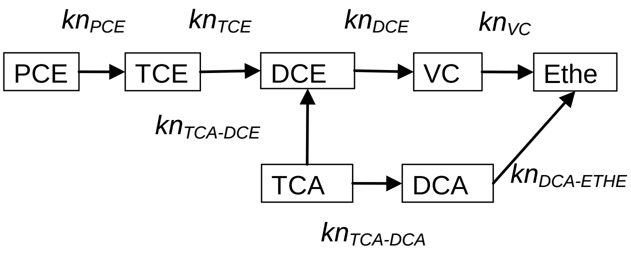


Figure 3: Natural attenuation reaction network used in the model. k_n are the first-order reaction rate coefficients.

Calibration methodology

Goal of the model calibration was to estimate model parameters (hydraulic conductivity and coefficients for contaminant release and degradation) from groundwater levels and contaminant concentrations measured at the site. Calibration was done with PEST software [12], using pilot points [12] for representing spatially variable parameters, and regularization and truncated singular value decomposition to maintain parameter identifiability. Due to the large number of model parameters and the computational burden the model calibration was divided in two steps.

In the first step, the horizontal hydraulic conductivity and the 3 drain conductances (DC) were estimated from 396 groundwater levels (GWLs). The horizontal hydraulic conductivity was parameterized using 100 pilot points and an exponential variogram was fitted to 15 slug test estimates of the hydraulic conductivity.

In the second step, the hydraulic conductivity was kept fixed and 7 degradation parameters (*kn*), 3 contaminant mass transfer coefficients (KLA) and longitudinal dispersivity (LDSP) were estimated from 2241 concentration measurements.

Table 1: Calibration steps. In brackets, the number of calibrated parameters and observations are given.

Calibration step	**Variable parameters**	**Constant parameters**	**Dataset**
1 (flow model)	HHK (100), DC(3)	SY	GWLs 2012 (396)
2 (transport model)	kn (7), KLA (3) LDSP (1)	SY, POR	VOCs measuraments 2000-2012 (2241)

RESULTS

Flow

The calibrated hydraulic conductivity field after calibration step 1 is shown in figure 5.

Estimated hydraulic conductivities at the slug test locations were on average 18 times higher than those obtained from the slug tests. A similar result was found by [13]. High values of hydraulic conductivity might compensate for an incorrect description of the recharge process, as the highest values are found in the pasture area of the model (fig. 5). Moreover, slug tests consider only the deep part of the aquifer close to the low conductivity clay layer. The conductivity estimated with pilot points is also determined by the shallow part of the aquifer, especially in the pasture area where the water table was found close to the ground surface. This part of the aquifer may have a higher hydraulic conductivity compared to the deep aquifer.

Transport

Results of the second calibration step are shown in figure 6. These figures show simulated groundwater levels and contaminants concentrations for January 2012. Groundwater levels and plume direction are well reproduced (compare figure 1a and 6a and figures 1b and 6b). PCE concentrations are overestimated because the calibrated mass transfer at the PCE source was too high. The simulated TCE plume does not extend downgradient of the barrier, which is also seen in the measurements (compare figure 1d and 6d). TCA is rapidly transformed to DCA, resulting in a small plume localized near the source. The greater discrepancy was observed for the VC plume. Observed VC concentrations were generally low, except those close to the TCA source (due to the degradation chain TCA-DCE-VC) and in one piezometer downgradient of the barrier (see figure 1f). In the latter case the high VC concentrations can be caused by local high values of the contaminant degradation rates. Separate batch experiments performed with aquifer material and contaminated groundwater indicate that the degradation rates are spatially variable and related to the organic matter content. Variability of the degradation parameters will be explored in future calibration experiments.

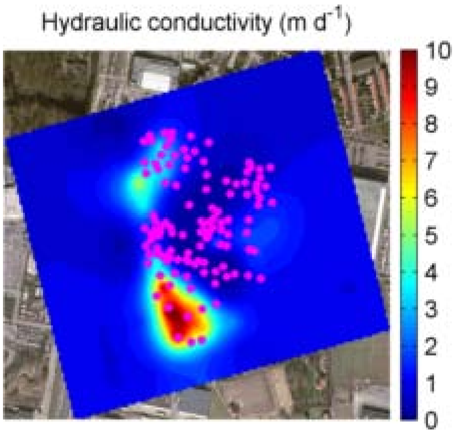


Figure 5: Horizontal hydraulic conductivity field after calibration step 1. Magenta dots show the locations of the groundwater level piezometers.

Model scenarios

Using the calibrated model three scenarios were simulated up to 2035. For the scenarios it was assumed that the NAPL contaminant mass at the source location is not consumed by contaminant dissolution and no deactivation of the iron barrier occurs. In a next stage the effect of mineral precipitation on the barrier reactivity will be considered.
In the first scenario, the barrier is not installed and the contaminants degrade only by natural attenuation. Natural attenuation degradation parameters were taken from the previously calibrated model. The resulting plume is shown in figure 7a. As can be seen from the figure, without the barrier the contamination spreads downgradient into the pasture area. Moreover, the source at the right side of the figure spreads further downgradient, without being substantially degraded.
The second scenario considers degradation by both natural attenuation and the PRB (installed in 2005). In this scenario the barrier is able to prevent further contaminant migration. Natural attenuation is not able to completely remove the contamination downgradient the barrier, resulting in a small plume in the pasture area (figure 7b).
In the third scenario, the remediation effect of the barrier and enhanced natural attenuation in the pasture area were considered. The values of the first order degradation rates shown in figure 3 were increased based on batch experiments where biological degradation was enhanced by addition of lactate. Enhanced natural attenuation was able to completely degrade contaminants downgradient of the barrier. The scenario assumes that degradation rates are maintained at a high level by repeated lactate additions.

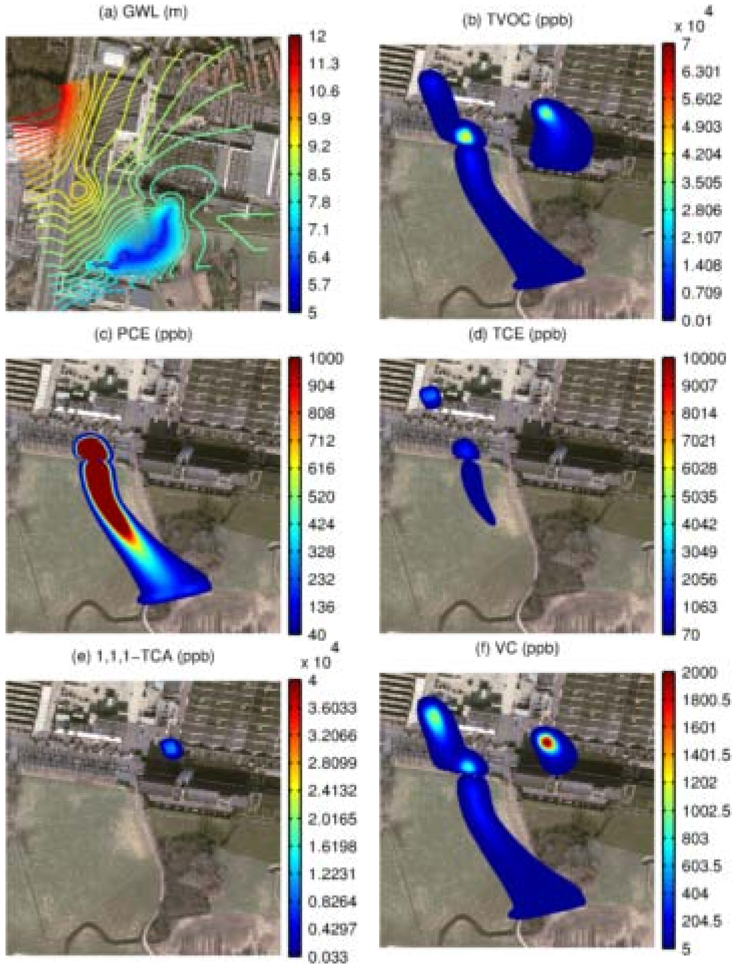
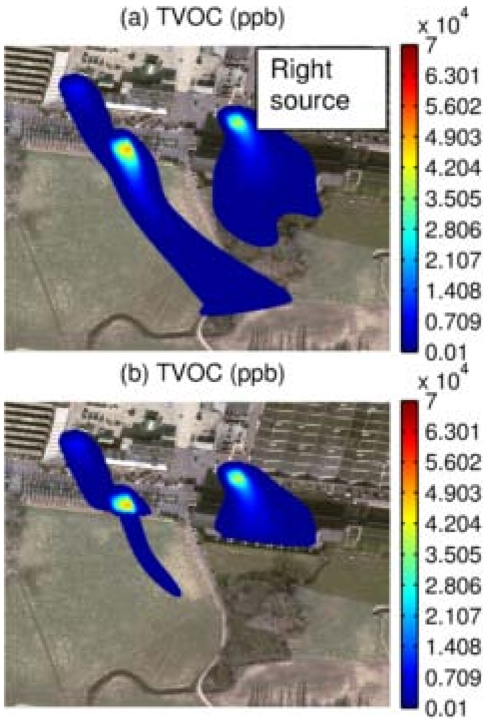


Figure 6: Simulated groundwater levels and contaminant concentrations for January 2012.



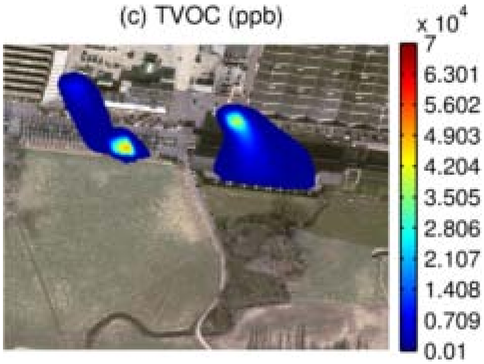


Figure 7: Simulated total contaminant concentration for the three scenarios.

CONCLUSIONS

In this study we developed a reactive transport model for a field PRB site. The model was calibrated on a large amount of groundwater levels and concentration data. Subsequently, three scenarios were simulated in order to predict the effect of different remediation actions (natural attenuation only, PRB and natural attenuation and PRB with enhanced natural attenuation).

The current groundwater levels and the plume direction were well reproduced by the model. Substantial discrepancies were found for the PCE plume and VC concentrations at the plume edge. Possible model improvements include a better estimation of the PCE mass transfer, spatially variable biodegradation rates and PRB passivation due to mineral precipitation.

Despite these limitations, the model correctly simulates the main features of the actual plume, such as the high contaminant concentrations found downgradient of the PRB after its installation. Model scenarios up to 2035 indicate that this contamination might not be removed only by natural attenuation and some additional remediation action, such as enhanced natural attenuation, must be undertaken.

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Hydrogeochemical modelling as a tool for planning and monitoring of in-situ soil and groundwater biogeochemical remediation

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ABSTRACT: The remediation of contaminated soils and groundwater is carried out not only on active industrialised areas but more often on areas of historical spills and now destined to revitalisation. The less invasive in situ remediation of polluted soil and groundwater, in comparison with ex situ techniques which require the removal of soil, becomes increasingly popular. Its most important feature is a feasibility to be conducted on densely built-up and industrialised areas as well as on transport routes, without a requirement for these to be out of use. The approach of the UPSOIL project is based on the combining of bio-chemical methods of remediation in situ within sites polluted by organic substances. The elaborated procedures/techniques may enable fast and cost-effective treatment of both: source and plume of contaminants at acceptable risk levels. Simultaneously, created method has to assure use of the natural potential of soil to attenuate organic contaminants. Hence, the approach assumes two stages of treatment: first – a quick and invasive oxidation, when the reactant is injected directly into the most contaminated places, and a rather slower phase in which pollutants are treated using bioremediation techniques together with the natural mechanism of attenuation. Performing chemical treatment in complex soil conditions, requires good planning and control of the injection parameters, control of soil matrix changes during the reactive phase, assessing the process efficiency in time, and evaluation of post treatment soil conditions. For that reason improvement in planning and monitoring are made within UPSOIL project. To achieve this a monitoring system based on automatic on-line loggers is coupled with modelling tools. The modelling results enable determination of critical values for parameters of risk and efficiency control which can be further used in assessing the on-line monitoring results. This approach is tested at sites contaminated with petroleum hydrocarbons and chlorinated compounds. The approach can secure timely made decisions on injections, locations of injection wells and injection parameters. At the same time cost-efficiency can be increased and remediation time shortened. The test's results show essential potential for improving remediation performance of in-situ chemical oxidation.

INTRODUCTION

The contamination of soil and groundwater by organic pollutants is a vital issue on industrialised areas, especially on previously abandoned and nowadays destined to the redevelopment. According to recent estimates, in the EEA (European Environment Agency) member countries there are nearly 250,000 soil contaminated sites, in turn, in USA the pollution of groundwater by organic compounds has occurred in 300,000 to 400,000 sites (Doust, Huang, 1992; USEPA, 2000). These numbers are expected to grow, because potentially polluting activities are estimated to occur at nearly 3 million sites (including the 250,000 sites already mentioned) (EEA, 2007).

Conventional treatment methods, such as pump-and-treat technology are often costly and semi-effective. The economic analysis has revealed that annual costs related to the performance of pump-and-treat treatment in the United States reaches 4.5 billion $ (Siegrist et al., 2011). Moreover, the application is often hardly possible on densely built-up areas. Due to these inconveniences, the implementation of alternative, lower-cost and lower-space technologies is inevitable. However, the conquest of the market by a new technology requires a very insightful field testing. The latter might be preceded by the modelling, which helps to predict the effect of remediation and to control the whole process. If the modelling tool works in a real-time and is fed by verified data, modelling might be parallel to the treatment. A full understanding of the process, supported by the frequent monitoring; real-time and periodical measurements can provide both: information about the long-term process and the verification of modelling results.

Within the last 10 years, the remediation of groundwater polluted by organics using in situ chemical oxidation (ISCO) has been developed. This technique involves multiple injections of oxidants directly into the source of pollution (ITRC, 2005). The reaction between oxidant and pollutant produces innocuous, non–reactive substances such as water, carbon dioxide and chloride. The ISCO method is continuously being improved by numerous batch and field studies. New challenges include the precise injection, i.e. outlining the targeted depth interval and providing the injection directly therein and matching the dose of oxidants with the contaminant load. Considering very dynamic and invasive character of the process, its control is also the issue of concern.

Because the modelling identifies chemical processes and enables predictions of their consequences; it should precede all clean-up actions. This paper describes the concept of modelling tool aiming to plan and optimise the ISCO process. The model is coupled with a simple toolkit displaying all collected monitoring data and performing the alarm while monitored parameters exceed thresholds accepted by the user. The alarm system can indicate a poorly-performed injection or/and the abnormal behaviour of environment. Hence, it helps to optimise and to plan the further injection campaigns.

STATE OF THE ART

During the ISCO actions, oxidants degrade COC's (contaminants of concern) such as chlorinated hydrocarbons, fuels, phenols, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, explosives and pesticides). Nowadays there are several oxidants which are commonly used or tested (e.g. permanganate, hydrogen peroxide, ozone, persulfate, peroxene, calcium peroxide, percarbonate) (IRTC, 2005; Huling, Pivetz, 2006; REGENESIS, 2007).

Degradation processes produce intermediates and follow the second-order kinetics (Siegrist et al., 2011). The understanding of pathways and the rate of reactions is a key driver in building of an accurate modelling tool and in controlling the process. The modelling tool can help in the successful performance of field tests. Such tests may eventually end up with fully commercial applications and the elaboration of best practices guidelines.

The ISCO laboratory tests and field demonstrations began in the 90s. The results were published in numerous articles, reports and books (e.g. Bellamy et al., 1991; Gates, Siegrist, 1995; USEPA, 1998; Gates-Anderson et al., 2001; Kim, Choi, 2002; ITRC, 2005). Numerical simulations of the ISCO processes have been developed at the same time as the first experiments and field tests. The majority of modelling studies have been concerned on the application of ozone within vadose zone (Hsu, Masten, 2001; Kim, Choi, 2002; Shin et al., 2004) and permanganate within saturated zone (Mundle et al., 2007; Henderson et al., 2009; Cha, Borden, 2011: Versteegen, 2011). Currently, modelling studies pertained to other oxidants are developed (Chang et al., 2011: Watts, 2011), however they are still rather in a phase of testing and quite aside from the modelling mainstream. It may result from the complexity of oxidation reactions and the lack of kinetic data required for the modelling. Codes and modelling tools describing use of oxidants other than permanganate are rarely available, thus the potential operators and ISCO users have to build them from the ground up. Usually, the ISCO models include following processes: advection, dispersion, NAPL dissolution, sorption/desorption of COC's, degradation of COC's using second-rate kinetics reaction and NOD oxidation using different approaches depending on reactions' rates (Hanning, 2007; Borden et al., 2010).

As it was mentioned, there are few models which can be tested against the ISCO experiments, for example 1D model CDISCO (Borden et al., 2010) (conceptual design for ISCO) and 3D model CORT3D (chemical oxidation reactive transport in 3D) (Illangsekare, 2006). The ISCO modelling might be also performed using modified by user models such as PhreeqC (Parkhurst, Appelo, 1999), Modflow-2000 (Harbaugh et al., 2000) or combination of both – PHT3D (Prommer, Post, 2010). However, any changes in the numeric code require a good knowledge of both the structure of the code and dynamics of the process. Besides, the already existing tools are rather suitable for planning than controlling of the ISCO process. They may help to select the most vulnerable zones, to predict the oxidant consumption, COC's degradation and the response of the physical parameters – pH, ORP, temp. Hence, future challenges of the modelling encompass: 1) application of different oxidants, 2) coupling the real-time monitoring and modelling and 3) building very detailed 3D models in user-friendly way.

MODEL CONCEPT AND REALISATION

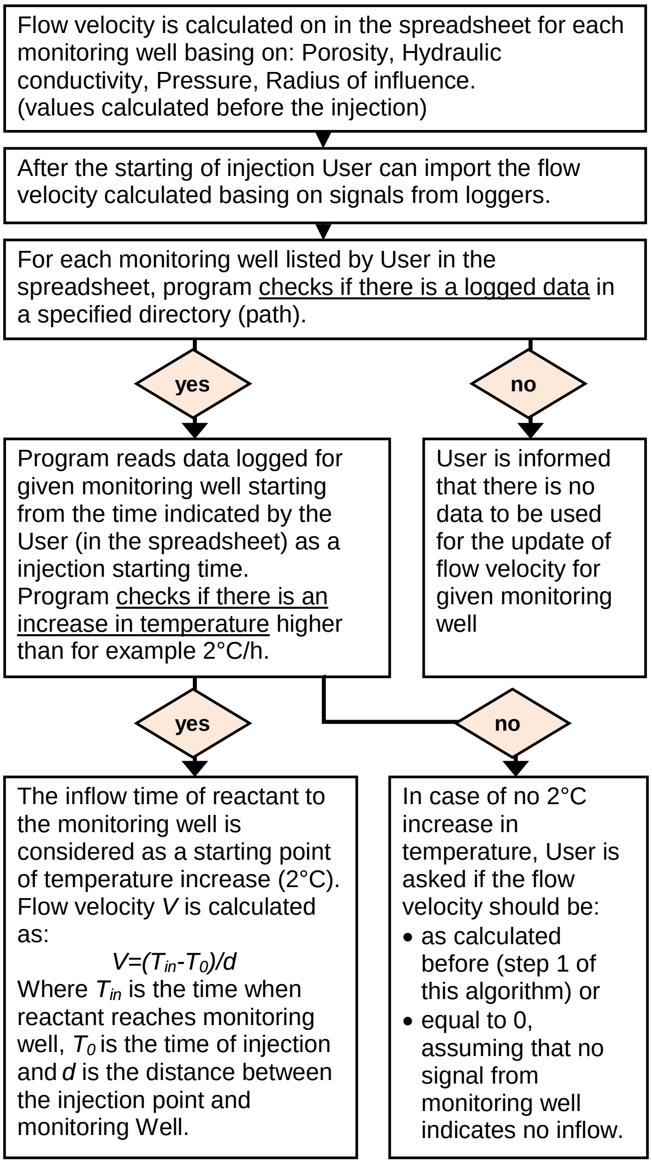
The model developed in UPSOIL project has a form of Microsoft Excel spreadsheet coupled with monitoring data and is composed of two main calculation parts. The first one is designed for the summarisation and estimation of initial physical and chemical conditions. These conditions are calculated for each monitoring point and are distance averaged for the injection point. Results of these calculations are used partially as an input to the second calculation part - hydrogeochemical model (PhreeqC), which calculates the future status of groundwater along flow paths between the injection point and each monitoring well. Subsequently, outcomes from the PhreeqC model can be imported to the spreadsheet together with the monitoring data as: 1) a table; 2) charts presenting changes of physical and chemical parameters (for given point and changing time or given time and each point on a pathway); 3) map of the monitored area with the interpolation of simulated parameters. Basic steps in the use of model are presented in Table 1. Except of the writing of the basic parameters into the spreadsheet (step 2 in the table), all other functions of this tool are executed using buttons and dialog boxes. All the functions are based on Visual Basic or Python language scripts hidden behind a simple spreadsheet interface.

Table 1: Basic steps in the use of model.

1	User sets the real-time monitoring devices in wells surrounding the injection point. Measured parameters include: pH, pE, temp.
2	User writes data into the spreadsheet: • Coordinates of injection point and monitoring wells; • Parameters of injection: rate, volume, concentration of reactant; • Physical and chemical parameters: o of injected fluid (or fluid planned to be injected) o in monitoring wells o of surrounding (clean) water o of water in micropores [optionally]: (parameters include: pH, pE, temp., concentration of pollutants and base ions, density, porosity, hydraulic conductivity)
3	Spreadsheet calculates basic parameters: • Radius of influence (ROI), • Total bulk treatment volume, • Velocity of water, • Time of reaching the ROI etc.
4	User sets in the spreadsheet the path to loggers data (to the real-time monitoring set in step 1)
5	[Optionally] User imports initial conditions from real-time monitoring for the time of injection (pH, pE, temp., flow velocity). Parameters are written into the spreadsheet - FEEDBACK 1 (see Figures 1 and 2).
6	User generates the input data for PhreeqC model and runs the model. Inputs are generated basing on data gained in steps 2, 3 and 5.
7	User imports the monitoring data and outputs from the PhreeqC model into the spreadsheet. Data are presented as graphs or maps – FEEDBACK 2
8	[Optionally] User can set threshold values for parameters included in real-time monitoring. Exceedances of these values will be shown in the spreadsheet and reported as messages sent via e-mail - FEEDBACK 3

As it was mentioned in step 5, 7 and 8 of the Table 1, the model includes three types of feedback which are designed to be used by ISCO operator during or after the injection. The feedback means here output data, based on real-time monitoring and calculations, which can be used to: 1) adjust the ongoing process of remediation, 2) modify the strategy of remediation after the first injection campaign or 3) to confirm that remediation is being done according to the plan.

The **first feedback** is the use of real-time monitoring to feed the mathematical model with up-to-date data including the pH, pE, temperature and flow velocity at the moment indicated by the user as a starting injection time. Without this feedback the model's simulations would be based on mentioned four parameters calculated or measured prior to the injection. Algorithms of this feedback are presented on Figure 1 (import of the flow velocity) and Figure 2 (import of pH, pE and temperature).



Flow velocity is calculated on in the spreadsheet for each monitoring well basing on: Porosity, Hydraulic conductivity, Pressure, Radius of influence. (values calculated before the injection)

After the starting of injection User can import the flow velocity calculated basing on signals from loggers.

For each monitoring well listed by User in the spreadsheet, program checks if there is a logged data in a specified directory (path).

Program reads data logged for given monitoring well starting from the time indicated by the User (in the spreadsheet) as a injection starting time. Program checks if there is an increase in temperature higher than for example 2°C/h.

User is informed that there is no data to be used for the update of flow velocity for given monitoring well

The inflow time of reactant to the monitoring well is considered as a starting point of temperature increase (2°C). Flow velocity V is calculated as:

$$V=(T_{in}-T_0)/d$$

Where T_{in} is the time when reactant reaches monitoring well, T_0 is the time of injection and d is the distance between the injection point and monitoring Well.

In case of no 2°C increase in temperature, User is asked if the flow velocity should be:

- as calculated before (step 1 of this algorithm) or
- equal to 0, assuming that no signal from monitoring well indicates no inflow.

Figure 1. Feedback - estimation of the flow velocity

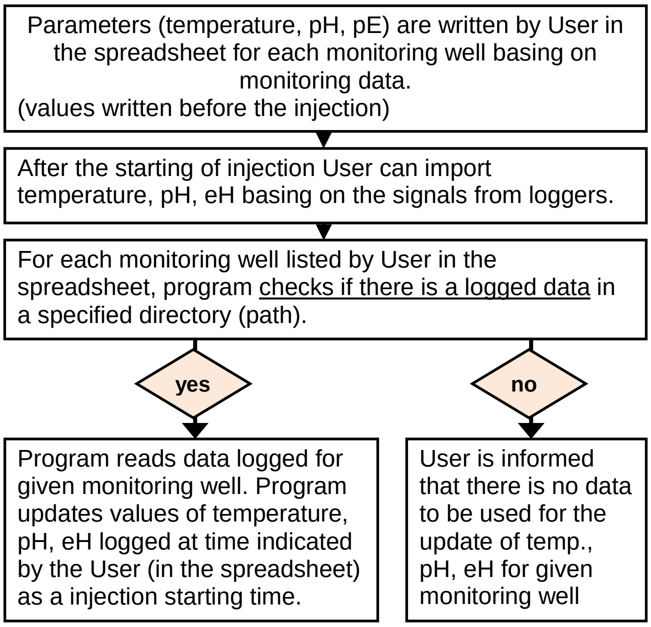


Figure 2. Loggers-based update of temp., pH, pE

The **second feedback** is based on monitoring data and outputs from the PhreeqC model imported into the spreadsheet. Data can be displayed as graphs presenting changes of physical and chemical parameters in time for given point on the flow path between the injection point and monitoring wells. The other options for graphs is presenting changes of parameters along the flow path for given time.

Imported data can be displayed also as a map presenting spatial distribution of modelled and measured parameters. The drawing of spatial distribution maps is performed using the IDW (inverse distance weighting) method (Azpurua, Dos Ramos, 2010). The interpolation is executed on the basis of Python (van Rossum, Drake, 2012) code using additional Python's numerical packages: Numpy, Scipy and Matplotlib (Dale et al., 2011).

The visualisation can be performed for chosen parameters for a given time, thus the user is allowed to track easily the immediate response of the aquifer system to the injected liquid. The comparison of maps drawn for: 1) different periods and 2) crucial parameters informing about the successful arrival of oxidant, may help to distinguish areas vulnerable for the oxidation from these more recalcitrant. Hence, the ISCO operator can plan further injections taking into consideration the zones wherein the level of the contaminants is still unsatisfactory high and water does not meet the quality standards.

The last, **third feedback** is a simple e-mail alarm system. The main concept of this system is to establish the thresholds for physical and chemical parameters (pH, pE, temperature) which may indicate the unexpected effects of injections (failure/danger) depending on the type of oxidant and pollutants.

A code written in Python imports to the spreadsheet's graph data recorded by loggers together with ranges typical for the oxidation process. When values of measured parameters exceed threshold values defined by the user, the alarm message is displayed and sent to the specified recipient as an e-mail message. The message includes names of parameters, values, date and time of exceedances.

CONCLUSIONS

There are several aims which this, designed for the Upsoil project modelling tool tried to fulfil. The first aim was the optimisation of injection. Using this tool for different scenario analyses (volumes and concentrations of the oxidant, pressure of the injection etc.) the user may understand better and predict the behaviour of environment during both injection and the post-injection phase. The latter phase of remediation may be crucial in the long-term use of the contaminated area and for incorporating other methods of the remediation (for example microbial enhanced remediation). This tool includes also the module where user can simulate releasing of contaminants from micropores. However, this part have been technically tested only but not validated.

Secondly, the modelling tool was aimed to gather results of both monitoring types: real-time (loggers) and periodical (field and lab tests). Collected data can be displayed as graphs (changes in time or along the flow path) and as spatial distribution maps.

Thirdly, the modelling tool gives the feedback for the further injection campaigns. The real-time data registered by loggers (pH, pE, temp.) can be instantly exported to the geochemical model, moreover changes in temperature can be used for the estimation of real velocity under the hydraulic conditions triggered by the injection. In addition, maps for chosen parameters can be used to point out areas wherein the injection should be repeated. Finally, the whole dataset recorded by loggers can provide the e-mail alarm for the ISCO process.

It is important to mention that this version of model was developed on the basis of literature sources and several field tests. Authors express their hope it will be further developed basing on experiences of knowledgeable specialists.

Broadly speaking, the tool should be thoroughly tested and developed by experienced users/modellers. Hence, authors encourage for modification and testing of developed software leaving it open for public use.

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Poster Presentations

Modeling Reductive Dechlorination of a CAH Containing Plume Entering the Zenne River

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Chlorinated solvents such as trichloroethene (TCE) remain one of the major groups of chemicals responsible for vast contamination of groundwater resources in many industrialized countries and pose a potential risk to human health and aquatic ecosystem integrity.

In our study, we have investigated a plume containing TCE and its daughter products dichloroethene (1,2 *cis*-DCE) and vinyl chloride (VC) entering the Zenne River near Brussels, Belgium.

The Zenne is a partly regulated lowland river with a mostly sandy, partly silty riverbed. Due to widespread use in numerous industrial processes in the past, perchloroethene (PCE) and TCE have entered the local aquifer at several locations and formed long-living DNAPL pools. Depending on local flow and transport processes, a slow dissolution of contaminants from these pools occurs and TCE as well as its daughter products are migrating toward the river. To assess variations in biodegradation parameters by *Dehalococcoides* spp. we have modeled different stimulated batch set-ups containing samples from various locations within the local alluvial aquifer and the hyporheic zone assuming Monod kinetics with competitive inhibition. Dechlorination parameters were estimated applying AMALGAM, a multi-objective parameter optimization routine. Simulation results showed that dechlorination parameters were comparable to results from previous studies and the observed parameter range substantiates the heterogeneity in biodegradation at the site. The obtained results could be used to design or improve field-scale *in situ* remediation measures.

Treatment Rinne – a new tool for toluene biodegradation modeling

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The contamination of soil and groundwater by organic pollutants is a vital issue on the urban and industrialized areas, especially on derelict and destined to the revitalisation. According to recent estimates, in the EEA (European Environment Agency) member countries there are nearly 250,000 soil contaminated sites, requiring clean up. Due to modelling identifies of biogeochemical processes and quantifying their consequences; it might precede all clean-up actions. Reactive transport of hydrocarbons should include both kinetics of the reactions, often microbial-mediated and flow, often within very heterogeneous medium. The combining of those elements is the greatest challenge of modellers working on the remediation of sites polluted by organic contaminants. It is a common practice to investigate the influence of heterogeneities on biodegradation processes using artificial aquifers, this research was also carried out in the indoor aquifer (Rinne). The experiment aimed to assess biodegradation process within heterogeneous aquifer included the pulse experiment, the steady-state toluene injection and the “accidental” spill of toluene. The user-friendly **T**heoretical **Rea**ctive **T**ransport **M**odel of microbial **En**hanced **T**oluene **R**emoval **IN** the **N**on-homogeneous aquifer **E**xperiment (Treatment Rinne) model has been built in order to simulate the biodegradation process and to display the results of the monitoring.

Session 6
Transport of injectable particles

Iron particles mobility in saturated porous media: influence of flow rate and fluid viscosity in column transport tests and transport modelling in radial geometry

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ABSTRACT: Microscale and nanoscale zerovalent iron particles (MZVI and NZVI, respectively), used for groundwater remediation, are not stable when dispersed in water, due to fast aggregation and sedimentation of the particles. Consequently, the use of shear thinning solutions of green biopolymers (e.g. starch, guar gum, xanthan gum) have been recently studied as viscous carrier fluids for the delivery of MZVI and NZVI. Shear thinning fluids exhibit high viscosity at low flow rates (which improves colloidal stability in static conditions) and lower viscosity at high flow rates, corresponding to the injection in the subsurface, when low viscosity (and consequently low pressures) is required. In this work, co-funded by European Union project AQUAREHAB (FP7 - Grant Agreement Nr. 226565), a modelling approach is described to simulate the transport in porous media of nanoscale iron slurries in both laboratory conditions (1-dimensional column tests) and field conditions (radial flow). When modelling the transport of highly concentrated slurries (in the order of several g/l) of NZVI and MZVI in porous media, clogging phenomena (i.e. reduction of porosity and permeability due to particles deposition) are to be taken into account, and the rheological properties of the carrier fluids are to be considered for a correct estimate of pressure drops. Colloid transport mechanisms are controlled by particle-particle and particle-collector interactions, typically modelled with kinetic terms of deposition onto the porous medium and corresponding release. Beside other parameters, deposition and release kinetics are affected by flow rate and fluid viscosity. In this work, column transport tests of microsized iron particles (BASF HQ, d_{50}=1.1 μm) are presented, performed at different flow rates and different polymer concentrations (guar gum at 1.5, 3 and 4 g/l). E-MNM1D is used for inverse simulations of the results, and the dependence of deposition and release kinetics on flow rate and fluid viscosity is modelled. The newly derived relationships are implemented in a radial transport model, E-MNM, which is used for the simulation of field-scale injection of MZVI slurries in porous media. The software 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.

INTRODUCTION

In the context of groundwater remediation, the use of zero-valent iron is known to be successful for the degradation of a wide range of contaminants. In particular, in recent years an increasing interest was found towards nanoscale and microscale zero-valent iron particles (NZVI and MZVI, respectively). 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 (Tiraferri et al., 2008; Tiraferri and Sethi, 2009; Dalla Vecchia et al., 2009).
Numerical modelling of transport processes of iron particles transport in porous media, as well as of their reactivity towards the contaminants, is necessary for the interpretation of laboratory tests, and for the simulation of injection

and reactivity at the field scale. Transport models for MZVI and NZVI are usually based on advection-dispersion equations, modified on purpose to include deposition and release phenomena, clogging, and other specific processes, as detailed below. In both one-dimensional and radial models (suitable for the simulation of field injection of MZVI and NZVI), the key aspects included in the model are clogging phenomena (i.e. reduction of porosity and permeability due to particles deposition), and the rheological properties of the carrier fluid (in this project, guar gum solution) for a correct estimate of pressure drops. Moreover, in radial geometry, the flow rate is not constant, but decreases hyperbolically with increasing distance from the injection point. For this reason, a space-variable flow velocity is to be considered, affected both by reductions in porosity and by increasing distance from the injection point. As all model equations are strictly coupled, changes in flow rate affect the non-Newtonian viscosity of the carrier fluid, and consequently the pressure drop, as well as the deposition and release kinetics, which depend on flow rate and fluid viscosity.

In this work, laboratory transport tests in one-dimensional columns are reported, exploring the effects of both flow rate and polymer concentration (in this study, guar gum) on particles mobility. A modelling approach is also proposed for the simulation of large-scale injection of iron micro- and nanoparticles, considering a radial geometry.

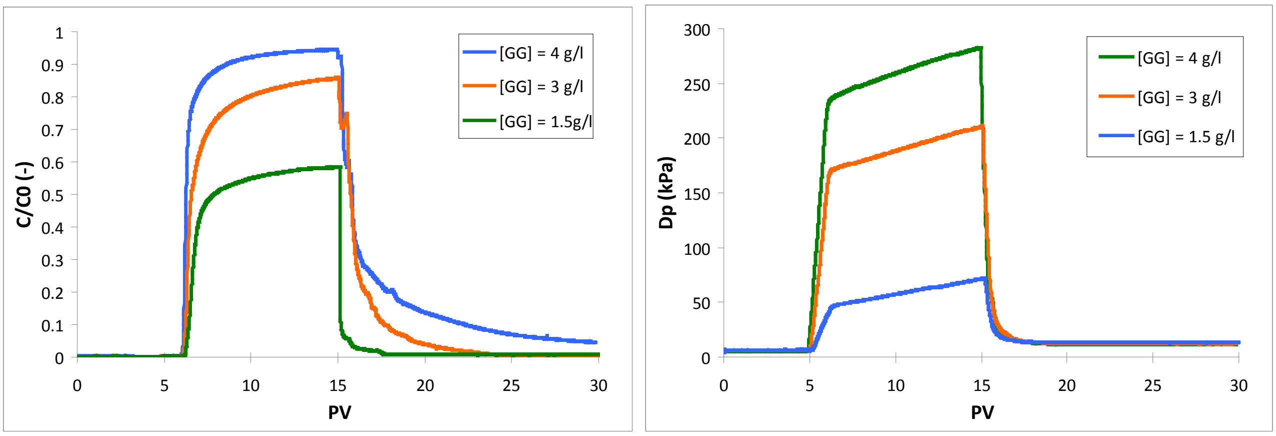
MATERIALS AND METHODS

Iron particles (HQ from BASF, d_{10}, d_{50}, d_{90} equal to 0.7, 1.2, 1.8 µm, respectively) 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, the guar gum concentration ranged between 1.5 and 4.0 g/l. The protocol for the preparation of the iron suspensions included the following steps: the iron particles were dispersed in water, sonicated for 5 minutes and mixed with the guar gum solution using a high speed rotor-stator (UltraTurrax). The guar gum solution was prepared using warm water to improve idration, and processed to remove residual undissolved particles. It was prepared 24 h prior to use, to ensure complete hydration of the polymer powder.

Column tests were performed in 42 cm long sand packed (Dorsilit 8) columns with 2.4 cm inner diameter, at constant flow rate ($1.2{\cdot}10^{-3}$ m/s) and included the following steps: pre-flushing of the column with D.I. water (5 PVs), iron slurry injection (10 PVs), post-flushing with D.I. water (15 PVs). Three values of flow rate ($2.8{\cdot}10^{-4}$ m/s, $1.2{\cdot}10^{-3}$ m/s, $5.3{\cdot}10^{-3}$ m/s) and guar gum concentration (1.5 g/l, 3 g/land 4 g/l) were applied. Inline continuous measurements of inlet and outlet iron concentration, as well as profiles of total iron concentration along the column were performed using susceptibility sensors. Also, pressure drop at column ends was monitored during the whole test.

RESULTS

Sedimentation and transport tests of selected Fe-based microparticles



(a) **(b)**

Figure 1: (a) Breakthrough curves and (b) evolution of pressure drop at column ends over time for HQ particles dispersed in guar gum at three different concentrations (1.5, 3 and 4 g/l) injected in sand packed columns at a flow rate v = $5.3{\cdot}10^{-3}$ m/s.

Figure 1 reports an example of results of the transport tests for HQ particles performed at the maximum explored flow rate ($v = 5.3 \cdot 10^{-3}$ m/s) for three guar gum concentrations (1.5, 3 and 4 g/l). Results include breakthrough curves and pressure drop at column ends. It is evident that increasing guar gum concentration the breakthrough of HQ particles is improved, the pressure increases. The dependence of the mass of iron retained inside the column as a function of guar gum concentration can be empirically modelled using an power function:

$$\frac{M_{ret}}{M_{in}} \cong A[GG]^B$$

where M_{ret}/M_{in} is the ratio of retained particles to injected particles, *[GG]* is the guar gum concentration, and *A* and *B* are empirical coefficients that are likely to depend on flow rate, iron particle size and grain size distribution of the porous medium. The values of M_{ret}/M_{in} for all tests performed using HQ particles are reported in Figure 2a, where fitting functions are also reported. The pressure increase at the beginning of the iron slurry injection, due to the higher viscosity of guar gum if compared to water, (almost) linearly increases when increasing guar gum concentration (Figure 2b).

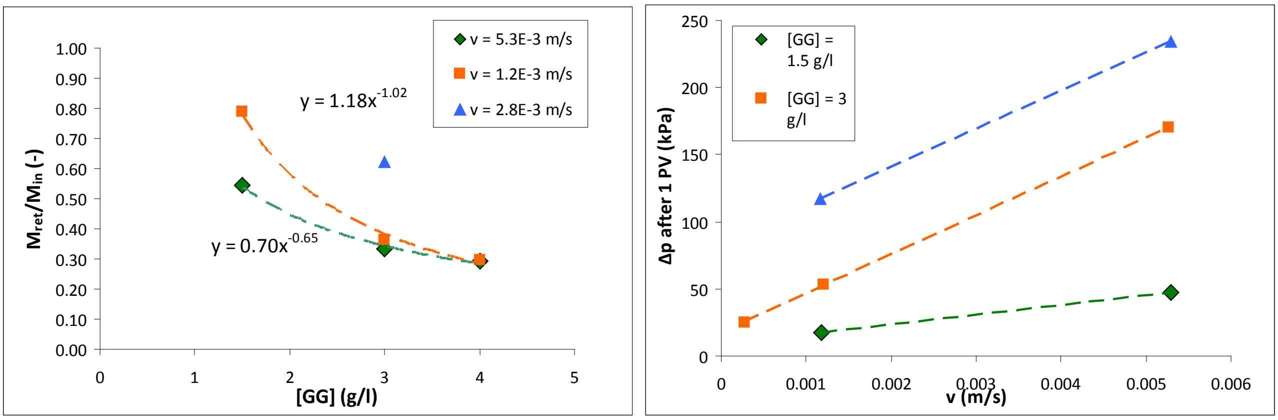


Figure 2: Dependence of (a) fraction of particles retained inside the column after injection and (b) pressure increase at the beginning of iron + guar gum slurry injection both reported as functions of the guar gum concentration, for different flow rates.

Iron transport modelling in radial geometry

The transport model E-MNM1D for micro- and nanoscale iron particles in saturated porous media (Tosco and Sethi, 2010), was extended to a radial geometry for the simulation of radial injection of iron microparticles via permeation.

The model equations were written under the hypotheses of purely radial flow (no changes along the vertical direction), no effect of gravity (supposed to be negligible compared to radial component of the flow velocity), and radial symmetry. The model equations are briefly discussed here.

Advection-dispersion-deposition equation:

$$\left\{ \begin{array}{l} \dfrac{\partial}{\partial t}(\varepsilon_m c) + \dfrac{\partial}{\partial t}(\rho_b s) + \dfrac{1}{r}\dfrac{\partial}{\partial r}(r q_{m,r} c) - \dfrac{1}{r}\dfrac{\partial}{\partial r}\left[r \varepsilon_m \left(D_{rr} \dfrac{\partial c}{\partial r} \right) \right] = 0 \\ \dfrac{\partial(\rho_b s)}{\partial t} = \varepsilon_m k_a c - \rho_b k_d s \end{array} \right.$$

where ε_m is the porosity, D_{rr} is the hydrodynamic dispersion along radial direction, q_m is the Darcyan velocity, ρ_b is the bulk viscosity, *c* is the concentration of suspended particles, *s* is the concentration of deposited particles (expressed as mass of deposited particles per unit mass of the porous medium), k_a and k_d are the kinetic parameters of colloid deposition and release kinetics (their dependence on flow rate is further discussed below). The first equation represents the mass balance for the liquid phase, the second one the mass balance for the solid phase, following a linear reversible deposition-release dynamics.

Darcyan flow rate can be expressed as a function of radial distance from the injection point, and used to calculate the pressure drop via Darcy's law modified for non Newtonian fluids:

$$\frac{\partial p}{\partial r} = -\frac{\mu_m}{K_m}\frac{Q_m}{2\pi rb}$$

The **dynamic viscosity** of the dispersion is a function of shear rate, polymer concentration and particles concentration, and this dependence can be described with a modified Cross model:

$$\mu_m(\dot{\gamma}_m, c, c_x) = \mu_{m,\infty} + \frac{M(c)c_x}{1+\left[\lambda_m(c)\cdot\dot{\gamma}_m\right]^{\chi_m(c)}} \quad where \quad \dot{\gamma}_m(s) = \alpha_\gamma \frac{q_m}{\sqrt{K\varepsilon_m}}$$

where M(c) is a function that can be derived from experimental data, and depends only on the concentration of suspended particles, λ_m(c) and χ_m(c) are two parameters of the Cross model, both functions of c, and γ_m is the shear rate of the fluid in the porous medium

Porosity and permeability coefficient. When colloids depose on the soil grains, the pore space available for the fluid•flow decreases, proportionally to the concentration of deposed particles *s*:, and the specific surface area increases. Both phenomena contribute to the reduction of the permeability coefficient

$$K(s) = \left[\frac{\varepsilon_m(s)}{n}\right]^3 \left[\frac{A_0}{A(s)}\right]^2 K_0$$

where K_0 is the initial permeability coefficient (i.e. without any particle deposed on the porous medium), n is the initial porosity, A_0 is the initial specific surface area of the porous medium. Equations describing the changes in porosity and specific surface area as functions of deposited concentration *s* are implemented, similar to those used in the 1D model.

Attachment and detachment rates. It is known from the literature that attachment/detachment rates depend on a number of parameters, and in particular on flow rate. As an example, an expression for the clean bed attachment was proposed by Tufenkji and Elimelech (Tufenkji and Elimelech 2004b):, while an empirical equation for the detachment rate was proposed by Brovelli and co-workers (Brovelli et al. 2009). Basing on these equations, a first approximation of the dependence of deposition and release kinetics on flow rate and fluid viscosity was adopted, and implemented in the radial transport model:

$$k_a = \lambda v_e^\beta \mu^\beta$$

$$k_d = \lambda' v_e^\gamma \mu^\gamma$$

where λ and λ' are empirical coefficients, dependent on a number of parameters (porosity, specific surface area, average grain size of porous medium and particles, etc.) and β and γ are exponents derived from the analysis of the correlations from the literature, here assumed equal, respectively, to -2/3 and 0.58.

An example of model output is provided in Figure 3 along with the model parameters used in the simulation. The reference particles used for the definition of colloid properties are Basf MS200, while for the rheological properties the Cross parameters corresponding to 4 g/l guar gum solution were adopted.

CONCLUSIONS

The experimental results evidenced a clear influence of flow rate and transport concentration on the mobility of the iron particles in porous media. This finding can be related to changes in deposition and release coefficients, as also suggested by literature correlations. Future work will include the development of new relationships expressing the dependence of transport parameters on flow rate and viscosity, obtained from the analysis of the experimental data deriving from the column transport tests. Breakthrough and pressure drop curves of each test will be inverse-modelled using the 1D version of the model, to derive attachment and detachment coefficients. The new empirically-derived relationships to be implemented in the final version of the radial model E-MNM.

ACKNOWLEDGEMENTS

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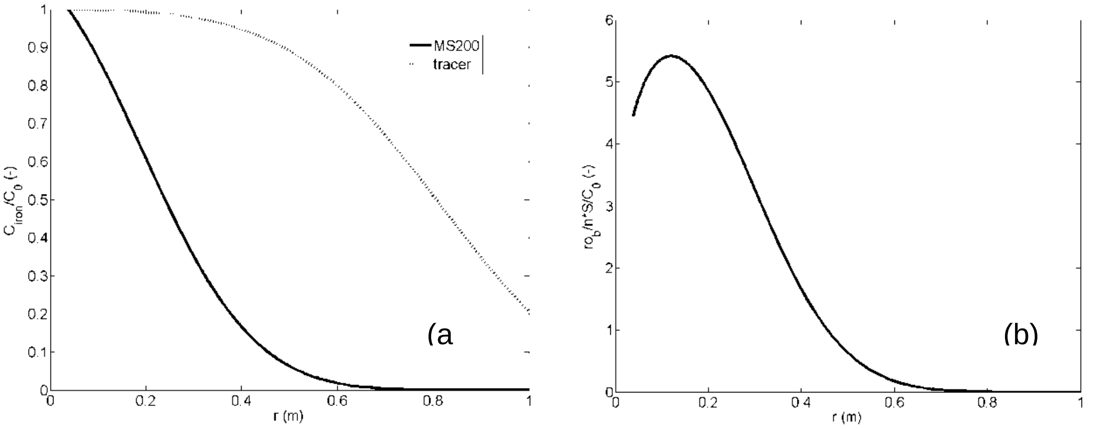

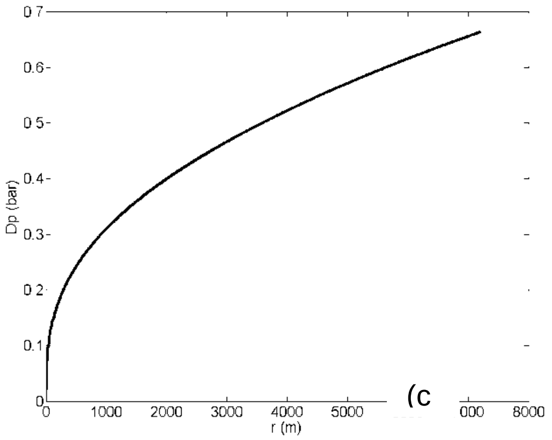

SLURRY PROPERTIES		
	Guar gum concentration	4 g/l
	Rheological model: Cross Model	
Carrier fluid: guar gum	μ_0	0.67 Pa s
	$\mu_?$	$1.34 \cdot 10^{-4}$ Pa s
	λ_m	0.2
	χ_m	0.645
Particles: MS200 (Basf)	*Injected concentration C_0*	20 g/l
	Density of bulk particles ρ_s	$7.80 \cdot 10^3$ kg/m^3
	Particle diameter d_p	$4.70 \cdot 10^{-6}$ m
FLOW + POROUS MEDIUM PROPERTIES		
Discharge per unit depth Q_m/b		$1.5 \cdot 10^{-4}$ m^3/s
Bulk density ρ_b		$1.35 \cdot 10^3$ kg/ m^3
Size of sand grains d_{50}		$2.10 \cdot 10^{-4}$ m
Initial porosity n		0.5
Initial permeability K_0		$3.5 \cdot 10^{-10}$ m^2
Initial specific surface of porous medium A_0		$1.61 \cdot 10^4$ m^2/m^3
INJECTION PROTOCOL		
1. *Initial condition: porous medium fully saturated with water, no particles dispersed nor deposited on porous medium*		
2. *Iron injection (iron + guar gum)*		
	injection duration	7200 s
PARTICLES INTERACTION KINETICS		
	λ	$2 \cdot 10^{-6}$ (Pa m s)$^{-1}$
Attachment	β	-0.67
	λ'	$2 \cdot 10^{-3}$ (Pa m s)$^{-1}$
Detachment	γ	0.58

Figure 3: Results of E-MNM run in radial geometry: radial profile of normalized concentration of suspended (a) and deposited iron (b), overpressure at the injection point as a function of time (c), and model parameters (d).

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Scaling-up Transport of ZVI Particles in Aquifers

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ABSTRACT: Injecting micro and nano scaled zero-valent iron particles into the contaminated aquifers has distinct advantages as compared to the emplacement in reactive barriers: Particles may be injected underneath buildings, at any depths and into the source zone, thus potentially decreasing both remediation time and cost. To obtain an efficient and targeted injection the transport of the particles has to be optimized for given aquifer and particle properties. Most transport experiments to date were carried out in columns, in other words in a constant velocity field. In a field injection, however, the velocity decreases hyperbolically with distance from an injection point, thus transport properties obtained in column experiment are not sufficient to describe transport of ZVI particles in a radial flow field. At VEGAS, container scale experiments were carried out to determine the transferability of column experiments of field scale applications. Zero-valent iron nano particles were injected in a colloid suspension, and the influence of different injection rates and techniques as well as achievable transport distances was observed.

INTRODUCTION

The seepage velocity around an injection well is not constant (as in a column experiment) but decreases, for confined conditions, hyperbolically with increasing distance from the well (Figure 1). Hence, transport data obtained in a column experiment cannot be transferred directly to radial flow.

To be able to get a better understanding of the transferability of the information gained from column experiment into the field scale, an intermediate scale experiment was developed at VEGAS, University of Stuttgart. The experiment consists of a triangular container which represents a 60 degrees portion of a full cylinder.

Assuming radially symmetrical flow, this will allow for a detailed investigation of flow and transport without a loss of generalization. In the container experiment this type of flow field can be created at a field realistic scale.

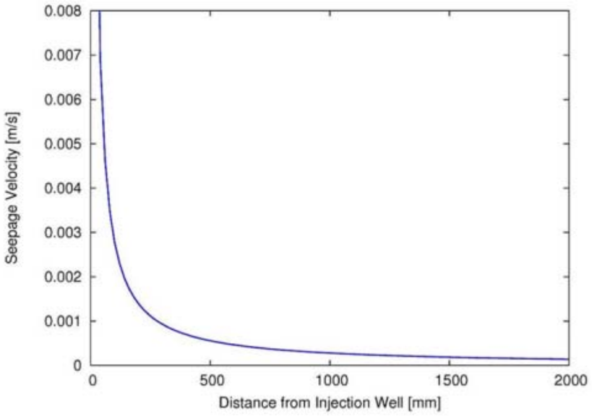


Figure 1: hyperbolically decreasing seepage velocity with increasing distance from the injection well

EXPERIMENTAL SETUP

The whole container was built from Polypropylene (PP) to avoid interference of the container material on the electromagnetic measurement system. The chosen triangular shape of the experiment (Figure 2) represents a 60 degrees portion of a full cylinder. This shape had to distinct advantages. a) It was possible to get a cross-sectional view of the experiment through a glass plate (40 mm security glass, Südwest Glas) and b) the total size was reduced without loss of generalization. The dimensions of the experiment (inside: H = 60 cm, R = 1.80 m) were chosen to be comparable to a real field situation. Sand was packed into the container to create the porous medium. The injection well (OD = 2,5 cm) was installed inside another well screen (OD = 12 cm), to allow for the emplacement of filter sand (Dorsilit, nr. 3, 2-3.5 mm, Dorfner, Germany). At the injection well flux boundary conditions were applied; the outflow boundary conditions were constant head. The iron slurry was diluted and dispersed to provide agglomeration of particle prior to being pumped into a reservoir (1m^3]. there it was mixed continuously while a pump was used to inject the suspension into the container (Figure 2).

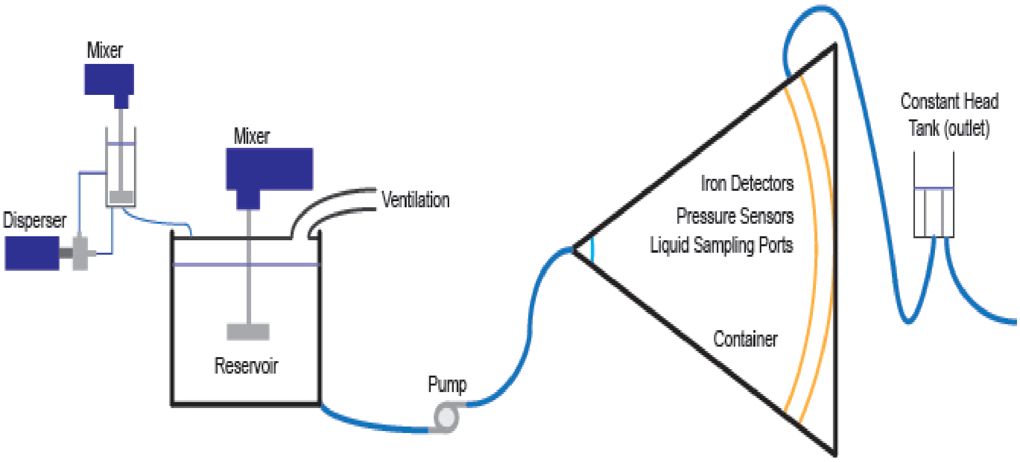


Figure 2: Schematic overview of the container experiment set-up

Specially designed sensors were installed to measure the concentration of iron at different locations within the container during the injection. The sensors consisted of two coils. One of them produced an electromagnetic field which induced a potential in the other coil. By measuring the current that flows through the first coil and the voltage that is induced in the second coil, the magnetic susceptibility of the medium (which is proportional to the concentration of iron within the medium) within the coils can be determined. In order to convert this magnetic susceptibility into iron concentration the system needs to be calibrated (either before or after running the experiment).

27 sensors were placed at five distances from the injection well and at two angles from the glass plate. They were buried in the sand during the container filling and placed in line with the flow field. Finally, the data was evaluated to obtain the change in magnetic susceptibility, which is directly related to the zero-valent iron concentration. The final concentration inside the coils was analytically determined after the excavation.

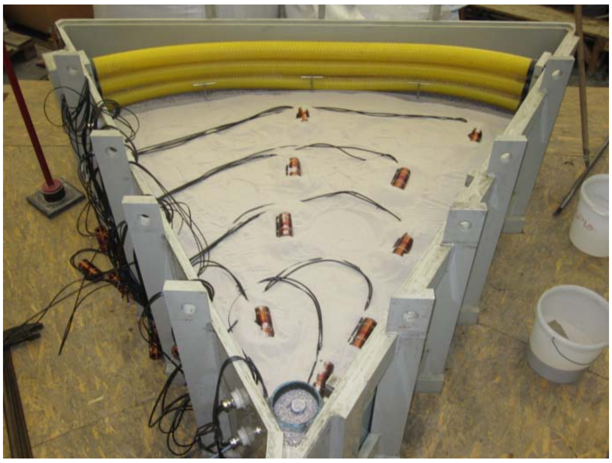


Figure 3: Large scale container during installation of coils (inflow in front, outflow in the rear)

INJECTION CONDITIONS FOR NANO-SIZED COLLOIDS

The container was packed with a well graded quartz sand (Dorsilit, nr. 8, 0.3-0.8 mm, Dorfner, Germany); the pore volume of the porous medium between injection well and the filter screens was approximately 375 litres. Each of the experiments consisted of three injection phases. In the first phase, five liters of tracer solution (Uranine, 0.5 g/l) were injected followed in phase two by 900 liters of nano-iron suspension without additional pre-treatment. The suspension concentration was 10 g/l (diluted with degassed tap water, Total Organic Carbon: 0.4 g/l, pH: 8.0, Dissolved Oxygen: ~ 1 mg/l, Electrical Conductivity: ~ 8.9 S/m). The third phase consisted of an injection of 900 liters of degassed tap water (DO: ~ 1 mg/l, pH: 7.0).

The conditions of the four experiments using nano ZVI in the injected suspension are presented in Table 1. Experiments 1 and 4 were performed as duplicates, for experiments 2 and 3 all conditions were equal save the injection rate which was reduced to 50%.

The main questions to be answered with these four experiments were:

- Which transport distances are possible for nano iron colloids under field realistic conditions?
- Are the results reproducible?
- What is the influence of injection rate on the transport distance?
- Which pumping mechanism is better for the transport; pulsating or continuous flux?

Table 1: Conditions for the container experiment using nano iron

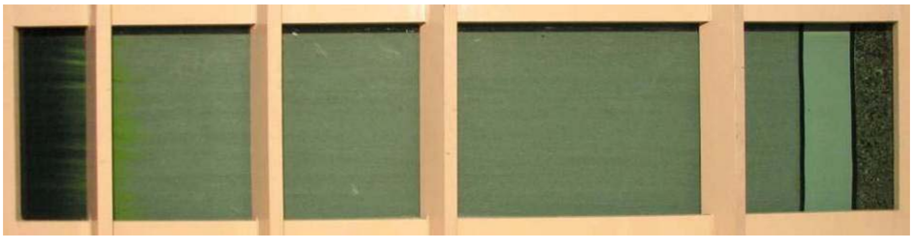
	Exp.# 1 & 4	**Exp.# 2**	**Exp.# 3**
Injection rate	1000 l/h Continuous	500 l/h Pulsating	500 l/h Continuous
Total volume of suspension	900 l	900 l	900 l
Total volume of water (flushing)	900 l	900 l	900 l
Duration of suspension injection	55 min	110 min	110 min
Duration of water flushing	55 min	110 min	110 min
Total volume of the container	1500 l	1500 l	1500 l
Volume of container contributing to flow	approx. 1000 l	approx. 1000 l	approx. 1000 l
Pore volume contributing to flow (calculated)	375 l	375 l	375 l
Porosity	0.39	0.39	0.39
Residence time (calculated)	22 min	44 min	44 min
Fe material	RNIP 10-E Toda Kogyo	RNIP 10-E Toda Kogyo	RNIP 10-E Toda Kogyo
Fe_{total} concentration set and measured	10 g/l set, #1: 7.7 g/l measured #4: 9.1 g/l measured	10 g/l set 9.9 g/l measured	10 g/l set 10.1 g/l measured

RESULTS

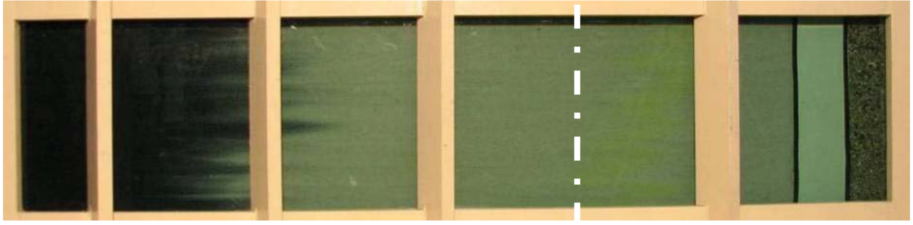
In total four experiments were carried out to test the transport of zero-valent iron nano colloids in a confined aquifer using the container setup.

Injection at 1000 l/h

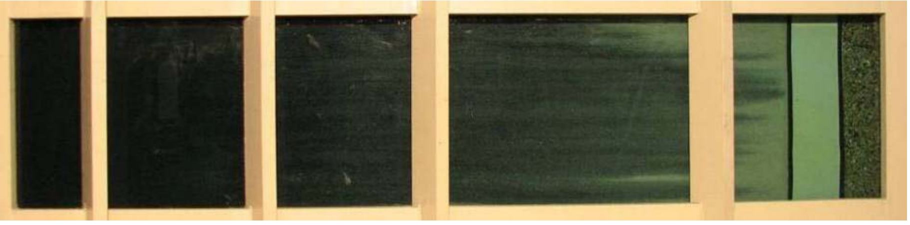
During the first experiment (#1 in Table 1) it was possible to get the iron colloids transported over the full length of the container. Visual observation through the glass plate showed that the iron colloids moved at a much smaller velocity through the sand than the carrier fluid (conservative tracer). The iron front visibly arrived at the outlet side after three pore volumes of suspension where injected (Figure 3), thus suggesting a retardation factor of approx. 3 to 4.



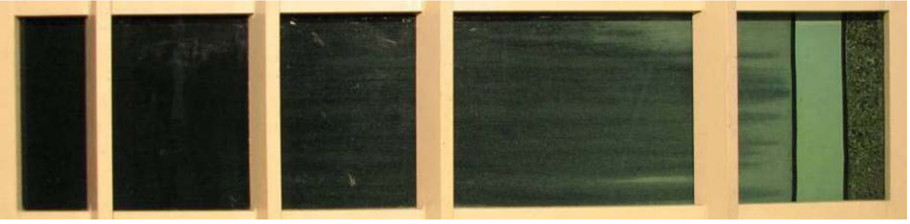
a) t = 200 s, Uranine front (green, — · line) directly in front of iron front (black)



b) t = 700 s, Uranine front (green, — · line), iron front (black) moving forward



c) t = 3600 s, Iron front (black) close to outflow



d) t = 6300 s, Iron front (black) very stable during water flush

Figure 3 a-d. Uranine (white dashed line)- and iron front during an injection at different time intervals

While visually the window was black throughout, the sensors showed a large gradient in concentration along the flow path. In Figure 4 (left) the magnetic susceptibility measured in the spools emplaced is shown as a function of the injection time for five successive locations inside the container. It can be seen that at each location the magnetic susceptibility initially increases strongly followed by a slight, steady increase until the injection of the nano iron suspension stopped. This indicates the break-through of the iron suspension at that position.

After the injection with iron, the suspension fluid was chased by degassed tap water, resulting in a drop of the magnetic susceptibility. This drop was caused due to an influence of the surfactants on the capacity of the coils. In subsequent trials the coils were covered with an epoxy resin, which prevents this jump and drop in the signal.

The susceptibility during the water flushing stage remained stable, indicating that the colloids no longer moved and hence, that the iron concentration inside the container did not change any more. The magnetic susceptibility is directly linearly related to the iron concentration, as can be seen by comparing the final magnetic susceptibility after water flushing (Figure 4, left) with the average of the measured concentrations through chemical analysis (Figure 4, right).

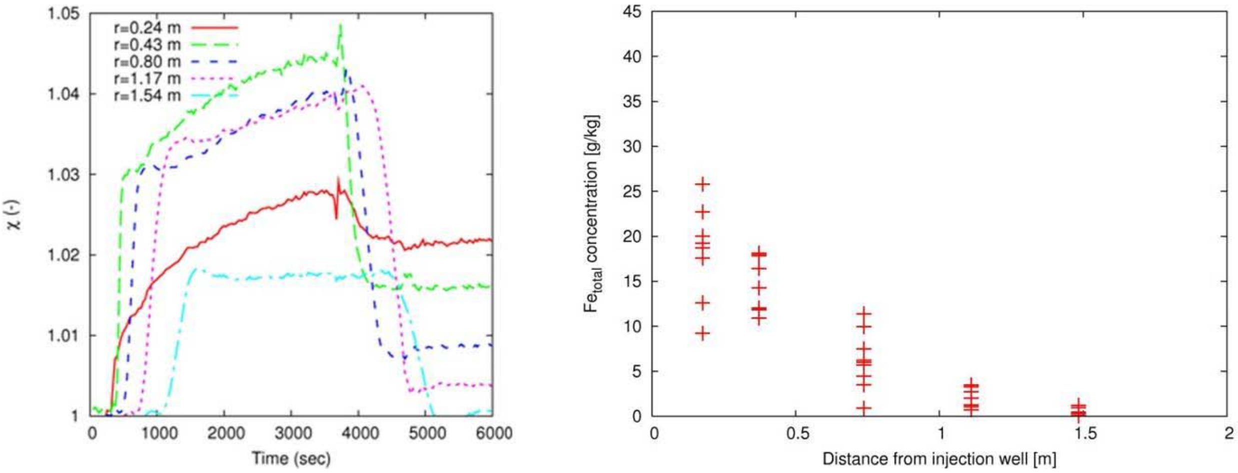


Figure 4. Left: Magnetic susceptibility changes during the injection of the iron suspension (100 – 3700 sec) and water flushing (3700 – 6000 sec). Each coil pair responded differently to the surfactants, after the water flushing the sensors showed the real susceptibility. Right: Zero-valent iron concentration inside the coils obtained by chemical analysis. From left to right the values represent the sensors at different distances; the final susceptibilities are directly related to the average values of the chemical analysis.

Influence of Different Injection Rates

Two experiments using the same continuous flux pump (Seepex, Germany) and total amount of iron suspension injected were performed to determine the influence of the injection rate on transport in a radial flow field: one at 500 l/h (exp. #3, Table 1) and the other at 1000 l/h (exp. #4, Table 1). In Experiment 4 (1000 l/h) the iron is transported slightly further, while Experiment 3 (500 l/h) shows higher concentrations closer to the well. At some distance from the well, the concentrations are very similar. The differences in concentrations close to the well are in accordance with the hypothesis that the transport of the nano iron colloids is mainly influenced in this region.
Since the concentrations in Experiment 4 (1000 l/h) are lower in the vicinity of the well and thus the danger of clogging is reduced, this higher injection rate is preferable.

Pulsating Flux Pump vs. Continuous Flux Pump

For a field application different types of pumps can be used. Two extremes were compared here; a pump providing a very stable and continuous flux through a rotor stator technique (Exp.# 3, Table 1) and one that provides a pulsating discontinuous flux through a large single membrane (Exp.# 2, Table 1). Both experiments were performed at 500 l/h. From the results it could be concluded that the pulsating pumping technique did not provide the improved transport of nano iron colloids as was expected. A possible cause could be that in the interval between the pulses the colloids can sediment out of the suspension faster due to the lack of shear forces and that the increased shear rate at the beginning of each pulse was not high enough to remobilize the attached or sedimented colloids.

CONCLUSIONS

From the injections performed with nano iron colloids it was shown 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. Notably, the concentrations close to the well were lower, reducing the risk of clogging.

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Numerical investigation and parameterisation of nZVI transport processes under different boundary conditions

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Using zero-valent iron particles at nanoscale (nZVI) as an *in situ* technology for groundwater and especially for source zone remediation is a promising alternative to conventional methods due to a high surface area and thus high reactivity. However, several physical and chemical processes can limit the mobility of nZVI particles and inhibit the effectiveness of this technology. Therefore, investigations of the governing processes and the effects of different conditions on the transport behaviour and an optimisation of particle mobility for field applications are the main challenges. While previous published numerical studies using different model approaches focus mainly on the effect of single boundary conditions (e.g. particle size, ionic strength, viscosity) on particle transport behaviour, multiple influencing variables are rarely considered and simulated so far.

The aim of this study in the context of the research project NAPASAN (FKZ 03X0097D) is to derive a model with one parameter set, which is capable to describe the nZVI particle transport behaviour with regard to commonly used deposition mechanisms under a wide range of boundary conditions. Therefore, extensive 1D column lab tests considering variable injection concentrations, injection velocities, and sediment permeabilities for commercial as well as project internal developed particles (see presentation of Strutz and Köber) provide the basis for the numerical simulations using the *E-MNM1D* code (Tosco & Sethi, EST 2010), which is developed for micro- and nanoparticle transport. Such a model can then be used as a helpful planning tool to set up remediation strategies and monitoring concepts for real sites in general and for a project pilot site in particular.

To date the model was capable to reproduce the measured Fe(0) concentration profiles of the deposited particles for most of the lab test setups (5 - 30 g/l injection concentration, 2 - 6 m/h pore water velocity, and hydraulic conductivities of about $4x10^{-4}$ - $4x10^{-3}$ m/s) at different time steps caused by kinetically controlled attachment processes like blocking and straining. Using one subsequent derived parameter set the simulated Fe(0) concentrations at the end of the injection periods fit the measured profiles to 60 and 80 % in the average for all and appropriate injection conditions, respectively. Model accuracy decreases at higher injection concentrations and higher initial hydraulic conductivities. The hydraulic conductivity affected by the attachment processes decreases during injection in the amount of one to two orders of magnitude, which coincide with the lab results as well. This can play an important role for site remediation by reducing source emissions and in cases of re-injection scenarios.

The results indicate that the model approach with the one parameter set can be used as a basis for optimisation of injection scenarios and predictions of particle spreading. In preparation for the field application these recent findings have already been used to support and conduct a successful preliminary particle injection test at the pilot site (see presentation of Martac et al).

In addition, the *OpenGeoSys* code (Kolditz & Bauer, J. Hydoinform. 2004) as a reactive transport simulator for multidimensional problems is actually adapted stepwise by implementing the derived governing transport processes and findings from the 1D column tests to simulate the nZVI particle spreading in 2D aquifer cells as well as at field scale for further model validation and predictions.

Poster Presentations

Characterisation and optimization of nano-iron particle transport for groundwater remediation

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Zero-valent nano-iron particles have shown a great potential for groundwater remediation, especially for groundwater contaminated with chlorinated hydrocarbons. For a successful and efficient remediation with nano-iron particles it is necessary to achieve a sufficient coverage and a homogenous particle distribution. For this purpose it is essential to determine the best site-specific performance of particle injection. Hydraulic conductivity (k), pore velocity (v) and the particle concentration will be of main importance for the achievable particle distribution, whereas only the latter two are adjustable during particle injection. Currently, no study is available showing the quantification of these influencing parameters that could be used for injection optimization. Furthermore, influences of nano-iron injections on aquifer permeability are still unknown. All these were the main issues addressed in the presented study.

Column and tank experiments with varying Fe(0) particle concentrations (1 g/L to 30 g/L), pore velocities (0,3 m/h to 18 m/h) and sediment permeabilities (10^{-2} to 10^{-6} m/s) were performed using commercial and newly developed nano-iron particles. In addition to measurement of the total Fe(0) concentration in the sediment by magnetic susceptibility scans, water samples were taken along the flow path and at the outflow of the experiments to analyse the reactive (Fe(0)) and the non-reactive (Fe(II/III)) mobile particle concentrations.

Based on the obtained data the best zero-valent iron concentration was determined to be approximately 10 g/L, and $v \approx 6$ m/h or higher is recommended to achieve far reaching and homogenous particle distributions. For sediments with k smaller than 1×10^{-3} m/s the pressure at the inlet increased and v decreased applying less injected mass of nano-iron than in the experiments with higher k. During the period of particle injection, k decreased for all experiments by at least half an order of magnitude. This can be advantageous for source remediation, because the contaminants' emission from the source zone decreases and the reaction time of contaminants with Fe(0) increases. However, decreasing k can impair further injections and can make plume remediation inefficient.

Based on the experimental results, a first pilot injection with the newly developed nano-iron was performed at a contaminated site. The desired distribution of the particles in the natural sediment could be proven with sediment liners. Results from ongoing field and lab experiments under heterogeneous conditions will also be presented.

Pore scale flow simulations for numerical validation of Darcy-Forchheimer law for shear thinning fluids used in colloidal zerovalent iron delivery

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ABSTRACT: The use of viscous, shear thinning fluids (eg. guar gum and xanthan gum solutions) has been recently proposed to improve colloidal stability of micro- and nanoscale zerovalent iron particles (MZVI and NZVI) for groundwater remediation. When modelling the colloidal transport of such suspensions, the rheological, non-Newtonian properties of the shear thinning carrier fluid are to be incorporated into the model, in order to correctly simulate pressure drops and viscosity of the suspension. For small flow rates, typical of laboratory column tests, the extended Darcy law is known to be applicable also to non Newtonian fluids. However, when field injection is considered, high Reynolds numbers are encountered close to the injection point, and linear flow cannot be assumed. The Darcy-Forchheimer law is known to be applicable for Newtonian flow and for simple models of shear thinning fluids (power law). However, this is not demonstrated for other, more realistic, shear thinning rheological models. In this work the validity of Darcy-Forchheimer law also for such fluids is demonstrated via pore-scale single-phase flow simulations. Simulations were conducted on synthetic two-dimensional porous media and performed via computational fluid dynamics for both Newtonian and non-Newtonian fluids, and the results are used for the extension and validation of the Darcy-Forchheimer law, herein proposed for shear thinning fluid models of Cross, Ellis and Carreau. The results of flow simulations show the superposition of two contributions to pressure drops: one, strictly related to the non-Newtonian properties of the fluid, dominates at low Reynolds numbers, while a quadratic one, arising at higher Reynolds numbers, is dependent only on the porous medium properties.

INTRODUCTION

Non-Newtonian flow is encountered in a wide range of industrial applications, including enhance oil recovery in petroleum engineering (Sethi 2011), and many processes in food and chemical industry involving in-line filtration (e.g., milk, most liquid food, oil, blood, etc.). Moreover, recent applications in groundwater remediation use shear thinning polymeric suspensions as carrier fluids for the injection of iron nanoparticles into the subsurface (Tosco and Sethi 2010; Dalla Vecchia et al. 2009; Tosco et al. 2012). In these applications, it is extremely important to correctly predict the pressure drop resulting from non-Newtonian fluid flow through the porous medium. In most cases, the problem can be solved at the macroscale, using extended formulation of the Darcy law (Pearson and Tardy 2002) or solving the transient flow using similarity solutions, at the micro-scale, using pore-network models or realistic pore-scale models.

The Darcy law (Darcy 1856) is used to describe steady-state flow of Newtonian fluids through porous media at small Reynolds numbers, when the relationship between hydraulic gradient and fluid velocity is linear. However, when increasing the Reynolds number non linearities arise. The Darcy-Forchheimer law introduces an additional quadratic term for the dependence of the hydraulic gradient on flow velocity, which is independent of the viscous properties of the fluid, and expresses the dependence of the pressure gradient on the square of the flow rate thorough a parameter β, the so-called Forchheimer coefficient. If non-Newtonian fluids are considered, the usual formulation of the Darcy law can be applied in the low flow regime, provided that all non-Newtonian effects are lumped together into a proper viscosity parameter, called "porous medium viscosity" (Sorbie 1991; Bird et al. 1977). Similarly, at higher Reynolds numbers the Forchheimer law could be applied under the same hypotheses. A possible strategy to demonstrate the validity of the Forchheimer term also for non-Newtonian fluids, as well as its independence of viscous properties, involves the use of micro-scale flow simulations in reconstructed geometries.

In this work, an extended formulation of the Darcy-Forchheimer law is proposed for shear-thinning fluids and validated by using micro-scale flow simulations. Four different model domains, characterized by different value of porosity and specific surface area, were considered, in the typical range of natural porous media in aquifer systems. Pore-scale flow simulations were performed by using the same non-Newtonian fluids, to explore the impact of different pore geometries on the macroscopic average pressure drop and effective porosity. The microscale flow simulation results are analyzed in terms of “macroscale” pressure drop between inlet and outlet of the model domain as a function of flow rate. The validity of the extended Darcy-Forchheimer law is shown for three shear-thinning models, namely Cross, Ellis and Carreau models. For all fluids, a broad range of flow rates was explored in the low flow and inertial flow regimes.

GOVERNING EQUATIONS

Macro-scale equations: extended Darcy law

The Darcy-Forchheimer law is an empirical non-linear equation expressing the relationship between pressure drop and specific discharge at high Reynolds numbers by including a quadratic term to the Darcy law:

$$\frac{\partial p}{\partial x} = \frac{\mu}{K} q + \beta \rho q |q| \, , \tag{1}$$

where p is the pressure of the fluid [M L^{-1} T^{-2}], q is the specific discharge of the fluid [L T^{-1}], K is the permeability coefficient [L^2], μ is the fluid viscosity [M L^{-1} T^{-1}], ρ is the fluid density [M L^{-3}], β is the so-called inertial flow parameter [L^{-1}], and gravity is neglected. Equation (1) reduces to the classical formulation of Darcy law for small q. The dependence of the flow inertial parameter β on porous medium properties was investigated by several authors, especially in the field of reservoir engineering, using approximated models for the pore-space configuration, or deriving empirical or semi-empirical relationships from experimental data (Macini et al. 2011). When modelling the laminar flow of non-Newtonian fluids in porous media, the Darcy law has to be modified: under steady-state flow conditions, the so-called generalized Newtonian fluid model can be adopted (Bird et al. 1977). The model relies on the hypothesis that the same equations used for Newtonian flow can be applied also to non-Newtonian fluids, provided that the constant viscosity μ is replaced in the equations by the “porous medium viscosity”, μ_m, which depends on both porous medium characteristics and fluid properties (Pearson and Tardy 2002; Lopez et al. 2003; Bird et al. 1977). As bulk viscosity is a function of the shear rate, also the porous medium viscosity is related to the so-called “porous medium shear rate”, defined as the average shear rate that the fluid experiences while flowing through the pores (Perrin et al. 2006)

$$\dot{\gamma}_m = \alpha \frac{|q|}{\sqrt{K\varepsilon}} \, . \tag{2}$$

Experimental tests confirmed that rheograms (i.e., plots of apparent viscosity as a function of shear rate) of the bulk fluid and those derived from injection in one-dimensional porous media are shifted by a constant value α, often referred to as shift factor. Unlike K and β, the shift factor α is not an intrinsic property of the porous medium, and is to be determined for each fluid and porous medium from laboratory flow tests or from pore-level flow simulations, which is the approach followed in this work. At high Reynolds numbers, also non-Newtonian fluids give rise to additional contributions to the pressure drop, characterized by a non-linear dependence on the specific discharge. They can be modelled by adding the Forchheimer term to the extended Darcy law. It is possible to hypothesize that the non linearities are due to inertial phenomena, and consequently do not depend on the viscous properties of the fluid (Hayes et al. 1996). The pressure drop can therefore be quantified with the modified Darcy-Forchheimer equation:

$$\frac{\partial p}{\partial x} = \frac{\mu_m(\dot{\gamma}_m)}{K} q + \beta \rho q |q| \, . \tag{3}$$

The purpose of this work is to verify the validity of this law also for several non-Newtonian fluids (Table 1). The validity of the approach is discussed by proving that Eq. (3) correctly models pore-scale simulated data of pressure drops versus discharge rate. The analysis can be carried out by making use of the concept of equivalent viscosity, μ_{eq}. This quantity is defined as the expression that must replace the viscosity in the Darcy law in order to result in the same pressure drop predicted by the Darcy-Forchheimer equation:

$$\mu_{eq} = \frac{\partial p / \partial x}{q} K = \mu_m(\dot{\gamma}_m) + \beta \rho K |q| \, , \tag{4}$$

where ∂p/∂x is the measured pressure drop and K is the Darcyan permeability (i.e., the permeability value obtained at very low discharge). The validity of the extended Darcy-Forchheimer law for non-Newtonian fluids is assessed in this work for shear thinning rheological models by using the pore-scale simulations described in the next section.

Table 1: Rheological models used for numerical flow simulations of non-Newtonian fluids.

Rheological model	Bulk viscosity	Equivalent viscosity

Cross	$\mu(\dot{\gamma}) = \mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + (\lambda \dot{\gamma})^\chi}$	$\mu_{eq} = \mu_\infty + \frac{\mu_0 - \mu_\infty}{\left[1 + \left(\frac{\lambda \alpha}{\sqrt{K\varepsilon}}\right)^\chi \lvert q \rvert^\chi\right]} + \beta \rho K \lvert q \rvert$
Ellis	$\mu(\dot{\gamma}) = \frac{\mu_0}{1 + (\lambda \dot{\gamma})^\chi}$	$\mu_{eq} = \frac{\mu_0}{1 + (\lambda \dot{\gamma})^\chi} + \beta \rho K \lvert q \rvert$
Carreau	$\mu(\dot{\gamma}) = \mu_\infty + \frac{\mu_0 - \mu_\infty}{\left[1 + (\lambda \dot{\gamma})^2\right]^{\chi/2}}$	$\mu_{eq} = \mu_\infty + \frac{\mu_0 - \mu_\infty}{\left[1 + (\lambda \dot{\gamma})^2\right]^{\chi/2}} + \beta \rho K \lvert q \rvert$

Pore-scale flow simulations

The four different model domains used in pore-scale simulations were obtained from scanning electron microscopy (SEM) images of natural unpacked sand grains. The region corresponding to the pore space of the medium was then discretized using GAMBIT® 2.4.6 (Figure 1). Numerical flow simulations for Newtonian and non-Newtonian fluids in the described two-dimensional domains were performed by solving the full continuity and Navier-Stokes equations by using the commercial computational fluid dynamics (CFD) code ANSYS Fluent 13.0. Laminar single-phase flow simulations were first run for Newtonian fluids with different values of viscosity (10^{-3} to 10 Pa s). Then non-Newtonian fluids, described by the Cross, Ellis and Carreau rheological models were simulated by replacing the constant Newtonian viscosity with the apparent viscosity calculated from the equations of Table 1. Boundary conditions of constant mass flow inlet in the upper edge, where the fluid enters the domain, and of outflow in the lower edge, where the fluid exits the domain, were applied. Symmetric boundary conditions were instead selected for the two lateral edges. For each simulation, the pressure integral drop between the entrance (top) and exit (bottom) of the computational domain was evaluated and analyzed by using the Darcy-Forchheimer equation, as discussed below.


(a) (b) (c)

Figure 1: Digitalization process for the construction of the model domains: SEM image of sand grains (a), digitalized contours (b) and computational grid (c).

RESULTS

Steady-state single-phase Navier-Stokes flow simulations for Newtonian fluids were run on all four computational grids, for the viscosity range 10^{-3} to 10 Pa s (Figure 1). The parameters K and β for each computational grid were both obtained via least-square fitting of data (fourth column of Table 2). Flow simulations for non-Newtonian fluids were run over a wide range of specific discharge (approximately 5 × 10^{-7} – 5 m/s) for all grids. The rheological models of Cross, Ellis and Carreau for guar gum and xanthan gum solutions were adopted. Simulation results, in terms of steady-state pressure drop between entrance and exit of the model domain, were then analyzed against flow rate. The permeability was assumed independent of the fluid properties, while the inertial coefficient β and the shift factor α were least-squared fitted, to prove the independence of β on fluid properties. Pressure data can be analyzed referring to the concept of equivalent viscosity μ_{eq}. For each micro-scale flow simulation, which provides a pressure drop Δp/L between inlet and outlet of the domain, a value of μ_{eq} can be calculated as (K/q)(Δp/L), following Eq. (4). When μ_{eq} is reported as a function of the porous medium shear rate the impact of inertial flow on pressure drops is highlighted (Figure 2). In this case, all data in the low flow regime collapse onto the rheological curve of μ_{eq}. Conversely, data in the inertial flow regime, usually for shear rates in the order of 10^4 s^{-1}, diverge from the bulk rheological curve, and are aligned along a straight line (in the log-log graph) which is specific of the porous medium.

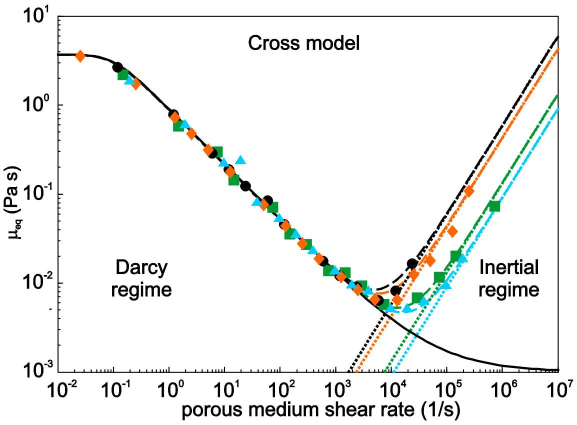

Figure 2: Data points of μeq obtained from micro-scale flow simulations (μeq=K/q·ΔP/L) plotted against porous medium shear rate (b) for the Cross model, for Grid 1 (♦), 2 (●), 3 (▲), and 4 (■).The calculated μm(γ˙m) (solid line) and inertial term Kβρq (dotted lines) are also reported.

Table 2: Parameters K, β, α calculated for the four grids from Ergun equation (Eq. 4) and obtained from inverse modeling of flow simulation results with the Darcy-Forchheimer's law (Eq. 2) for Newtonian and non-Newtonian fluids (Cross, Ellis and Carreau rheological models).

Grid	Parameter	Darcy-Forchheimer			
		Newtonian fluids	Cross fluid	Ellis fluid	Carreau fluid
1	K (m^2)	5.98×10^{-10}	5.98×10^{-10} *(not fitted)*		
	β (m^{-1})	5.28×10^5	5.94×10^5	6.59×10^5	5.40×10^5
	α (-)	-	1.60	1.70	1.75
2	K (m^2)	1.54×10^{-10}	1.54×10^{-10} *(not fitted)*		
	β (m^{-1})	7.59×10^5	6.92×10^5	9.61×10^5	8.04×10^5
	α (-)	-	2.48	2.56	2.55
3	K (m^2)	3.91×10^{-10}	3.91×10^{-10} *(not fitted)*		
	β (m^{-1})	1.67×10^5	1.18×10^5	1.20×10^5	1.37×10^5
	α (-)	-	4.17	4.18	4.09
4	K (m^2)	1.82×10^{-10}	1.82×10^{-10} *(not fitted)*		
	β (m^{-1})	1.37×10^5	1.29×10^5	1.32×10^5	1.37×10^5
	α (-)	-	5.26	4.70	4.67

For non-Newtonian flow, three macroscale parameters are required for the prediction of pressure drops, namely the permeability K, the inertial coefficient β, and the shift factor α. Like for Newtonian fluids, also for the shear thinning fluids the pressure drop data from pore-scale flow simulations were fitted against the Darcy-Forchheimer law. The permeability was here assumed independent of fluid properties, and only β and α were determined, for each grid and rheological model (Table 2). For all grids, the values of inertial coefficient β from non-Newtonian flow simulations are in agreement among them, and with the values obtained for Newtonian fluids. No evident influence of the fluid rheology is observed. Figure 2 shows the results of μ_{eq} versus shear rate for the Cross model. The values of equivalent viscosity calculated from micro-scale flow simulations (symbols) are compared with the least-squares fitted curves obtained by using Eq. (4). The contribution of the two components, namely the porous medium viscosity μ_{eq} and the inertial term βρK|q| are also highlighted (solid and dotted lines, respectively). For all three rheological models the figures show that, in the low flow regime, shear thinning effects dominate, and the data points of μ_{eq} for all grids are correctly modelled by the fluid rheological curve μ_{eq}. Conversely, when increasing flow rate, the additional contribution to the pressure drops due to inertial phenomena increases, and the viscosity term βρK|q| dominates (dashed lines).

CONCLUSIONS

In case of Newtonian flow the porous medium can be fully described by two macroscopic parameters, namely permeability K and inertial coefficient β. Conversely, inverse modeling of pressure drops with the Darcy-Forchheimer law evidenced that, in case of non-Newtonian flow, an additional parameter is required, represented by the shift factor α, which depends on the properties of both porous medium and fluid. Therefore, in case of non-Newtonian fluid flow, the estimation of the pressure drops requires three macroscale parameters. From a practical point of view, permeability and shift factor can be easily determined in laboratory from column flow tests, performed using the non-Newtonian fluid. Conversely, the determination of the inertial coefficient β from column tests with a highly viscous fluid may be difficult in some cases, due to the high pressures and flow rates involved. As an alternative, if the pore-level structure of the medium is known sufficiently in detail (for eg. from 3D micro-tomography imaging), all three parameters can be determined from 2D or 3D pore-scale flow simulations, following the approach which was adopted in this work. This method has the advantage of allowing exploring a (potentially) unlimited range of fluids (both Newtonian and non-Newtonian), as well as a wide range of flow rate and pressure, which may be in turn prohibitive in laboratory tests.

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Quantification of mobile nano-iron as a monitoring tool for NZVI field injections

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Nanoscale zero-valent-iron (NZVI) is ascribed by numerous researchers to have a promising potential for remediation of a variety of relevant groundwater contaminants during the last years. But since this technique has not been established as a standard remediation approach so far, more extensive monitoring efforts are needed for first field applications to demonstrate its capabilities and remaining challenges. One key issue for a successful site remediation is to achieve far reaching and a most homogeneous distribution of the NZVI particles starting from the infiltration or injection point. Different approaches of particle surface modifications showed promising results relating to this task. Reliable monitoring evidence from field applications is nevertheless still needed, since indirect indications like changes in pH, redox potential or contaminant concentrations do not necessarily prove the presence of NZVI particles at the point a groundwater sample was taken. Such changes can also be caused, if NZVI is present upstream of the sampling point. Possible methods for the proof of present NZVI are digestions of sediment from drill cores, magnetic susceptibility core scans or in-situ magnetic susceptibility measurements which are currently tried in the German NAPASAN R&D project. These methods deliver reliable information, but can lack in application flexibility, repeatability or sensitivity. It was therefore investigated in the presented study, if measurement of mobile NZVI particles in the water phase can be used as an alternative for detection and quantification of total NZVI concentrations in the sediment.

For this task pore water samples were taken along the flow path of several column experiments (2 m) performed with different injection rates and suspenspension concentrations. Preliminary test series were run to determine an appropriate sampling procedure. The samples were finally taken using a peristaltic pump operated at low flow to avoid mobilisation of deposited particles. Reactive particles containing Fe(0) were analysed by acidification and subsequent measurement of developing H_2 using gas chromatography. Non-reactive particles consisting mainly of Fe(II/III) minerals were determined by additional ICP measurements and subtraction of reactive particle concentrations.

The results clearly showed that reactive Fe(0) particles can be detected in the mobile phase even days after NZVI injection at a constant concentration. Compared to the concentration of the injected suspension (e.g. 10 g/l) and the total Fe(0) concentration in the sediment (e.g. 5-40 g/kg), concentrations of mobile Fe(0) particles were relatively low (1-10 mg/l). The correlation between the total Fe(0) concentration in the sediment and the mobile Fe(0) fraction is not very strong but evident. Quantification of mobile nano-iron in pore water can therefore be used at most for detection of NZVI in the sediment. Concentrations of total Fe(0) concentration in the sediment can further be estimated within the range of one order of magnitude. Mobile Fe(II/III) particles were detected in higher concentrations than mobile Fe(0) particles, representing higher mobility of Fe(II/III) particles. The lower mobility of Fe(0) particles may be caused by magnetic forces causing higher agglomeration and sedimentation. Quantification of mobile iron particles can thus deliver valuable information for the monitoring and evaluation of NZVI injections and should be part of a monitoring plan.

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Session 7
Remediation technologies: Lessons learned from the field

Oral presentations

Pilot Scale Injection of Guar Gum Stabilized Micro-sized Zero-valent iron via Hydro-fracturing

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ABSTRACT: Within the FP7 AQUAREHAB project, injectable micro-sized zero-valent iron particles (mZVI) are being 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). In contrast to nZVI, mZVI suspensions need to be stabilised to prevent sedimentation in storage vessels and injection tubes.

Here we report on a field scale injection of guar gum stabilized mZVI that was performed in November 2011 as a joined endeavor of several AQUAREHAB partners. At the test site (located in Belgium) a TCE and 1,1,1-TCA contamination is present at 4-11 m bgs. The aquifer has a relatively low permeability and the gradient is very small resulting in an estimated groundwater velocity of approximately 10 m per year. Different injection techniques and approaches were considered. Based on the site characteristics, the final pilot test was performed with direct push injection (Geoprobe) at 5 depths (1 location) at high pressure to induce fracturing. Multilevel monitoring wells were installed at different distance around the injection point, along with temperature sensors and devices specifically developed to detect magnetic particles via measurement of electromagnetic susceptibility. In total, 100 kg of mZVI was injected suspended in 1.5 m³ of guar gum (6 g/l) slurry. The objectives of the field test were:

- To evaluate the preparation procedure and injectability of guar gum stabilized mZVI
- To understand the pressure range developed during the injection
- To test the applicability of the newly developed monitoring probes
- To determine the vertical and horizontal distribution of mZVI particles in the subsurface after injection
- To evaluate the reactivity of mZVI after the injection

A short overview of the approach followed, is described in this paper.

INTRODUCTION

The use of millimetric ZVI (mZVI) for aquifer remediation is a consolidated technology [1-2], that allows to treat contaminated plume at shallow depth (lower than 20-30 m). The increasing interest in nanoscale and micrometric ZVI, is mainly due to the possibility to overcome geometrical limitations and directly inject ZVI particles in water based slurries at a source level. The precipitation of mZVI in the injection fluid is a point of attention when up-scaling the technology to the field scale. Attempt has been performed in the past decade in order to overcome these limitations [3-10]. A strategy to enhance iron slurry stability and as consequence mobility in the subsurface, consists in dispersing the particles in non-Newtonian fluids, such as guar gum (a green biopolymer) solution [11-12].

There are two different main approaches to inject ZVI particles in the subsurface: permeation and fracturing [13-14]. The first approach is a low pressure injection where the injection fluid flow via the soil pores without causing a preferential flow path. This approach is feasible only if iron particles are sufficiently small to avoid mechanical filtration in the porous media, and in presence of highly permeable porous media. In low permeability formation, fracturing, being the injection under higher pressure and creating preferential flow paths may be the only option.

The case study described in the following paragraphs consist in the injection (direct push) of a highly concentrated guar gum stabilized mZVI slurry in a contaminated site characterized by low hydraulic conductivity and small grain size distribution.

SITE DESCRIPTION

The injection of mZVI took place in the Aarschot site (Belgium) in November 2011. The polluted site is in an industrial area, not subject to regulation for drinking water protection areas. From 1975 to 1980, wet paintings (solvent based) were produced in this plant, and since 1980 the production has been changed to powder coating. The pollution consists of CAHs, in particular chlorinated ethanes (1,1,1-TCA and 1,1-DCA) and chlorinated ethenes (TCE and cis 1,2-DCE) originating from 2 sources (Figure 1) In order to design the mZVI injection is necessary to characterize both site and contaminant source. The hydrogeological structure of the site includes:

- Layer 1 (0 to 3 m bgl): shallow sandy aquifer, water table at approximately 2 m-bgl (unless seasonal variation);
- Layer 2 (3 to 8 m bgl): fine clayey-sandy aquitard;
- Layer 3 (8 to 20 m bgl): deep sandy aquifer (grain size distribution: d_{50} = 211 μm, d_{10} = 94 μm). This layer is the target of the injection test of iron particles.

The hydraulic conductivity was estimated based on available data using both empirical approximations, and interpretation of pumping and slug test data. The average K estimated is 1.2e-4 m/s. The vertical hydraulic conductivity is assumed equal to 10% of horizontal, the hydraulic gradient ranges from 0.0009 to 0.0025 and the effective porosity, estimated on grain size distribution data is about 18%.
The TCE plume reaches the depth of 15,5 m-bgl, while the TCA plume13,5 m-bgl,

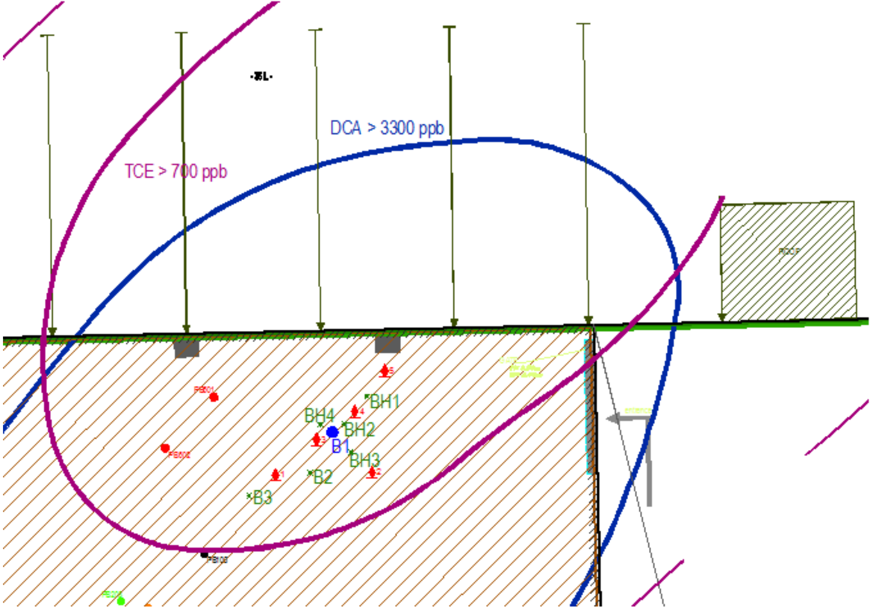

Figure 1: Aarschot contaminated site. B1 is the injection point and the extraction point. Monitoring wells are M1, M2, M3, M4 and M5. Soil cores were extracted in points B1, B2 and B3, and more recently in BH1, BH2, BH3 and BH4

PRELIMINARY TEST

Preliminary laboratory tests were conducted to design the pilot test. Reactivity tests were performed with different mZVI particles to select the most suitable for site contamination, and to estimate the mass needed for contaminants reduction. Further, sedimentation tests were performed to determine the guar gum concentration needed to avoid iron particles sedimentation and to establish a procedure for slurries preparation at pilot scale.

PILOT TEST

Injection and extraction

For the pilot test, a one-spot injection (Figure 1) at high pressure (fracturing) via direct push was selected. A volume of 1,5 m^3 of slurry consisted of guar gum (6 g/l) and mZVI (total 100 kg) was injected at 5 different depths between 10,5 to 8,5 m-bgl, (300 litres each 0,5 m).

The guar gum suspension was prepared by dispersing guar gum powder in hot water (about 50°C) and subsequently high shear mixing (Collomix Cx200) to hydrate the polymer the day before injection. In order to avoid sedimentation, iron particles were added just before the injection: 300 litres of guar gum suspension were put into a conic vessel and 20 kg of iron powder is added, mixed at high shear and recirculated for 10 minutes before each injection.

The injection was performed from bottom to top with a Geoprobe GS2000 dual piston pump, which is able to inject at flow rate ranging from 3,5 to 13 L/min. Table 1 shows the time needed for each injection as well as the average flow rate; the time needed for each injection is lower than the sedimentation time of the slurries determined in laboratory experiments (which is approximately 1,5 hours).

Table 1 Volume injected, time needed and average flow rate needed for each injection

Injection level	***Depth (m-bgl)***	***Volume (l)***	***Injection time Ti (min)***	***Average Flow Rate (l/min)***
1	10,5	300	34,53	8,69
2	10	300	31,15	9,63
3	9,5	300	33,583	8,93
4	9	300	35,7	8,40
5	8,5	300	40,283	7,45

Once it could be assumed that no more particle movement was to be expected (two weeks after injection) an extraction well was installed near the injection point. Next, 4m^3 of water was extracted from the extraction well (Figure 1) to remove excess guar-gum if possible and to simultaneously pull contaminated water into the reactive zone.

Monitoring strategy

Before the injection, 5 multilevel detection and monitoring systems (MDSP) were installed in the subsurface at different distance of the injection spot, using a Geoprobe machine (Figure 1) Each of the monitoring MDSP systems consisted of five coils that measured magnetic properties of iron, five temperature sensors and seven ports (4,5 - 8 - 8,5 - 9,0 - 9,5 - 10,0 - 10,5 m bgl) to take water samples[15]. The electronics (5 slave systems) were put next to the arrays to keep the cable length as short as possible. A master module (not shown in the photo) was controlling the data acquisition and the storage of the data. The arrays were designed such that they could be installed in the subsurface by direct push in the depth were the injection was planned.

Every five weeks, groundwater samples were collected from the MDSP systems with a peristaltic pump, to measure geochemical composition, redox parameters, chlorinated ethenes and ethanes, and dechlorination products. To support degradation of all chlorinated compound, specific isotope analysis were performed.

Two weeks after the injection, undisturbed core samplings were performed at three different distances from the injection point (about 0 m, 1 m and 2.5 m). The presence of the iron was examined visually and via H_2 measurements. To observe H_2 evolution, treatment with 1M HCl has been done. Further, to evaluate the distribution of iron particles around the injection well, guar gum has been extracted from the soil samples. In May 2012 four additional soil cores were collected to examine the presence and distribution of iron: (1) visually, (2) via H_2 measurements, and (3) through magnetic susceptibility measurements [16].

Figure 2: Monitoring system around injection point (red mark in the middle)

MONITORING RESULTS

Injection pressure

Monitoring of this parameter helps to understand phenomena occurring in the subsurface during injection process. As an example one of the pressure logs is shown in the graph below (Figure 3), in which the peak in pressure value is due to fracture formation and the subsequent decline to fracture propagation. At the end of the injection the instantaneous dropdown can be reasonably due to fracture propagation in the layer characterized by coarser material.

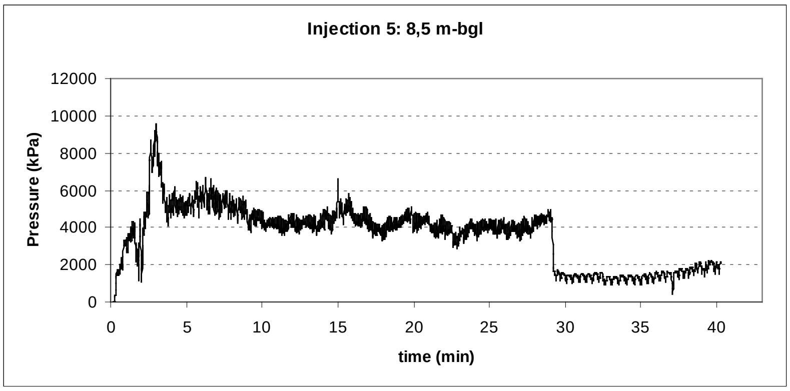

Figure 3: Pressure log during injection at 8,5 m-bgl (clayey layer)

Iron distribution

During the first campaign, performed two weeks after injection, three soil cores were extracted respectively at a radial distance of 0, 1 and 2.5 m from the injection well. 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 2.5m (data not shown). The same kind of measurements was performed to analyze soil core sampled during the second campaign (May 2012). In this case the highest mZVI concentration was detected 0.5 m from injection point in the direction of M4 (BH2) at the depth 310 cm (4 g Fe / kg aquifer) and 440 cm (8 g Fe / kg aquifer), but due to fracturing injection, the mZVI distribution is probably different in all directions..In order to check results magnetic susceptibility measurements were performed on the same soil cores aiming to detect the presence of iron. Preferential flow paths were created as could be deduced from Figure 4, which clearly highlight the presence of iron at different depth around the injection point and the non-homogenous distribution or iron particles. Data obtained with the different analyses were in agreement.

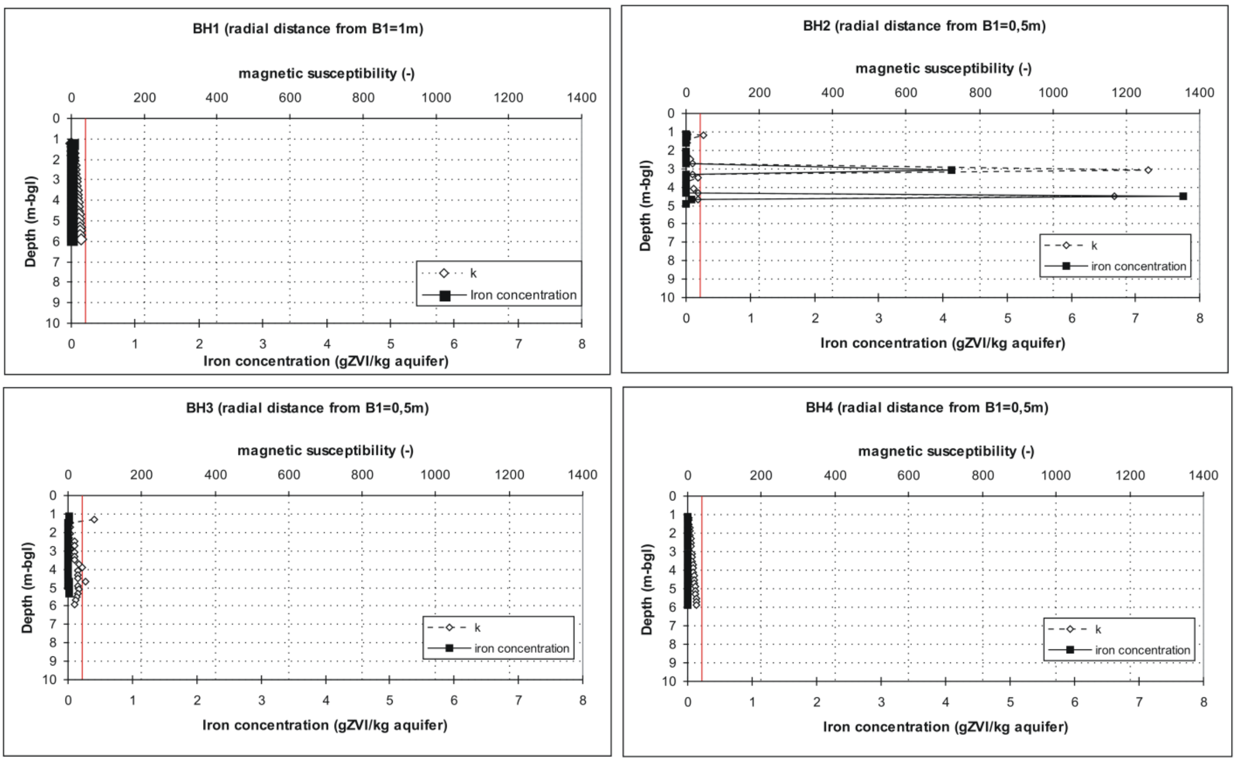

Figure 4: Iron concentration determined with H2 measurements and magnetic susceptibility profiles of soil ores extracted from 4 boreholes around injection point

Contaminant degradation

One day after ZVI injection, the oxidation reduction potential (ORP) and conductivity decreased significantly in the monitoring well at 1 m from injection point (4.5 m bgl). In the same direction iron was distributed (Figure 5). After guar gum stabilized ZVI injection, 1,1,1-TCA decreased significantly in the well M4 at 1 m (4.5 m bgl) and in well M5 2.5 m far from injection point (8 m bgl). The same was observed for TCE and 1,1-DCE. Total CAHs reduction in the well M4 (4.5 m bgl) ranged up to 75%. One of possible explanations for reduction of CAHs is abiotic degradation.

Fourteen days after the injection, extraction was occurred. Extracted groundwater compartments revealed constant isotope values of contaminants with one exception. 1,1,1-TCA exhibited clear isotope enrichment in the primary three samples (≤ 1 m^3) indicating stimulated degradation in the close vicinity of the injection well. Moreover, Figure 5 presents temporal dynamics of 1,1,1-TCA concentration and its carbon stable isotope values after 1 day and after 3, 8 and 13 weeks after extraction (4.5, 9 and 10.5 m bgl). 1,1,1-TCA data and isotope values for 1,1,1-TCA suggested that the changes in M4 are due to the iron reactivity towards 1,1,1-TCA.

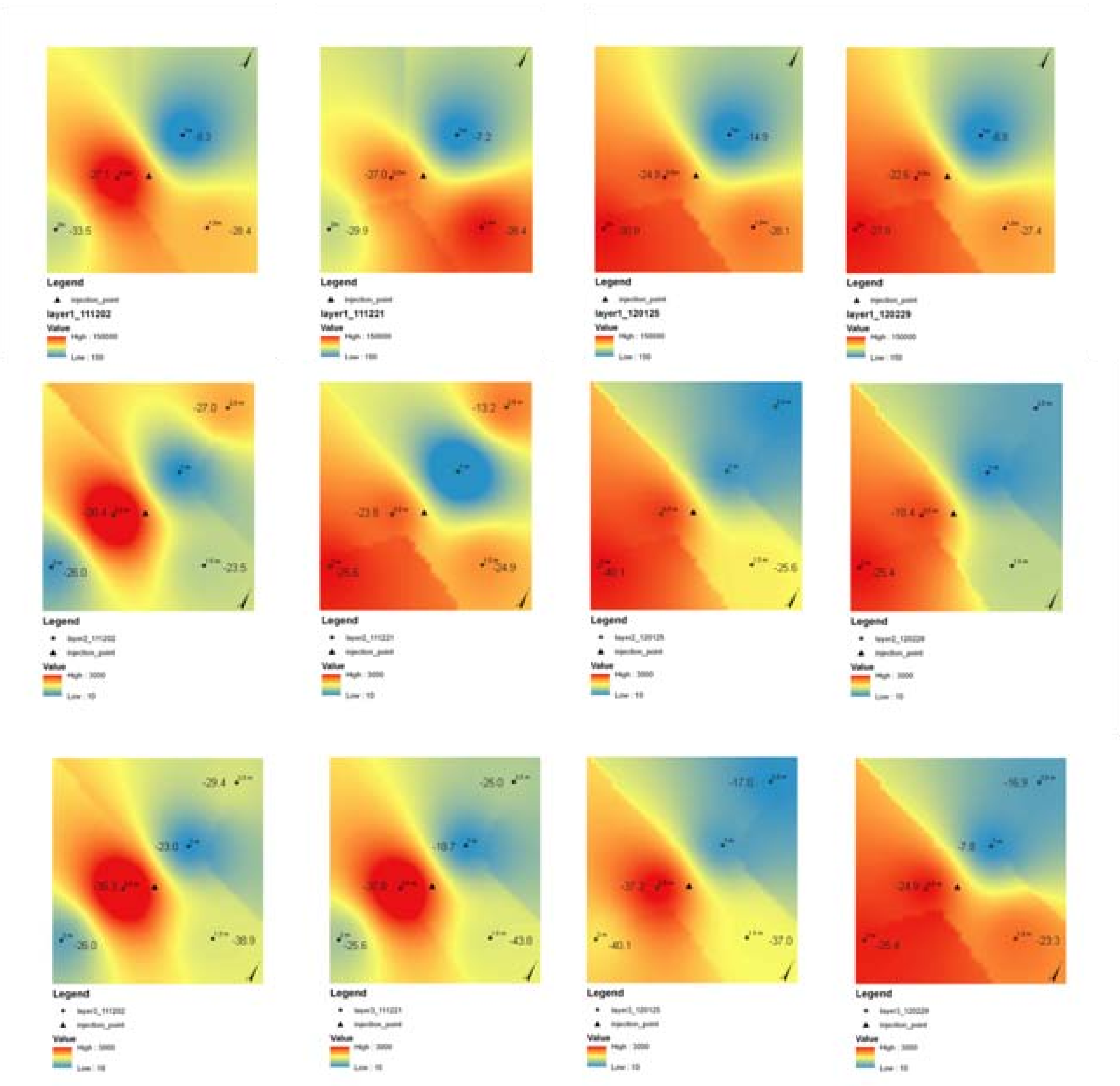

Figure 5: Temporal dynamics of 1,1,1-TCA concentration and its carbon stable isotope values (layer1 – 4.5m-bgl, layer 2 – 9 m-bgl and layer 3 – 10.5 m-bgl).

CONCLUSION

The pilot test demonstrated that mZVI slurries stabilized with guar gum can be prepared at pilot scale and delivered in the subsurface. Direct push fracturing injection has been selected as injection strategy taking into account: iron mass required for dechlorination, the ratio between average particles dimension and average porous media size distribution, and the sedimentation time of the slurry determined by screening laboratory experiments. Monitoring data show an heterogeneous distribution of iron, due to the injection technology, and a maximum distance of ZVI particles from the injection point equal to 2.5 m. Once emplaced, the mZVI particles are capable for significant dechlorination of 1,1,1-TCA and 1,1-DCE.

ACKNOWLEDGEMENTS

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

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Combined innovative remediation by bioremediation and ISCR of a VOC groundwater pollution

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At a former production site of bicycles near Antwerp, Belgium, a historical groundwater pollution with volatile organic chlorine compounds (trichloroethene (TCE)) was detected. Due to the sandy subsoil, the presence of a nearby groundwater extraction and surface water, a rapid dispersion of the groundwater pollution in a highly urbanized industrial area was established leading to an enormous and complex pollution. The source zone consists of a splitted DNAPL until 12,5 m depth with a volume of about 2.000 m³, and a contamination plume until 25 m depth with a volume of about 550.000 m³. A cost efficient and feasible soil remediation is needed.

The remediation plan, designed by Ecorem, consists of a combination of innovative remediation techniques to remediate the splitted DNAPL-zone (source) and the plume. Three boundary conditions were taken into account: (1) a traditional remediation technique was not feasible nor cost efficient, (2) both the DNAPL and the contamination plume needed to be remediated and (3) an nearby groundwater extraction, influencing the hydrogeological situation.

(1) The remediation technique in de DNAPL-zone consists of an *in-situ* chemical reduction using zerovalent iron nanoparticles (ZVI) injection. The detailed engineering has been based on previous investigation results, a successful laboratory test and on-site pilottesting with ZVI.
(2) To remediate the contamination plume until an acceptable level, Ecorem designed a sustainable and cost-effective remediation technique. The combination of a bioremediation technique with the *in-situ* chemical reduction (DNAPL) should meet the sustainability criteria of a lively soil matrix. Based on the previous investigation results, stimulated bioremediation (reduced anaerobic biodegradation) has been evaluated as a feasible remediation solution.
(3)

The influence of the nearby groundwater extraction on the contamination and suggested remediation techniques, has been evaluated in a groundwater model. The combined remediation solution offered by Ecorem, resulted in an innovative and cost-effective remediation concept.

Injection of nZVI to remediate a CHC source zone – Pilot site Braunschweig

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ABSTRACT: In the backyard of a former dry cleaning facility downtown Braunschweig, Germany, the contaminated zone has an extension of about 10 x 20 m. Main contaminant is PCE while towards the boundaries of the source TCE and cis-DCE concentrations increase. The source zone extends throughout the unsaturated zone (5 m bgl) and into the saturated zone to 14 m bgl. Most of the source is located underneath a parking lot with small portions underneath buildings. Total volume of contaminated zone is estimated at about 1000 m³ and it is estimated that 500 kg of contaminants are present. In April 2011 test injections for the injection of nano Zero Valent Iron (nZVI) particles were conducted. The slurries contained nZVI particles produced by UVR-FIA as well as, in some cases, Guar Gum to increase the buoyancy. Soil cores were taken afterwards at various distances from the injection well and their ZVI content was measured. Based on the results, a full pilot application was designed (spacing of injection wells, injection rates, injection pressure, particle and guar gum concentration etc.) and implemented in July 2012. The presentation will lead from the initial site investigation through the preliminary injection to the pilot injection. Design parameters, monitoring results and lessons learned will be discussed.

INTRODUCTION

The NAPASAN research project financed by the German Ministry for Education and Research aims to validate the ability of nano-sized zero-valent iron (nZVI) to perform successful remediation at chlorinated hydrocarbons contaminated sites. One of the main tasks of the project was to develop large-scale 2D and 3D injection experiments able to calibrate and prove the nZVI behaviour under field conditions. Such experiments should reveal the optimal site-specific injection boundary conditions and validate them through a field pilot-test. A successful nZVI based remediation faces challenges related to the presence and persistency of the iron in the close vicinity of the contaminants. Reliable investigation and injection technologies build up therefore the central point of any in-situ remediation.

DIRECT PUSH BASED INVESTIGATION AS BASIS FOR SITE MODEL DEVELOPMENT

Traditionally, site investigation relies on a predefined survey grid with nodes where soil boring/monitoring well and fixed-laboratory investigations are combined, in order to provide a knowledge status capable to enable remediation-related decisions. A major shortcoming is the small number of boreholes and sampling points, hampering a reliable characterisation of the subsurface and a successful in-situ remediation. To overcome these shortcomings and to enable both screening and detail subsurface investigations in comparatively short time periods and at low expenses, Direct-Push (DP)-based technologies were applied in an adaptive manner at the NAPASAN model-site Breite Straße, a former dry cleaning facility in Braunschweig, Germany. This technique was performed by pushing and hammering small diameter hollow steel rods into the ground to acquire high-resolution depth profiles of different physical and chemical parameters. Soil and groundwater samples were taken and various sensors were added to the DP equipment in order to obtain subsurface information at a high level of detail without the compulsory need for permanent monitoring devices.

Site Characterisation for adaptive site model development

In the backyard of a former dry cleaning facility downtown Braunschweig, the contaminated zone has an extension of about 10 x 20 m. Within the source area the contamination is strongly PCE dominated, while towards the boundaries of the source TCE and cis-DCE concentrations increase. The source zone extends throughout the unsaturated zone (5 m bgl) into the saturated zone down to 14 m bgl. Most of the source is located underneath a parking lot with small areas underneath buildings. Total volume of contaminant body is estimated at about 1000 m³, the contaminant mass at about 500 kg. During the project development, several high-resolution DP technologies were adaptively applied (Figure 1):

- Electrical conductivity (EC) for pointing out the site lithology
- Hydraulic Profiling Tool (HPT) and Slug Tests (ST) to estimate the hydraulic behaviour
- MIP (Membrane Interface Probe) to characterise the contaminant body
- Depth oriented groundwater and soil samples to calibrate the MIP-findings.

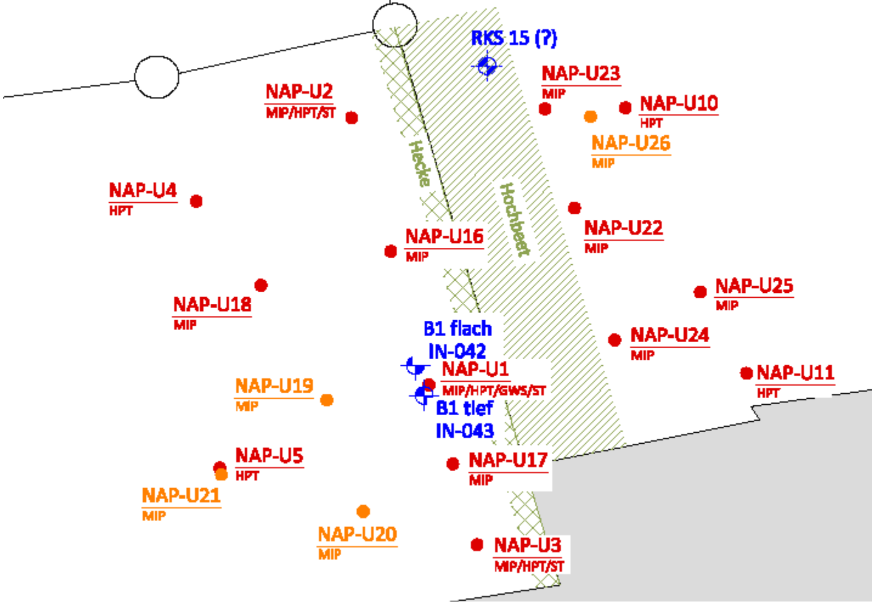


Figure 1: Site map with the present stand of investigation at the model site Breite Straße

Such a stepwise investigation allows an adaptive site model development, which emphasizes the main lithology, hydraulics and contamination specifics. Constructed 3D-Models of the spatial distribution of the hydraulic conductivity estimated for the target horizon (around 10-15m bgl.) values between 1-5 x 10^{-5}m/s (Figure 2). Many interbedded layers appear even more permeable (K-values above 1 x 10^{-4}m/s, see Figure 2). Such estimations provided the starting key points in identifying the possible technical solutions for the future field nZVI injection experiments.

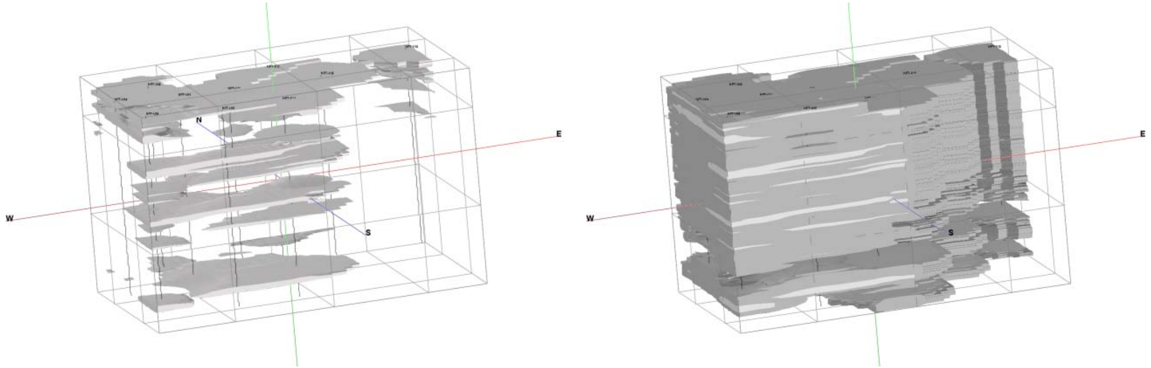


Figure 2: 3D-Model of the hydraulic conductivity displayed exemplary for K-values >1x 10-4 m/s (left, grey - values > 1 x 10-4 m/s) respectively for K-values between 1 - 5 x 10-5 m/s (right: grey - values >1 x 10-5 m/s, light grey: values >1 x 10-4 m/s, gaps: aquitard)

Contaminant situation in the source area and in the plume was delineated by a series of MIP investigations, followed by groundwater and soil sampling. A total of 30 MIP-profiles, 20 depth-oriented Liner-sampling and 25 target-oriented groundwater sampling delineated in the first step, then verified the extension of the contaminant body (Figure 3). Based on estimated contaminant distributions, the target horizon between 10 – 14 m bgl. is characterised by concentrations between 10 - 50 mg/l (Figure 3).

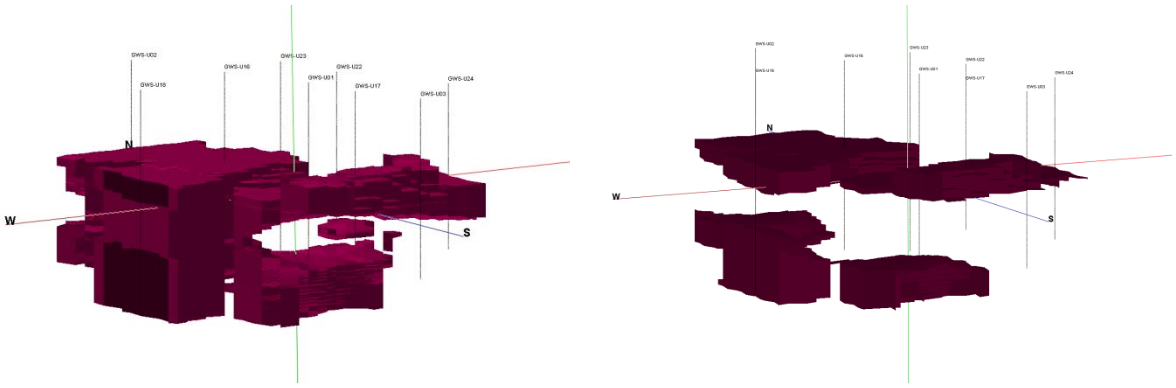


Figure 3: 3D-spatial distribution of contaminant concentrations (left > 50mg/l respectively right > 100mg/l)

FIELD SCALE INJECTION EXPERIMENTS FOR ESTIMATION OF OPTIMAL SITE SPECIFIC INJECTION CHARACTERISTICS

Strategy and performance

In order to reliably assess and validate the newly developed concepts and sensors for measuring the magnetic susceptibility, a large-scale pilot-test was vital. A proper dimensioning of the pilot-test in terms of spatial configuration and time resolution of the monitoring system could not be achieved without a preliminary field scale injection experiment. Such an experiment was designed, dimensioned and performed in April 2012 around point NAP-U3 (see Figure 1). DP-Direct injections of nZVI slurries with Uranine as dye tracer respectively Guar-Gum to increase the nZVI buoyancy were followed by monitoring of the spatial nZVI distribution around the injection points through DP-Liner-sampling at the same depth (Figure 4).

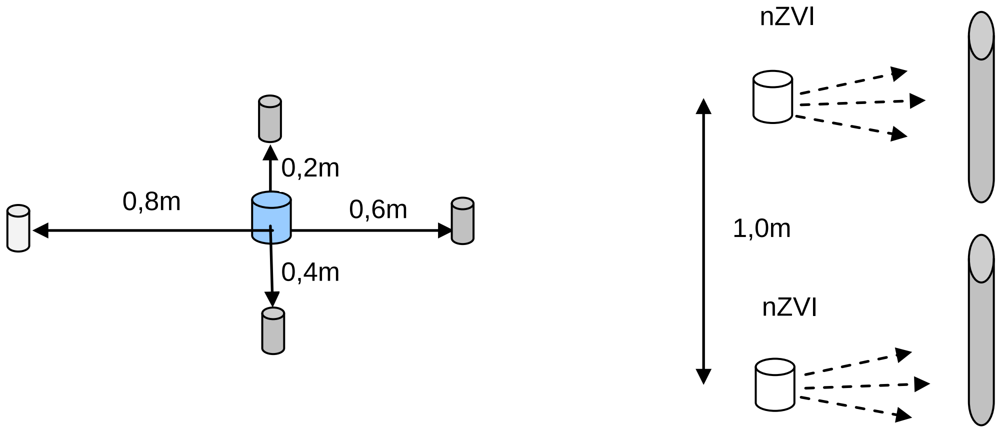


Figure 4: Layout of field scale nZVI injection experiments with lateral (left) respectively vertical (right) monitoring of iron distribution around the injection points through DP Liner-sampling followed by lab magnetic susceptibility measurements

At two different points, viscosity-based injection changes were investigated by injecting at two different injections points (U resp. G in Figure 5) depth-oriented (5,40 m and 6,10 m bgl. by point G resp. 6,60 m and 7,00 m bgl. by point U) 2 m³ of nZVI (2,5 g/l) with resp. without Guar-Gum (1,5 g/l). Injection was performed at about 13 l/min. under a pressure of about 5-6 bar.

Results

Spatial distribution of nZVI around the injection points was validated through liner-soil sampling (4,40-5,60 m bgl. and 5,60 - 6,80 m bgl. by point G resp. 5,60 - 6,80 m bgl. and 6,80 - 8,00 m bgl. by point U). The results confirm a radius of influence of about 1 m (Figure 5).

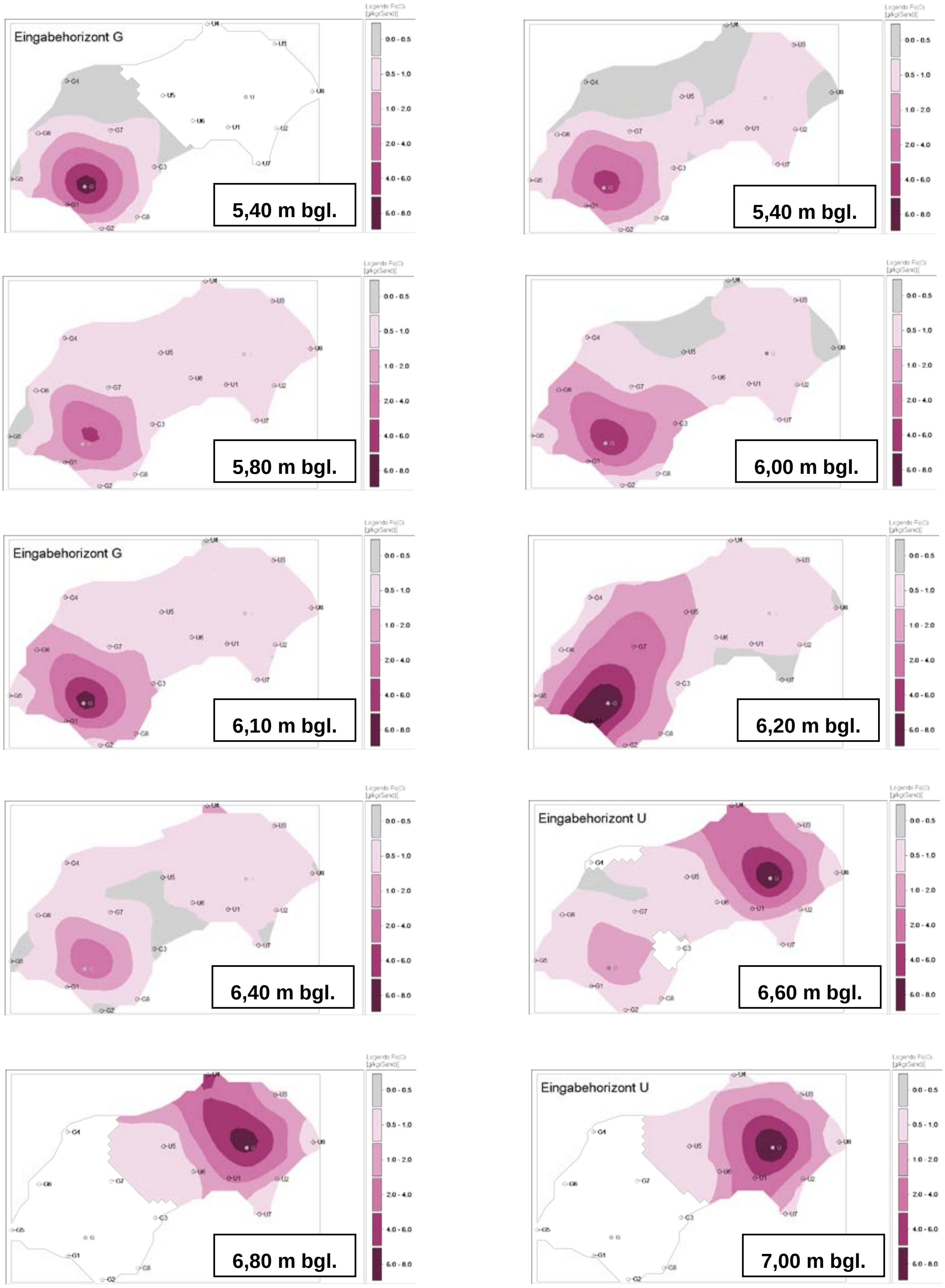
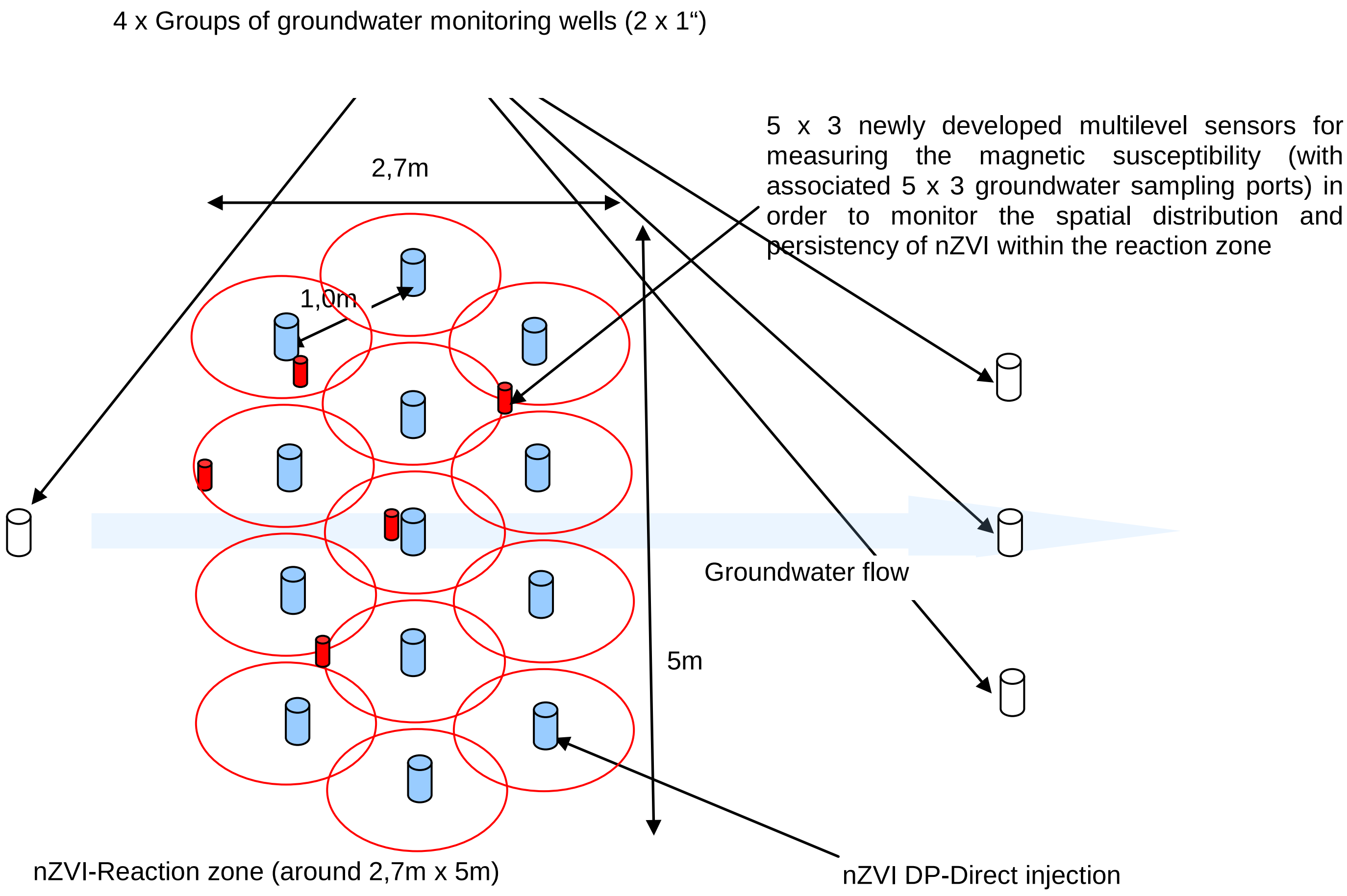


Figure 5: 2D-overview: Spatial distribution of nZVI in soil (g/kg)

CONCLUSIONS

Based on the findings of the presented preliminary injection experiments, a full pilot application was designed (spacing of injection wells, injection rates, injection pressure, depth, art of injection, nZVI resp. Guar Gum concentration) and implemented in July 2012 (Figure 6). The concept was implemented around investigation point NAP-U2 (see Figure 1). The measurement systems were installed in July 2012. 300 kg of iron in a suspension containing 10 g/l of nZVI were injected at 14 injection points during the first two weeks of August 2012 in four depths between 10 and 12 m below ground. The first preliminary results pointed out the arrival of nZVI, emphasizing the success of the pilot-test design. The data is presently under processing, comparisons between magnetic susceptibility based vs. groundwater based presence and persistency of nZVI are under development, the monitored signal variability will be studied in relation to the investigated underground heterogeneity.



4 x Groups of groundwater monitoring wells (2 x 1“)

5 x 3 newly developed multilevel sensors for measuring the magnetic susceptibility (with associated 5 x 3 groundwater sampling ports) in order to monitor the spatial distribution and persistency of nZVI within the reaction zone

nZVI-Reaction zone (around 2,7m x 5m)

nZVI DP-Direct injection

Figure 6: Spatial setting of pilot-test nZVI (reaction zone by NAP-U2)

Within the next weeks, core samples will be taken to prove the findings. The newly developed procedures and technologies are expected to significantly contribute to the success of nZVI application as remedial substrate.

ACKNOWLEDGEMENTS

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Application of Engineered Anaerobic Bio-Oxidation for Groundwater Remediation – Pilot Trial

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ABSTRACT: A pilot trial was completed to begin in assessing the feasibility of Anaerobic Bio-Oxidation (ABO) using sulphate injection to remediate groundwater impacted with petroleum hydrocarbons beneath a former, disused, decommissioned petrol filling station. A single injection event of soluble terminal electron acceptors was carried out at the site to stimulate the local microorganism population to enhance the biodegradation of dissolved phase petroleum hydrocarbons beneath the site.

The results collected during post injection performance monitoring indicated that a significant concentration reduction up to about 90% was achieved within the influence zone of sulphate injection and a carefully designed multiple injection of sulphate can successfully be used to address dissolved phase petroleum hydrocarbon contamination economically and sustainably.

INTRODUCTION

The engineered application of non oxygen electron acceptor for enhancement of degradation of Petroleum Hydrocarbon Contamination (PHC) under anaerobic condition has been previously developed (Lunardini and Dickey, 2003). Biogeochemical data collected from many petroleum hydrocarbon contaminated sites revealed anaerobic groundwater condition beneath the site indicating that anaerobic degradation could be more favourable than aerobic degradation of PHC.

The engineered application of Anaerobic Bio-Oxidation (ABO) involves introduction of soluble electron acceptors other than oxygen into the saturated zone in order to stimulate the biodegradation of petroleum hydrocarbon. The ABO via sulphate application gives a number of advantages. High solubility, the capability of naturally occurring microbes to utilise the sulphate and persistence in the In situ Reactive Zone (IRZ) following introduction are some of the key advantages which make that sulphate driven ABO is more efficient way to provide the electron acceptor and hence reduce the remediation timeframe at a site (Suthersan et al., 2011). In comparison to oxygen, there is a minimum non contamination demand for sulphate in the matrix, therefore the reduction in sulphate within a IRZ is predominantly due to biologically-mediated sulphate reduction (Atlas and Bartha, 1998). Furthermore, it is more likely to achieve an elevated dissolved electron acceptor concentration with sulphate than oxygen due to its high solubility, resulting in prolific bio degradation of PHC.

The sulphate reduction of benzene under natural pH is given in the Equation 1:

$$C_6H_6 + 3.75\ SO_4^{2-} + 3\ H_2O \Rightarrow 1.875\ H_2S + 1.875HS^- + 6HCO^-_3 + 0.375\ H^+ \quad (1)$$

As shown in Equation 1, by-products of sulphate reduction can alter the geochemistry within the aquifer. Therefore, a careful assessment and control of sulphate reduction by-products for effective ABO would be critical. During sulphate reduction, hydrogen sulphide can be produced as a by-product, however, it is rarely documented as an issue in the field as naturally occurring iron will help to restrain the sulphide accumulation beneath the site (Cunningham et al. 2001). The potential for production of bicarbonate in sulphate reduction may effectively increase the alkalinity and which in turn increase pH in the groundwater. The rate of sulphate reduction may reduce at pH values outside of the 5.5 and 9 range. (Hao et al. 1996). In addition, in a calcium-rich aquifer, precipitation of solids could effectively alter the hydraulic conductivity of aquifer, limiting the effective delivery of reagent in subsequent injections.

In general, the overall cost associated with sulphate driven ABO is lower than that with many active remediation technologies. The ABO appears to be more sustainable than many of the other in situ remediation technologies when evaluate against the SURF UK social, environmental and economical indicators. Therefore, a pilot trial of ABO was undertaken in a former petrol filling station in order to assess the suitability of this technology to address the dissolved phase residual petroleum hydrocarbon contamination plume beneath the site. This paper describes the outcomes of the pilot trial.

PILOT TRIAL

The scope of pilot trial comprised of a single injection of sulphate solution using a injection well installed and three events of post injection performance groundwater monitoring.

Site Location and Description

The site is a disused, decommissioned petrol filling station, located in West Midlands in the UK. The ground conditions encountered during intrusive investigation carried out by ARCADIS, comprised Made Ground (MG), consisting of sandy gravel and gravely sand proven to a maximum depth of 4.5m below ground level (bgl). The MG overlaid gravely sand and sandy gravel, interpreted as the Alluvium and River Gravel deposit, proven to a maximum depth of 6.0m bgl.

The rest groundwater levels beneath the site were recorded at depth of approximately 3.5mbgl. The groundwater elevation data suggested a groundwater flow direction to the north.

The site layout plan is presented as Figure 1.

Contaminant Distribution

Based on the results of groundwater monitoring undertaken prior to sulphate injection, the highest petroleum hydrocarbon concentrations were measured in groundwater sampled from the monitoring wells located in the vicinity of the former tank farm and fuel distribution infrastructure. The highest Total Petroleum Hydrocarbon (TPH) concentration was measured in groundwater sampled from monitoring well MW201 (28,000 µg/L) and comprised predominantly Petrol Range Organics (PRO).

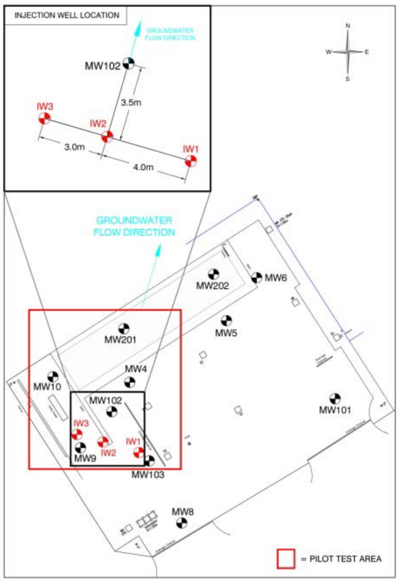


Figure 1: Site Layout Plan

Elevated concentrations of TPH were measured in soils sampled from the same area. These samples were primarily collected from the smear or saturated zone of the site and comprised predominantly PRO. Dissolved phase TPH distribution beneath the pilot trial area, prior to sulphate injection, is presented in Figure 2.

No Light Non Aqueous Phase Liquid (LNAPL) was encountered beneath the site.

Sulphate Injection

The injection and monitoring well layout is presented as Figure 1. A total volume of 8,000 L of 25g/L sodium sulphate solution was injected in to IW2 with an approximate injection rate of 0.56L/s. The variation of electrical conductivity and sulphate concentrations, due to the sodium sulphate injection, within the surrounding does response wells (IW1, IW3 and MW102) were measured during injection. These parameters were considered as appropriate indicators for a short time period to assess the distribution of sodium sulphate around the injection well.

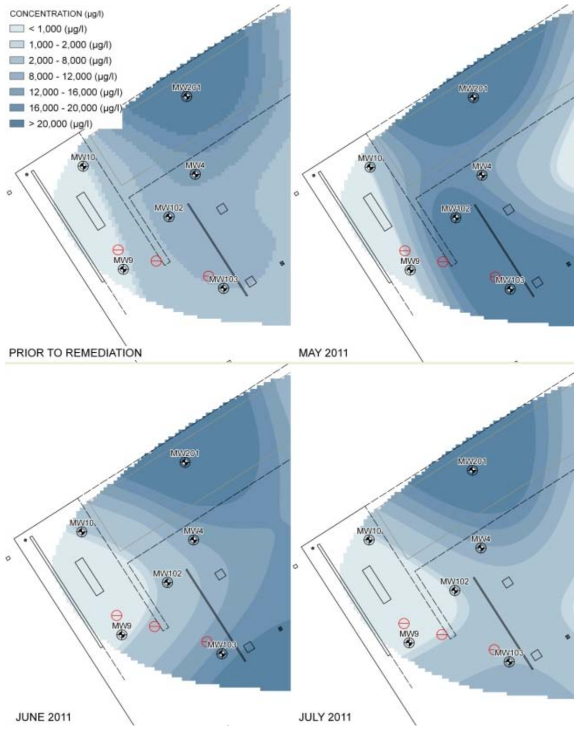


Figure 2: ***Spatial Distribution of TPH concentrations in groundwater within pilot area***

RESULTS

Figure 3 shows the results collected during sodium sulphate injection at the site. As shown in Figure 3 the electrical conductivity and sulphate concentration were seem to increase within dose response wells indicating that the sodium sulphate solution reached monitoring wells IW1, IW3 and MW102. The measured data indicated that the distribution of sulphate, with the given volume, was possible up to about 4 m from the injection point. Accordingly, the effective Radius of Influence (RoI) was estimated as 3-4m beneath the site.

Post Injection Performance Monitoring

Performance monitoring was carried out for three months on a monthly basis in May, June and July 2011 in order to evaluate the effects of the sulphate injection on the dissolved phase PHC plume beneath the site.

No LNAPL was encountered resting on groundwater within the monitoring well network across the site, during performance monitoring conducted from May to July 2011.

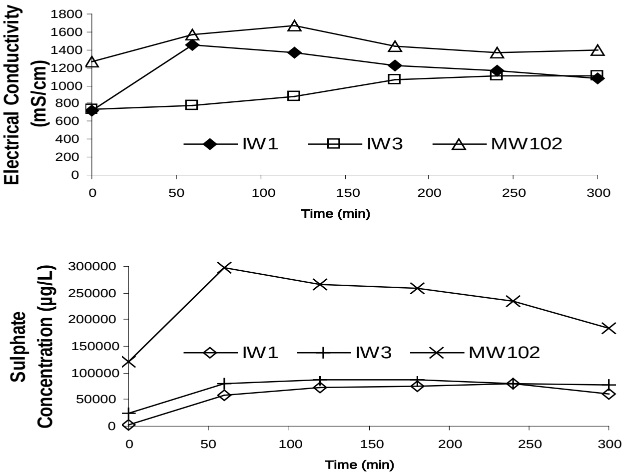
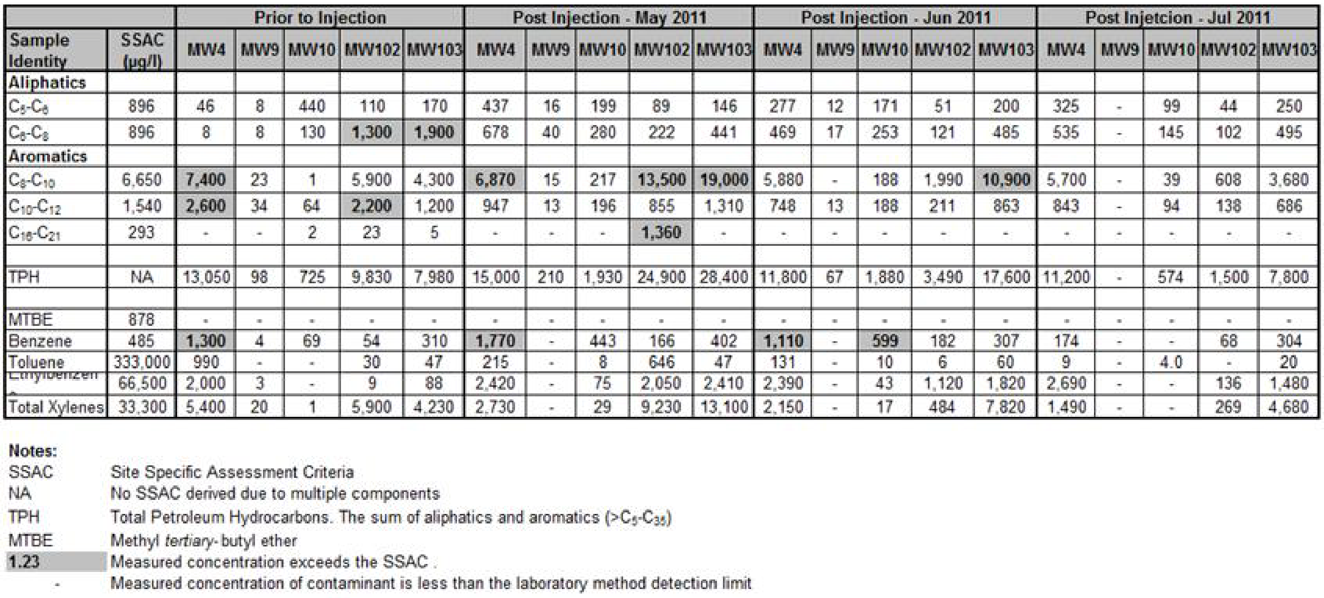


Figure 3: ***Variation of Electrical conductivity and Sulphate concentrations in dose response wells during sulphate injection***

The measured concentrations of CoC during performance monitoring, together with comparison of Site Specific Assessment Criteria (SSAC), derived for the site based on the intended end use, are presented in Table 1. The measured concentrations of CoC in groundwater sampled during May 2011, following the sodium sulphate injection, showed an increasing trend. This may be due to the disturbance made during the injection of sodium sulphate. The concentrations of CoC in soil, measured during the site investigation, indicated that a reasonable contamination mass remained within the smear zone. Therefore, desorption and dissolution of PHC remaining within the smear zone may have occurred with the sulphate injection as temporal raise of groundwater level during injection contributing for increased concentrations of CoC in groundwater identified immediately following the sulphate injection.

The concentration increase of CoC due to potential desorption following sulphate injection brings an added benefit to the site remediation. The adsorbed contamination mass, which may act as an on-going contamination source for groundwater, significantly controls the potential for rebound of contaminant concentrations during post remediation verification monitoring. Therefore, the reduction of adsorbed contamination mass should reduce the potential for future rebound of concentrations of contaminants during post remediation validation monitoring

Table 1: ***Measured Concentration of CoC during Pilot trial***



		Prior to Injection					Post Injection - May 2011					Post Injection - Jun 2011					Post Injetcion - Jul 2011				
Sample Identity	**SSAC (µg/l)**	**MW4**	**MW9**	**MW10**	**MW102**	**MW103**	**MW4**	**MW9**	**MW10**	**MW102**	**MW103**	**MW4**	**MW9**	**MW10**	**MW102**	**MW103**	**MW4**	**MW9**	**MW10**	**MW102**	**MW103**
Aliphatics																					
C_5-C_6	896	46	8	440	110	170	437	16	199	89	146	277	12	171	51	200	325	-	99	44	250
C_6-C_8	896	8	8	130	**1,300**	**1,900**	678	40	280	222	441	469	17	253	121	485	535	-	145	102	495
Aromatics																					
C_8-C_{10}	6,650	**7,400**	23	1	5,900	4,300	**6,870**	15	217	**13,500**	**19,000**	5,880	-	188	1,990	**10,900**	5,700	-	39	608	3,680
C_{10}-C_{12}	1,540	**2,600**	34	64	**2,200**	1,200	947	13	196	855	1,310	748	13	188	211	863	843	-	94	138	686
C_{16}-C_{21}	293	-	-	2	23	5	-	-	-	**1,360**	-	-	-	-	-	-	-	-	-	-	-
TPH	NA	13,050	98	725	9,830	7,980	15,000	210	1,930	24,900	28,400	11,800	67	1,880	3,490	17,600	11,200	-	574	1,500	7,800
MTBE	878	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzene	485	**1,300**	4	69	54	310	**1,770**	-	443	166	402	**1,110**	-	**599**	182	307	174	-	-	68	304
Toluene	333,000	990	-	-	30	47	215	-	8	646	47	131	-	10	6	60	9	-	4.0	-	20
Ethylbenzene	66,500	2,000	3	-	9	88	2,420	-	75	2,050	2,410	2,390	-	43	1,120	1,820	2,690	-	-	136	1,480
Total Xylenes	33,300	5,400	20	1	5,900	4,230	2,730	-	29	9,230	13,100	2,150	-	17	484	7,820	1,490	-	-	269	4,680

Notes:

SSAC	Site Specific Assessment Criteria
NA	No SSAC derived due to multiple components
TPH	Total Petroleum Hydrocarbons. The sum of aliphatics and aromatics (>C_5-C_{35})
MTBE	Methyl *tertiary*-butyl ether
1.23	Measured concentration exceeds the SSAC .
-	Measured concentration of contaminant is less than the laboratory method detection limit

As shown in results collected in June and July 2011, the measured concentrations of CoC decreased in the area of the ABO pilot. As shown in results collected in July 2011, none of the measured concentrations of CoC were found above the applicable SSAC. The measured concentrations of sulphate in the groundwater sampled from the monitoring wells during post injection performance monitoring are presented in Table 2. The measured sulphate concentrations, particularly within the wells with elevated concentrations of CoC, have diminished with the time. This, together with reduction in the CoC, indicated the potential utilisation of sulphate by microorganism to stimulate the anaerobic bio oxidation of hydrocarbon contamination dissolved in the groundwater beneath the site.

Table 2: ***Measured Sulphate Concentration (µg/L) during Performance monitoring***

Date	MW4	MW9	MW10	MW102	MW103
May-11	26,700	74,800	2,500	323,000	20,400
Jun-11	4,000	63,100	3,000	105,000	<2,000
Jul-11	<2000	53,900	<2000	57,200	<2000

The variation of groundwater TPH concentrations measured during performance monitoring is shown on Figure 2 and the overall percentage reduction of TPH concentration in each monitoring location is presented in Table 3. In general, a significant concentrations reduction can be noted within wells sampled in the pilot trial area.

Monitoring wells MW4, MW10 and MW102 were located hydraulically down gradient from the injection well IW2 and the overall TPH concentration reductions of 14%, 21% and 85%, respectively have been achieved in these locations. MW102 is located within the radius of influence of the injection well, therefore the increased availability of sulphate at this location is considered to have enhanced ABO resulting in higher contamination mass reduction in the vicinity of MW102. Monitoring wells MW4, located further down from the influence of sulphate injection, and MW10, located out of the immediate influence zone of the injection, resulted a lower sulphate concentration to stimulate ABO and hence a limited TPH concentration reduction.

Monitoring well MW9, which is located within the radius of influence of sulphate injection, showed 90% concentration reduction. The least concentration reduction of 2% has been noticed within the monitoring well MW103, which was located hydraulically up gradient and out of the influence zone of sulphate injection well.

In general, a clear correlation between TPH concentration reductions and sulphate concentrations within monitoring wells can be noted. A higher TPH concentration reduction was observed in the wells where greater sulphate concentration was available. This supports the utilisation of sulphate for contaminant removal through ABO.

Table 3: ***Contamination reduction percentage observed during pilot trial***

Monitoring Well	TPH Concentration (µg/L) Prior to ABO Trial	TPH Concentration (µg/L) Post ABO Trial (July 2011)	Percentage Reduction
MW4	13,050	11,200	14%
MW9	98	<10	90%
MW10	725	574	21%
MW102	9,830	1,500	85%
MW103	7,980	7,800	2%

The results indicate that ABO has potential to achieve significant reduction in groundwater concentration of TPH compounds at the site. However, concentration reduction will diminish with the reduction of sulphate concentration beneath the site. Furthermore, as shown in Figure 2, no concentration reduction was observed in monitoring wells located out of the influence zone of injection well. Accordingly, frequent sulphate injections with a series of injection wells would need to be utilised to reduce the PHC mass from beneath the site through ABO and hence to manage the environmental liabilities associate with the site.

The remediation cost and energy utilisation associated with the sulphate injection are relatively low. There is no significant generation of waste and secondary waste treatment (e.g. extracted water treatment and disposal). It appears that the remediation time frame can be relatively rapid. The potential disturbance on the site and to the neighbouring properties and site users are low. Enhanced ABO is unlikely to create noise, dust or odour nuisances to the surrounding land users. Therefore, enhanced ABO is a sustainable remediation technique which can be used to address the dissolved phase PHC in a site effectively and economically.

CONCLUSION

An ABO pilot trial has been undertaken to determine the potential effectiveness of an ABO approach using sulphate to manage environmental risks from previously identified groundwater impacts at the site and to collect field data that would assist in designing a wider scale remediation approach for the site.

The results of the pilot trial indicated that anaerobic bio oxidation was an effective technique that could be capable of achieving significant reduction in PHC concentrations in groundwater.

The results collected during post injection performance monitoring indicated that a concentration reduction up to about 90% can be achieved within the influence zone of sulphate injection. Concentration reductions in monitoring wells located out of the influence zone of sulphate injection were relatively small due to the limited availability of sulphate to promote the ABO of contamination. The results indicate that carefully designed multiple injections of sulphate in a series of injection wells successfully be used to address the petroleum hydrocarbon contamination plume beneath a site. Furthermore, ABO is sustainable and economical remediation technology to be used for treatment of dissolved phase petroleum hydrocarbon contamination plume beneath a site.

ACKNOWLEDGEMENTS

A sincere thank to the ARCADIS UK project team including Field Services for their contribution for a successful pilot trial conducted at the site.

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Poster Presentations

Robustness and Reliability of an Inoculated Bioreactor for MTBE/TBA-Removal from Groundwater

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Methyl tertiarty-butyl ether (MTBE) is a synthetic car fuel additive. However, it's widely use resulted in groundwater contamination (up to 830 mg/L) with MTBE. Tert-butyl alcohl (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 drinkingwater winning areas. 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 exists, 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. 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. 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, is investigating the robustness and reliability of biotechnologies like the inoculated bioreactor, which is important to come to innovation, being the full scale applications. Results from lab scale and pilot scale tests, related with robustness and reliability, will be presented. On the one hand, on **lab scale**, the MTBE/TBA-removal performance of the bioreactor was systematically evaluated under different conditions (influent concentration, pH, T, oxygen concentrations, hydraulic retention times, co-pollutants). The extensive quantitative data collected on environmental conditions which allow MTBE/TBA degradation by the M-consortium (Debor at el., 201X), show (1) that bioremediation is an 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. On the other hand, **a pilot scale** inoculated bioreactor was operated in the field at a petrol gas in Belgium for about 6 months. The prototype bioreactor was shown to be a relatively fast starting and stable system, removing MTBE & TBA from groundwater in an efficient way, able to meet the discharge limits. Currently, the pilot bioreactor is being operated at other sites with other groundwater compositions, to evaluate further the robustness & reliability under real life conditions.

Large scale injection of soy bean oil emulsion using biostimulator technology

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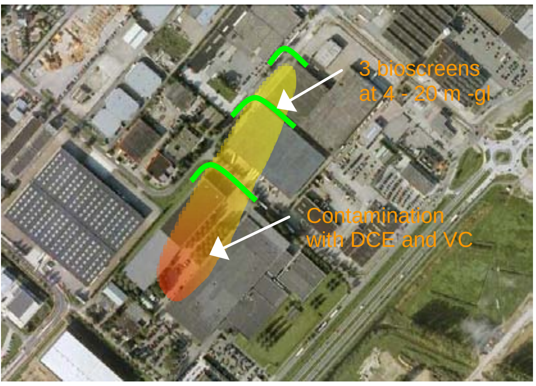
An innovative injection technology has been developed to enhance natural attenuation in large contaminations with chlorinated solvents. HMVT created the biostimulator to prepare a fine emulsion of soy bean oil in large quantities with local groundwater. Soy bean oil is a slow release substrate for biodegradation and has a life time of approximately 5 years in the groundwater. The biostimulator has two mixing tanks of 8 m^3 and a special mixing pump. The mixed emulsion is distributed by a fire hose over a few hundred meters to a manifold on a trailer. From this manifold the emulsion is injected into 10 to 20 injection wells at the same time. By application of the biostimulator HMVT has managed to triple the production and injection rate. Enhanced natural attenuation (ENNA) has become more cost effective now by scaling up the injection process.



Experiences at the Vanderlande NL site

At the site of Vanderlande Industries in the Netherlands 3 bioscreens with multiple injection wells were installed transverse in the contamination plume of 5 hectares. The 3 bioscreens contain more than hundred injection wells at 4 levels between 4 and 20 m below ground level. In about 2 weeks the biostimulator injected 160 m^3 substrate into 80 injection wells.

The process monitoring shows the concentrations of DCE and VC decreases in the bioscreen by some 90% in the first year. The formation of ethene confirms the complete biodegration. In the bioscreen sulfate is completely reduced by enhanced natural attenuation. The level of dissolved organic carbon has been increased by the injection of soy bean oil. The results show there is enough substrate for the biodegradation. In the presentation at the symposium we will discuss the application of the biostimulator and the results of the process monitoring.

Characterization and remediation of an industrial site polluted by a spill of MCB in Huesca (Spain)

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In the 40's began the installation of metallurgical and chemical industries in an alluvial valley effluent of the Ebro river. Over time the industrial area has changed considerably and its footprint on the environment has been significant, both on the upper terrace (+10m) and also on the river valley. The terrace is formed by heterometric gravels with abundant silt fraction of dark color, which fossilize an erosive Miocene relief (sands, silts, clays and marls). The gravels forming the main aquifer, have a thickness ranging from 4 to 10 m and the groundwater level is about 5 m deep (about 5 m above the current level of the river).

At the end of 1995 monochlorobenzene (MCB) was detected in the alluvial aquifer. Later, it was established that the contamination was originated in the area of a buried storage tanks, in the upper terrace. The MCB free phase shifted by the base of the alluvial aquifer of the upper terrace and in aqueous phase through the same aquifer that discharges mainly to the lower terrace and finally to the river. Since the contamination was detected, several actions were conducted in order to prevent pollution reaching the river and to remove all traces of MCB in groundwater.

The first emergency actions that took place were pump and treat groundwater before being discharged into the river and removing the MCB tanks. Later began the characterization works (piezometers, sampling campaigns,…) to delineate the magnitude and extent of contamination. Remediation works started in parallel such as (1) removal of MCB free phase from the base of the aquifer, (2) pump and treat water (air-stripping) from the lower terrace, and from the upper terrace by new piezometers distributed as an hydraulic barrier, (3) water injection into the leakage area to accelerate the remobilization of contaminant attached in the vadose zone. Moreover, recently, a bioremediation pilot test has been implemented in order to assess the technical feasibility and applicability at a larger scale.

The air-stripping plant is in operation since 1999 and has treated 900.000 m^3 of water, which represents 16.000 kg of MCB.

Feasibility Study on Remediation of PCE/TCE Contaminated Groundwater using a Permeable Reactive Barrier

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Permeable Reactive Barrier (PRB) is a recognized technology for *in-situ* treatment of contaminated groundwater. Studies have shown that one of the key factors leading to problems and failure of PRB performance is the inadequate site characterization. The objective of this paper is to describe a detailed site characterization for the evaluation of the potential installation of a PRB that is intended to clean up the aquifer supplying drinking water to 20,000 inhabitants in Nowa Dęba (South-East Poland), which is contaminated by tetrachloroethylene (PCE) and trichloroethylene (TCE). For the present work, a conceptual site model was developed using field information from previous investigations. Additionally, the intrinsic biodegradation potential was evaluated to assess Natural Attenuation (NA) as the first remediation option. Results show exceeding limit concentrations of TCE and PCE in groundwater. The contaminant source is believed to be located within the area of a former metal works and ammunition factory with concentrations up to 6130 µg/L for TCE and 694 µg/L for PCE. Receptors of contamination are the wells of the municipal waterworks. TCE concentrations of 631 µg/L and 149 µg/L were measured in two extraction wells of the waterworks. Presence of PCE on the other hand, was detected only in piezometers close to the suspected contamination source. Results suggest inadequate evidence of intrinsic biodegradation of TCE and PCE and therefore, limited potential for NA as a remediation alternative. On the contrary, PRB system may be effective to reduce TCE and PCE concentrations under the site specific conditions diminishing risk and meeting the drinking water standards established in the Polish regulations DZ. U.2007.61.417 and Dz.U.2010.72.466. No indication has been found of any conditions that may limit the effectiveness of the technology at the site of concern. Currently, laboratory test are performed for the selection of the most effective reactive materials to be used at the PRB system. The obtained results will be verified by the pilot installation at the case study area.

INTRODUCTION

Trichloroethylene (TCE) and tetrachloroethylene (PCE) are primary contaminants of concern common in aquifers in Europe and North America. They have been widely used for a variety of industries (ammunition, electronics, automotive parts, textile and dry cleaning) as cleaning and degreasing solvents, especially TCE for its effectiveness, non-corrosity and non-inflammable properties (Mccarty, 2010). PCE and TCE are considered to be health concern and are included in the list of probably carcinogenic to humans (WHO, 1997). Both substances can be transformed by biotic and abiotic processes, leading to the production of daughter products that are also health concern. PCE can be biologically degraded into TCE, and later TCE can be converted into cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC) which are more hazardous than their parental contaminants. VC is a known human carcinogen. Physical and chemical properties of TCE and PCE determines their behavior, fate and transport in the environment (Russell et al., 1992). The understanding of these properties is the first step when selecting a remediation technology. Chlorinated solvents and many of their daughter products have densities higher than water and, thus they can penetrate deeper into an aquifer forming denser-than-water non-aqueous phase liquid (DNAPL) plumes. These compounds have low solubility in water, which means that the loss of contaminant by dissolving in water is rather a slow process (Mccarty, 2010). Additionally, they demonstrate low sorption affinity indicating that they do not sorb strongly into aquifer solids. Because of their characteristics chlorinated solvents are among the contaminants that have proved to be difficult to remediate, representing a technical and economic challenge to engineers. A permeable reactive barriers (PRB) technology may offer a low cost and efficient option to remediate these contaminants. The main objective of the technology is to intercept and remediate dissolved contaminants passing through the barrier. Success of the PRB technology depends greatly on how well the site characteristics and aquifer hydrology are understood. The aim of this paper is to present the preliminary assessment of a site contaminated with TCE and PCE for the installation of a PRB to decide whether or not this technology will be appropriate to meet the remediation goals.

SITE DESCRIPTION

The area under study is located in the northern part of the Carpathian Foredeep in vicinity of the town of Nowa Dęba (South-East Poland). The site covers an approximately area of 30 m^2 that lies above a Quaternary aquifer body QDK (Quaternary fossil valley) which belongs to the Groundwater Body (GWB) No. 135, and partially to the Major Groundwater Basin (MGWB) No. 425 according to the Polish hydrological classification. This aquifer is the main drinking water source for the town of Nowa Dęba for approximately 20,000 inhabitants and some industries. In the southern part of the site is placed an industrial complex with mainly metal works activities and an ammunition factory operating since 1939. Groundwater extraction wells of Nowa Dęba waterworks are located to an approximately distance of 1600 m northwest from the industrial complex (Fig. 1). The groundwater of this aquifer is contaminated with TCE and PCE with concentrations up to 6130 µg/L and 694 µg/L respectively. Groundwater chemical analysis indicates TCE and PCE to be the main contaminants of concern in the site, although there were also found high pH and high concentrations of Al, Ni and Fe. In general, the groundwater chemical status of the aquifer was qualified as “poor quality” (Kret et al., 2011).

METHODOLOGY

Preliminary technical assessment to determine the suitability of the site for PRB application was based on the site characterization and conceptual site model. Both were used to determine any practical constraints to the barrier installation or that may limit the performance of the technology after installation. This is a crucial step in the technology design, because unlike other technologies such as ‘pump and treat,’ a PRB is a permanent installation for which the location and materials must be carefully selected; once it has been constructed it is difficult to relocate it. In general, aquifer hydrogeology, groundwater flow conditions, groundwater chemistry, contaminants concentrations and distribution in the aquifer were analysed to assess if the contaminants are amenable to treatment by the PRB technology and, if it enables to intercept the contaminant plume.

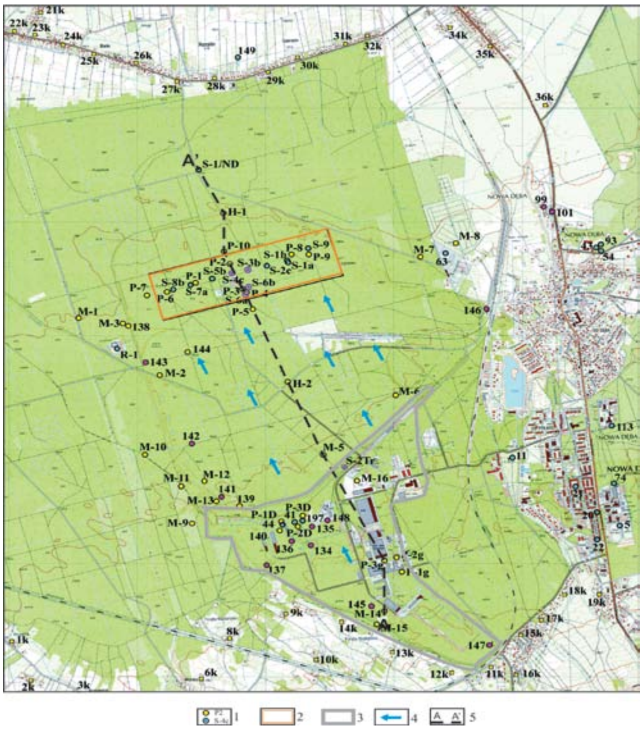

Figure 1: Map of the studied area

Notation: 1 – observation points (piezometeres and wells), 2 – waterworks area, 3 – industrial complex, 4 – Groundwater flow direction, 5 – Cross-section line.

RESULTS

Site Hydrogeology

The Quaternary aquifer consists of alluvial and terrace deposits of sand, silt, clay, and gravel. The aquifer is unconfined with depths to groundwater from 0.5 to 16.5 m. The thickness of the quaternary deposits is of approximately 30 m, lying on an impermeable layer of Miocene clays (Fig. 2). Recharge to the alluvial and terrace deposits comes mostly from infiltration of precipitation. Average annual rainfall is 847 mm from which 20-25% is infiltrated into the soil (238 mm/year). Drainage of the aquifer under natural conditions occurs on streams Koniecpólka, Deba and Bystrzyk. The groundwater levels are influenced by the water extraction from the waterworks. In 2010 the water withdraw ranged from 73 to 1240 m^3/d. Groundwater flows from South to North-West part of the studied area with an average velocity of 0.4 m/d. The hydraulic conductivity ranges from 0,009 to 34 m/d.

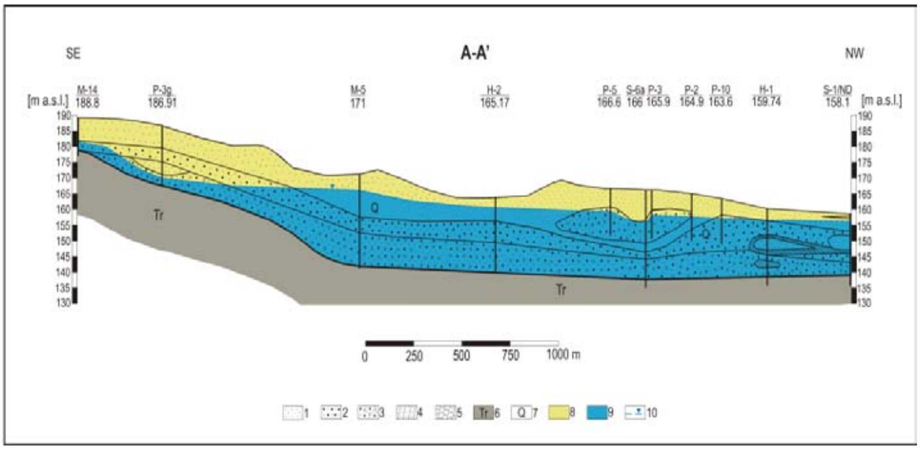

Figure 2: Hydrogeological cross-section of the studied area (Szklarczyk et al., 2011).
Notation: 1 – fine-medium sands, 2 – fine-medium sands with gravels, 3 – sandy gravel, 4 – sandy clay, 5 – clays and silts, 6 – Miocene – Krakowieckie clays, 7 – Quaternary deposits, 8 – unsaturated zone, 9 – saturated zone, 10 – groundwater level (status for 2010).

Contaminants in Groundwater

Concentrations of PCE and TCE recorded in 2009 and 2010 are presented in figures 3a-3d. Highest concentrations of contaminants were found in piezometers: M-16 and P-3g close to the suspected source. It was also identified that TCE plume have already reached drinking water wells: S-6b, S-3 and S-5, while PCE was less widespread. It can be observed that both TCE and PCE concentrations exceed the threshold value of 10 μ/L (Σ TCE and PCE) established in the Polish regulation (Dz.U.2010. 72.466). Since there is not data recorded for previous years, no comparison can be made to determine trend changes in concentrations during a longer period of time. The isopleth maps of TCE and PCE concentrations for the site can be found in Kiecak et al., 2012.

Source-Pathway-Receptor Sequence

The distribution of TCE and PCE suggest that the contaminant source is located within the area of the industrial complex (Kiecak et al., 2011). The causes of contaminants releases, periods of leakages and the volumes of contaminants lost are unknown. It is thought, however, that contamination of the aquifer occurred by systematic discharges of TCE and PCE during the history of industrial activity in the site. Contaminants have probably been released gradually as a result of inadequate storage, accidentally spills into unsealed soil, and lack of environmental awareness. PCE and TCE are denser than water, and when spilled on the ground in quantities great enough to overcome the residual saturation, may migrate vertically downward through an aquifer (Fetter, 1993). As relatively soluble in water, they may also migrate in a dissolved phase in the direction of a groundwater flow. Thus, potential routes of migration for PCE, TCE and associated degradation products in the site are principally through groundwater flow towards the waterworks (Kiecak et al., 2011). The first receptor of contamination is the groundwater of the Quaternary aquifer. Primary targets are the municipal drinking water extraction wells located 1600 m down-gradient of the suspected contaminant source. Secondary targets are surface water streams – the drainage base of the aquifer.

Natural Attenuation

The intrinsic biodegradation potential was assessed based on biogeochemistry and hydrogeochemistry of the site as well as hydrogeological conditions, for a first approximation of NA as a remediation strategy (Kiecak et al., 2012). Three indicating points in the area under study were selected: a piezometer M-5 located 1100 m from the source and wells S-2Tr and S-6B located approximately 900 m and 2400 m from the source respectively (Fig. 1). Geochemical indicators included: Dissolved Oxygen (DO), nitrates and sulfates concentrations, pH, Oxidation-Reduction Potential (ORP), Total Organic Carbon (TOC), temperature, DCE and VC. Results suggested that intrinsic biodegradation of TCE and PCE via reductive dehalogenation was not enough for risk reduction at the site and, it was concluded that there is a limited potential for NA as a remediation alternative.

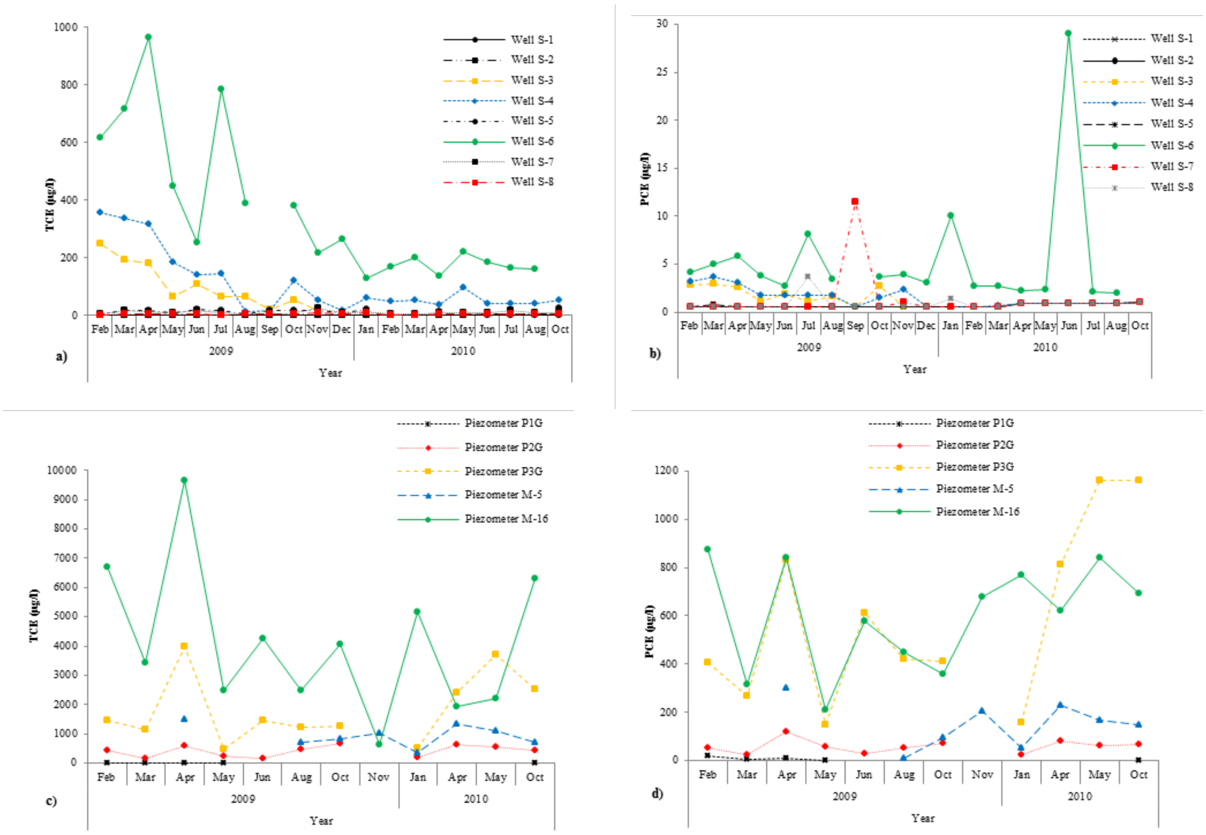

Figure 3: Concentrations of: (a) TCE and (b) PCE in wells, and (c) TCE and (d) PCE in piezometers in the vicinity of the waterworks.

POTENTIAL FOR PRB TECHNOLOGY

Success or failure of a PRB depends on the ability of the barrier to (i) intercept the contaminant flow and provide an appropriate residence time; (ii) promote remediation *in situ* so that contaminants are reduced to target concentrations within a reasonable time scale. The feasibility study was performed to identify possible constraints that may impede the barrier installation or may limit its performance. The source-pathway-receptor sequence confirmed the risk the current contamination represents to the aquifer and evidenced the necessity for remediation measures to be applied to the site. NA as a remediation option showed limited potential, thus an alternative or complementary technology for the site is required. The amenability of TCE and PCE treatment by PRB technology has been widely demonstrated with initial concentrations higher than those found at Nowa Dęba and achieving contaminant removals up to 99% (some examples can be found in Muegge 2008; Gavaskar et al. 2002; Vogan et al. 1999; Borden and Lee, 2001; Kiilerich et al., 2000).The initial characterization of the site indicates that the aquifer depth does not represent a constraint that may require expensive construction methods. Any underground structure or geological feature were identified that may impede the installation of the barrier or interfere with the trenching or excavation. Groundwater velocity of the aquifer is considered manageable, and it may not signify an increase in costs by the construction of a barrier with high thickness to achieve desired residence time. Additionally, the stratigraphy of the aquifer at the Nowa Dęba site with a low-permeability clay layer at the bottom makes it optimal for the installation of the barrier to prevent contaminant underflow. Treatability tests need to be performed to determine specific contaminants removal rates by selected reactive materials. Retention times, production and degradation of byproducts, as well as time to achieve target concentrations need also be assessed during treatability tests. These tests accompanied by groundwater flow and contaminant transport numerical modeling will help to decide upon the appropriate location of the barrier and will allow for predicting its long term behavior.

CONCLUSIONS

Concentrations of TCE and PCE in groundwater extracted by the waterworks are much higher than the limit threshold values for drinking water quality, thus, remediation measures need to be considered.Natural attenuation as a remedial option showed a limited potential, thus an alternative or complementary technology need to be considered. Preliminary site characterization proved that there are not constraints for installation of the permeable reactive barrier system to reduce TCE and PCE concentrations to target values.Further studies including the selection of reactive materials suitable for PRB that are capable of treating chlorinated solvents need to be undertaken. Additionally, a detailed groundwater flow and transport model needs to be constructed for the final design of the barrier.

ACKNOWLEDGEMENTS

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WATERDISS 2.0, Dissemination and uptake of FP water research results (FP7 - ENV – 2010)

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The implementation of the Water Framework Directive is not a 'Business-as-usual approach', and needs new knowledge and know-how. In this sense, it is demonstrated that the actual knowledge connection between research and policy is not efficient. WATERDISS aims at adding an intermediate step after research, like a marketing team in the industry. This 'step-further' will be developed closely with the stakeholders, by involving them within a social network, the European Water Community, for promoting exchanges. WATERDISS develops a process tailored to every typology of target groups, which can be differenced into the following groups:

- The practitioners group, with decision-makers (basin authorities, municipalities), and 'doers', (suppliers of technologies, consultancies, operators).
- The researchers group, as individual knowledge holders and at international level, as members of European consortiums, and at national level, as member of the research funding bodies.

The project activities involve the collection of information on about 60 water-related FP6/FP7 research projects outputs, the analysis of their potential future uptake in close collaboration with the research teams and the design for each project of an Individualised Dissemination Strategy. The transfer of outcomes to the targeted stakeholders is supported by both Web 2.0 features and events designed for specific audiences.

Keywords: Water Framework Directive⁄knowledge ⁄ technology transfer ⁄ Dissemination

Biodegradation of Explosives: From the Laboratory Tests to the Field Pilot-Scale Application

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ABSTRACT: In-situ biodegradation was identified as a cost-effective and sustainable remediation option to clean-up sites contaminated by various contaminants (petroleum hydrocarbons, chlorinated hydrocarbons). In the presentation results of the research project focused on development of in-situ anaerobic degradation process for remediation of soil and groundwater contaminated with 2,4,6-trinitrotoluene (TNT) and other nitrated toluens will be discussed. These toxic and recalcitrant chemical compounds may be present in the military areas or in explosives production facilities. Since the TNT biodegradation is assumed to be mainly of co-metabolism character, laboratory tests in batch and in column design were performed to choose the most suitable organic substrate, which will be consumed by autochthonous microorganisms, while TNT will be degraded under anaerobic conditions. Whey cheese was found to be the most suitable organic substrate compared to ethanol and acetate. Effect of the substrate concentration on the biodegradation rate and possibility to enhance biodegradation by addition of an anaerobic sludge from wastewater treatment plant were evaluated during the laboratory experiments. During the first pilot test, three repeated injections of whey cheese suspension into the sandy aquifer were performed during 10 months period. In total, approximately 5 m^3 of whey was used. Decrease of TNT concentration in groundwater from 5 mg/l down to concentration less than the detection limit of the used laboratory method (0.1 mg/l) was detected in all injection wells while concentration of TNT biodegradation products (4A-2,6DNT, 2A-4,6DNT and 2,4DA-6NT) increased significantly.

INTRODUCTION

2,4,6-Trinitritoluene (TNT) is a nitroaromatic compound, formed by an aromatic ring symmetrically surrounded by three nitro groups. TNT is a recalcitrant, xenobiotic and ecotoxic in nature environment. TNT has been used as an explosive compound throughout the world for military as well as engineering purposes since the beginning of the 20th century. The number of sites (production and storage facilities, military firing ranges) contaminated with TNT is estimated to be in order of first thousands in Europe and USA (Adrian 2003). In this paper are described results of the research project focused on remediation of soil and groundwater contaminated with TNT by means of in-situ biodegradation technology. Despite the fact it was reported in the literature that TNT undergoes aerobic microbiological degradation (Nunez 2001), this project was focused on research of TNT biodegradation under anaerobic conditions, since the aerobic biodegradation is often incomplete with condensed dead-end products as azoxynitrotoluenes. Given the high oxidation state of the TNT molecule, which is caused by the presence of electronegative nitro groups, TNT is highly susceptible to reduction processes, which are more complete under anaerobic conditions. It is understood that the main mechanism of TNT degradation cometabolism (Nunez, 2001), during which organic substrate other than TNT is consumed by fermentative microorganisms for energy production. High substrate consumption yields to overproduction of reduced electron carriers, which are regenerated (oxidized) meanwhile TNT is being degraded (reduced). Simplified biodegradation pathway of TNT is shown on Figure 1 where nitro groups of TNT are sequentially reduced forming aminodinitrotoluenes (2-A-4,6-DNT and 4-A-2,6-DNT), diaminonitrotoluene (2,4-DA-6-NT) and triaminotoluene (TAT). TAT undergoes deamination process, which yields to p-cresol, which is finally being reduced to toluene. Toluene can be further biodegraded under anaerobic as well as anaerobic conditions. Formation of TAT is not very often reported in the literature (Hawari, 2000). It is supposed that TAT reacts with organic substances present in the soil (e.g. humic acids) forming larger molecules and it is stabilized in the soil matrix without any negative ecotoxicological effect.

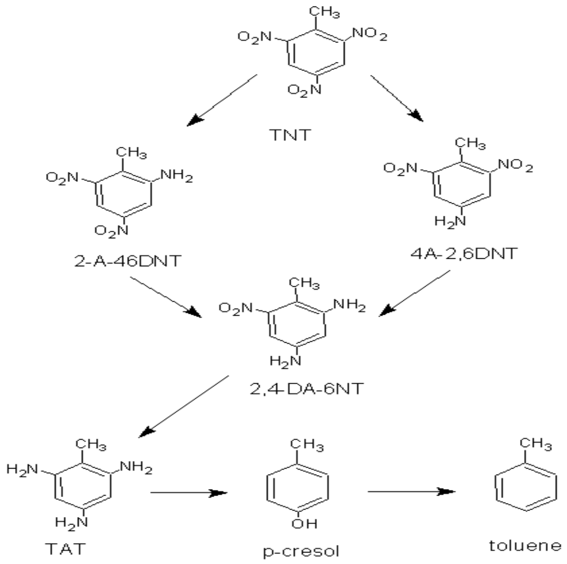

Figure 1: Simplified biodegradation pathway of TNT under anaerobic conditions.

EXPERIMENTAL SECTION

LABORATORY EXPERIMENTS

An overall goal of the laboratory experiments was to find the most suitable organic substrate to be consumed by consortium of microorganisms present in the soil and groundwater originated from the site contaminated with TNT and the optimal concentration of the organic substrate. Three sets of laboratory experiments where performed: (1), benchscale tests in 500 ml bottle, (2) batch scale tests in 30 L barrels and (3) column tests. The methodology of individual experiments is described in the chapters below

Benchscale Tests

In the first stage of experiments, three organic substrates (acetate, molasses and cheese whey) were tested at one concentration level of 0.5% (weight of substrate per weight of soil). The initial TNT concentration was 11.0 mg/kg in soil and 13.8 mg/l in groundwater. For each substrate modification with addition of anaerobic sludge from the municipal wastewater treatment plant was also prepared. Experiments were performed in triplicates in 500 ml bottles, into which 125 g of contaminated soil together with calculated mass of the substrate was placed and then the rest of the bottle was filled with contaminated groundwater without any head-space.

Batch-scale Tests

Batch-scale laboratory experiments were conducted in larger scale to confirm results of the benchscale experiments and to assess substrate concentration effect on the biodegradation rate. Only the best organic substrate determined during the benchscale experiments (cheese whey) was used during this test at three concentrations (0.25%, 0.5% and 1%) when contaminated soil (4 kg) and groundwater (20 L) was placed into 30 L closed plastic barrels equipped with special ports for soil sampling to avoid contact of the tested material with oxygen. The initial TNT concentration in soil was 9.07 mg/kg and 12.5 mg/l in groundwater. Barrels were left at controlled temperature of 10°C. The testing period was 4 months. Only soil was subject to sampling during the batch-scale tests.

Column Tests

Finally, column tests were performed to confirm results of the previous experiments in design, which more reflects the real conditions in the field. The column experiments were operated in two equal parallel columns made of Plexiglas, with height of 1 m and 20 cm in diameter.. The columns were packed with the original contaminated soil mixed with sand in ratio 1:1 to increase its permeability. The flow rate of contaminated groundwater through the column was 1 ml/min, which corresponds to the volume retention time of 5.2 days. Initial TNT concentration of contaminated groundwater at the column was determined repeatedly during the test, initial TNT concentration in soil was 4.77 mg/kg. The cheese whey as a substrate was mixed with groundwater in the tank A, concentration of used whey was 5% (v/v). Fresh mixture was prepared every 24 hours. The column tests were conducted for two months

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PILOT FIELD-SCALE APPLICATION

Two pilot field-scale applications were performed in the former production facility where explosion of the TNT production unit occurred in 1950´s. After the explosion, the facility was not reconstructed and was left unused. Apart of TNT, subsurface at the facility is impacted by toluene and complex mixture of mononitrotoluenes and dinitortoluenes isomers, in which 2-nitrotoluene and 2,4-dinitrotoluene dominate. Certain areas of the facility are characterized by low pH close to 4 and elevated concentration of sulphates and nitrates in order of hundreds of mg/l, most likely caused by the leakage or the nitration mixture (nitric and sulphuric acid) in the past.

A shallow aquifer is related to fine-grained sandy sediments, occasionally interlaid with clayey layers. The groundwater table can be encountered at the depth of 1 – 2 m below ground surface (bgs.). The shallow aquifer is isolated from deeper layers by the impermeable siltstone layer located at the depth 3 - 4 m bgs. The thickness of the aquifer is low, approximately 1 m in average. The velocity of the groundwater flow is very low due to low groundwater table slope, which is approximately 2 cm/m.

Both pilot tests consisted of repeated application of the cheese whey solution (30%) to the subsurface via injection wells and monitoring of groundwater affected by whey decay. The groundwater monitoring was performed regularly every first and third month after the whey injection. Groundwater was analyzed for broad range of constituents (TNT and its biodegradation products (4A-2,6DNT, 2A-4,6DNT and 2,4DA-6NT), TOC, basic cations and anions including final electron acceptors, total nitrogen, density of microbial population (anaerobic and facultative anaerobic bacteria, psyhrophile bacteria and sulphates reducing bacteria) and ecotoxicity measurement based on decrease of bioluminescence by bacteria *Vibrio fischeri*. In selected wells, concentrations of dissolved gases (methane, ethane, hydrogen sulphide) and concentration of simple organic acids (acetate, propionate, lactate and butyrate) were also monitored.

The First Field-Scale Pilot Application

The first pilot test (Pilot I) was initiated in June 2011 in the area characterized by low groundwater contamination with TNT in order up to 10 mg/l. Since then, three whey injections were performed (June 2011, October 2011 and April 2012). In total, 4,780 litters of whey solution were applied to the subsurface within the framework of the Pilot I. The layout of Pilot I is shown on Figure 2.

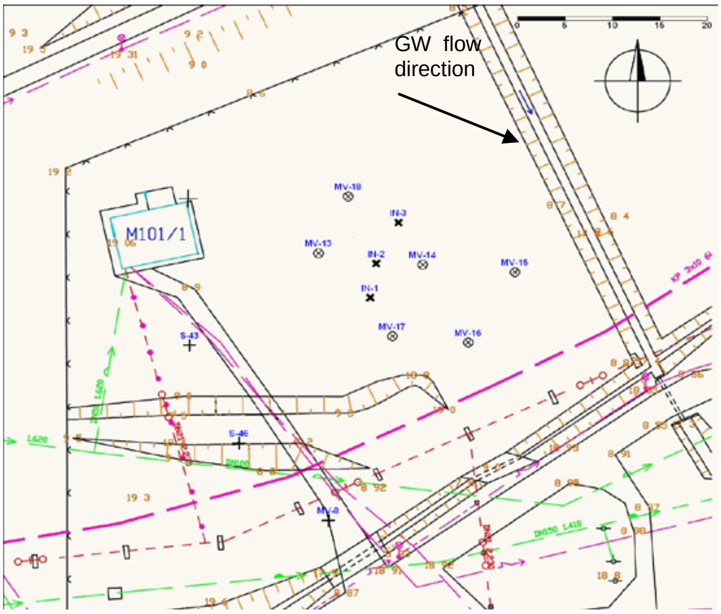

Figure 2: Layout of the first field pilot-scale application of cheese whey for TNT biodegradation, with marked injection wells (☐), monitoring wells (⊗) and other wells (+), not used in the field test

RESULTS

LABORATORY EXPERIMENTS

Benchscale Tests

Observed decrease of TNT concentration in tested groundwater during the benchscale tests is presented in graphical form on Figure 5 below.
The results of benchscale tests showed that the cheese whey is the most suitable organic substrate for TNT biodegradation in comparison with other tested organic substances (molasses and acetate). TNT concentration in tested groundwater decreased to 7% of the initial concentration after 35 days. No significant improvement of TNT degradation rates was achieved by addition of an anaerobic sludge. Nevertheless, very good results were obtained when molasses was used as a substrate with addition of anaerobic sludge, when TNT concentration in tested groundwater decreased to values close to the detection limit of the laboratory method (0.1 mg/l).

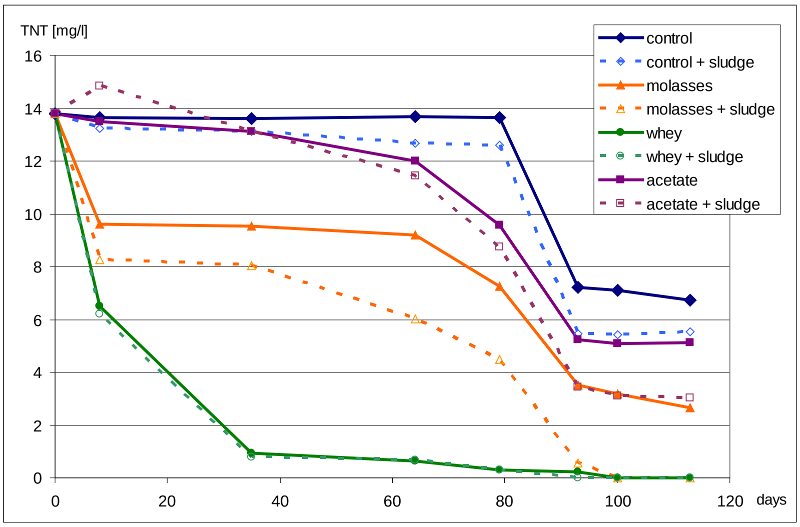

Figure 3: Progress in TNT concentration in tested groundwater [mg/l] during the benchscale tests with molasses, cheese whey and acetate as organic substrates at one concentration level with and without addition of anaerobic sludge in comparison with control

Batch-scale Tests

Decrease of TNT concentration in tested groundwater during the benchscale tests are presented in graphical form on Figure 4.

No significant differences in TNT biodegradation rate were detected with regards to the concentration of the organic substrate (cheese whey). The lowest tested concentration of cheese whey (0.25%) was sufficient to achieve significant removal TNT reaching approximately 8% of the initial concentration after 87 days.

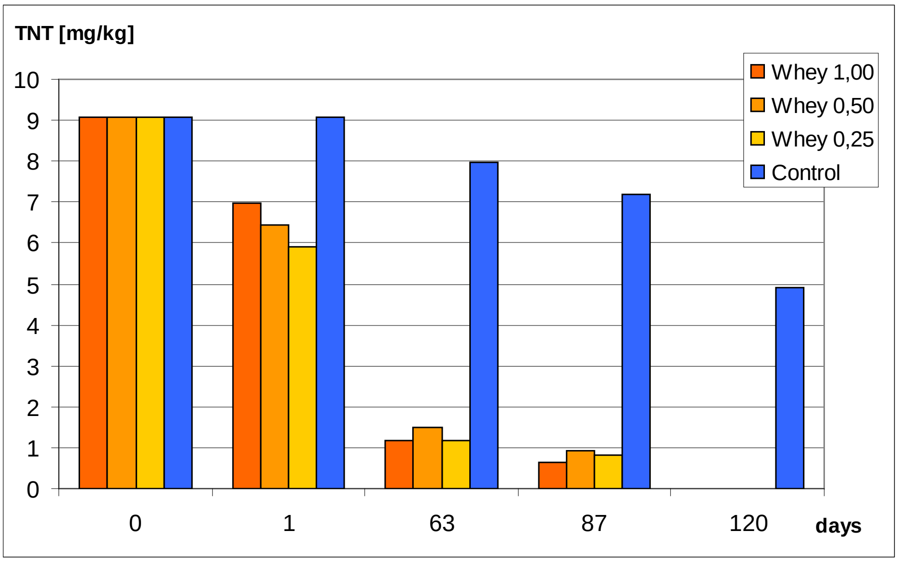

Figure 4: Progress in TNT concentration in tested soil [mg/kg] during the batch-scale tests with cheese whey as organic substrates at three concentration levels (0.25%, 0.50% and 1.00%) in comparison with control

Column Tests

Experiments with though flow column showed that microbial activity was sufficient to completely utilize groundwater contaminated with TNT in concentration around 12 mg/l at inlet already after 1 month of operation. Similar results were obtained for other contaminants present in the groundwater (nitrotoluenes and dinitrotoluenes). Surprisingly, the detected concentrations of TNT biodegradation products (4-A-2,6-DNT and 2-A-4,6-DNT) were higher at the inlet to the column than at the outlet, suggesting that these compounds undergo further transformation to not identified products.

Table 1: Concentration of contaminants in tested water (mg/l) flowing into the column (INLET) and out of the column (OUTLET) including TNT and its biodegradation products 4A2,6DNT, 2A4,6DNT and 2,4DA6NT

Date	**Sampling Point**	**2-nitrotoluene**	**3-nitrotoluene**	**4-nitrotoluene**	**2,6-dinitrotoluene**	**2,4-dinitrotoluene**	**TNT**	**4A2,6DNT**	**2A4,6DNT**	**2,4DA6NT**
26.8.2011	**INLET**	2.99	0.66	0.77	6.87	8.65	12.73	0.32	0.36	<0.1
	OUTLET	0.71	0.42	0.31	7.23	6.79	12.38	0.4	0.44	<0.1
26.9.2011	**INLET**	0.75	0.5	<0.1	7.53	7.86	13.68	0.34	0.36	<0.1
	OUTLET	0.23	<0.1	<0.1	<0.1	<0.1	<0.1	0.17	0.16	0.39
19.10.2011	**INLET**	0.31	0.44	<0.1	7.43	5.82	12.11	0.45	0.4	<0.1
	OUTLET	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

PILOT FIELD-SCALE APPLICATIONS

The First Field-Scale Pilot Application

A cross section profile of TNT concentration in groundwater is presented on Figure 5. The well MW-13 represents the groundwater flowing into the injection zone, the well IN-2 is located within the injection zone and the wells MW-14 and MW-15 are located down the groundwater flow from the injection zone. It is evident that TNT concentration decreases significantly in time to the detection limit of the used laboratory method (0.1 mg/l) mainly in the injection well IN-2. However, significant decrease in TNT concentration can be observed also in the nearest monitoring well MW-14. Concentrations of TNT metabolites in groundwater reached level of the first mg/l. The highest concentrations were detected in the well MW-14 in the period after the second injection form November 2011 to March 2012 (4-A2,6-DNT: 3.38 mg/l, 2A4,6DNT: 1.87 mg/l and 2,4DA6NT: 1.98 mg/l).

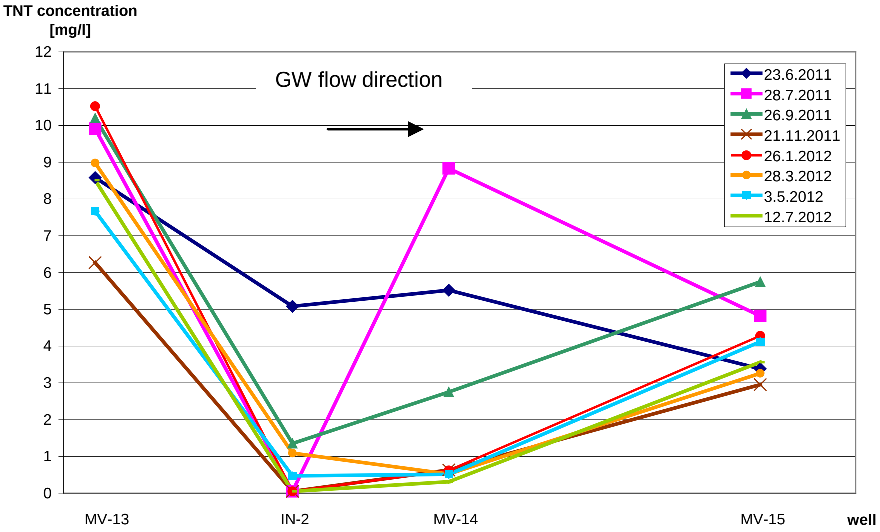

Figure 5: Cross section profile of TNT concentration in groundwater [mg/l] of wells MW-13, IN-2, MW-14 and MW-15

CONCLUSIONS

Results of this project showed that the anaerobic in-situ biodegradation is a feasible remediation technology for treatment of soil and groundwater contaminated with TNT in concentrations up to 10 mg/l (10 mg/kg). The feasibility was verified by the pilot scale application in field conditions. Relatively cheap organic substrate – cheese whey, which is a waste product of the food industry was determined to be the most suitable substrate for TNT reduction among other tested organic substances (molasses, acetate). No significant dependence of TNT biodegradation rate on the used concentration of the organic substrate was observed during the laboratory experiments. Addition of the anaerobic sludge did not improve TNT biodegradation rate significantly. Further work within the framework of this project will be aimed on treatment of the more contaminated material, identification of the TNT biodegradation metabolites and ecotoxicological aspects of the anaerobic biodegradation.

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Performance assessment of the bioremediation of a TCE source zone

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The SABRE project investigated the bioremediation of a zone of TCE DNAPL in a controlled field experiment. The source zone was contained in a cell 30 m long, 4 m wide and 6 m deep. Biodegradation was stimulated by the addition of a commercial edible oil product as a carbon source, SRS™ (Terra Systems, Inc., Wilmington, DE) and by the addition of specialized anaerobic microorganisms, KB-1™ (SiREM Guelph, Ontario, Canada), a commercial dechlorinating bacterial consortium containing *Dehalococcoïdes ethenogenes*. The cell was monitored in two transects of multilevel samplers, as well as a number of other monitoring points, with five sampling rounds over the two year experiment. The expected outcomes of the biostimulation were that there would be (1) reduced discharge of TCE, (2) increased production of daughter compounds, and (3) increased dissolution of TCE from the source.

Our new geostatistical analysis (Cai et al. 2012, *Ground Water,* doi: 10.1111/j.1745-6584.2012.00916.x) was used to estimate mass discharge of TCE and its daughter compounds through the first transect of monitoring wells which formed a flux monitoring fence. This approach took account of the spatial variability of concentrations and groundwater velocities. Conditional simulation was used to take into account the uncertainty of these variables and to produce uncertainty estimates on the mass discharges.

Analyses of dissolved parent and daughter compounds demonstrated that the engineered bioremediation has elevated the degradation rate of TCE, resulting in a two-thirds reduction in the TCE mass discharge from the source zone. The biologically enhanced dissolution of TCE was not significant (~ 5%), and was less than expected. However, the discharges of the daughter products cis-1,2, dichloroethene (cDCE) and vinyl chloride (VC) increased, probably because of the rapid transformation of TCE from the source zone to the measurement transect. This suggests that enhancing the biodegradation of cDCE and VC will be crucial to successful engineered bioremediation of TCE source zones.

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

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ABSTRACT: In 2005, a 200 m long zerovalent iron (ZVI) barrier was implemented at a site in Belgium to contain a chlorinated aliphatic hydrocarbon plume. The ZVI barrier (30 cm thick) consists of 20% fine ZVI and 80% of coarse sand, and 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, several 40° angled core samples were taken comprising (1) aquifer 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 in 2-4 cm slices under anaerobic conditions. A first core was sacrificed to determine the porosity profile and characterize the minerals formed. The porosity was found to be at least 33% in the whole ZVI transect, which was either similar or higher than the porosity of the surrounding aquifer material. Two core samples (one taken in the contamination plume, and one at the edge of the barrier outside the contamination plume) are being used for characterisation of the microbial population on DNA and RNA level, using quantitative PCR and 16S tag-pyrosequencing. Further, the reactivity of the barrier material was compared to the reactivity of the original barrier filling via batch degradation experiments. The tests proved the barrier material was still reactive.

INTRODUCTION

The use of granular zero-valent iron (ZVI) for in-situ remediation of groundwater contaminated with chlorinated solvents is a proven technology (Matheson & Tratnyek; 1994; Gillham, 1996; Gavaskar, 2000). Chlorinated solvents like tetrachloroethylene (PCE) and trichloroethylene (TCE) can be degraded abiotically by reductive dehalogenation in the presence of zerovalent metals like iron: ($Fe0 + RCl + H^+ \text{ ---->} Fe^{2+} + RH + Cl^-$). However, secondary mineral precipitation in ZVI systems, has been shown to reduce their reactivity and efficiency (Schoups et al., 2007). Also interactions between biological and chemical processes in ZVI barrier systems may influence the long-term performance of the passive technology both in a positive and negative way (Van Nooten et al., 2007). ZVI barriers are mostly designed for abiotic degradation of pollutants, but for several years already, it is known that bacteria are active in the presence of ZVI (Van Nooten et al, 2010; Philips et al;, 2010; Muchitsch et al, 2011;). More general, the exploitation of combined biological and physiochemical processes is not yet optimised. The parameters that are crucial to understand and predict the performance of these combined processes are not yet completely described.

Within the FP7 project AQUAREHAB, angled core samples were taken across the ZVI-barrier and characterised in detail in respect to porosity, minerals, degradation capacity and microbial population. The aim was to increase our understanding of processes influencing the life-time of ZVI-barriers, and to derive parameters to make predictions in the future.

SITE INFORMATION & CORE SAMPLINGS

At an industrial site in Belgium, a groundwater contamination plume is present in the subsurface. In 2005, a 200 m long zerovalent iron (ZVI) barrier was implemented at a site in Belgium to contain a chlorinated aliphatic hydrocarbon plume. The ZVI barrier (30 cm thick) consists of 20% fine ZVI and 80% of coarse sand, and 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, five 40° angled core samples were taken (see figure 1) comprising (1) aquifer upstream of the ZVI-barrier, (2) a transect of the ZVI-barrier as well as (3) aquifer material just downstream of the barrier (figure 1). After sampling, the core samples were frozen immediately and afterwards stored at -80°C. The analyses planned on these core samples comprise: porosity measurements, characterization of precipitates, and of the microbial community composition across the ZVI-barrier and the nearby aquifer. Also the reactivity of the ZVI was evaluated.

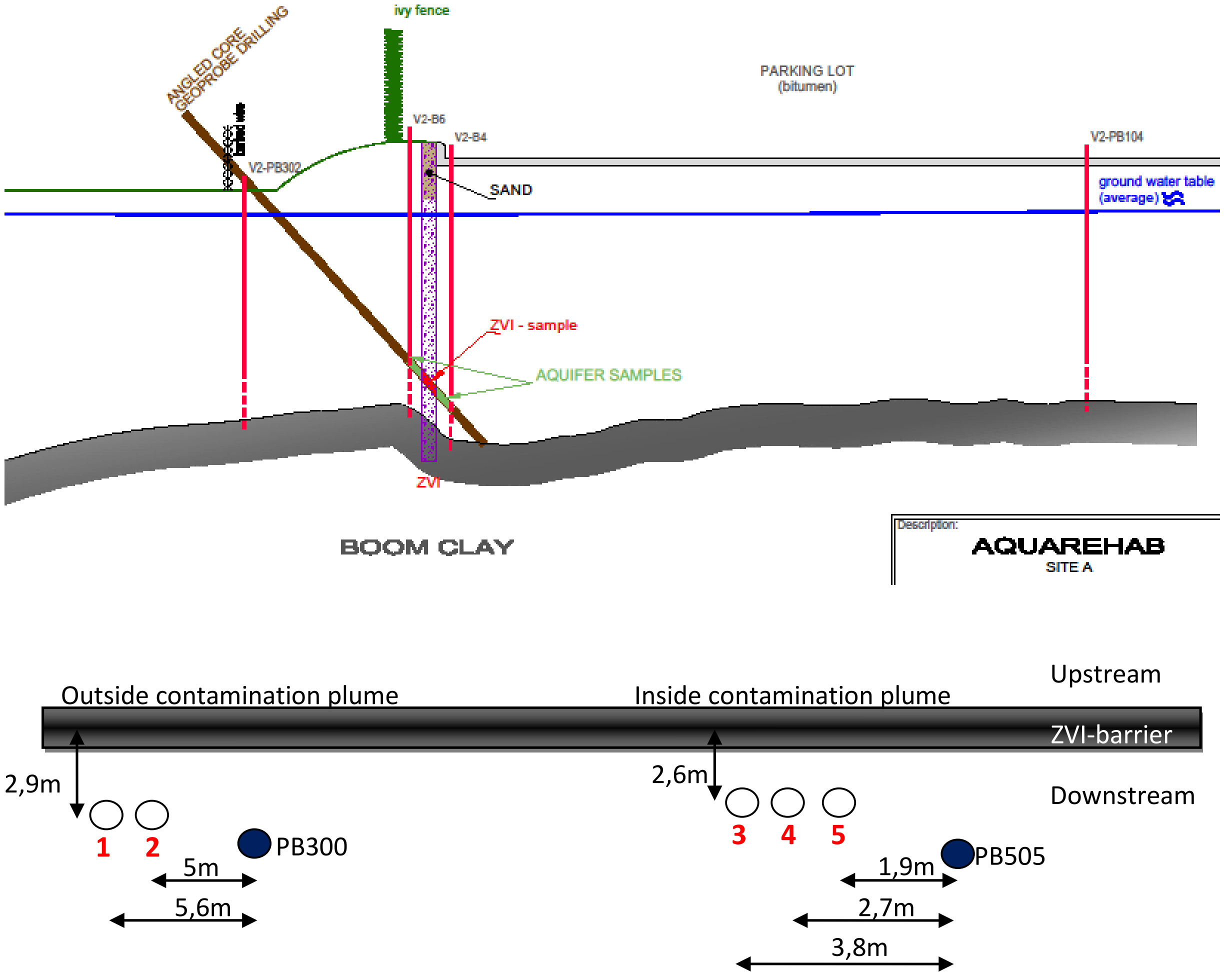

Figure 1: overview of angled core samples taken from the ZVI-barrier at site A

RESULTS

Porosity measurements

Method: Core sample number 5 (inside contamination plume) was used for porosity measurements and analyses of precipitates. The frozen core was cut in to small pieces of 2 cm each. The internal diameter is 3 cm. Each section was weighed and then dried under anaerobic conditions. Porosity data were obtained by the loss of weight and the volume per section. Results are shown in Figure 2

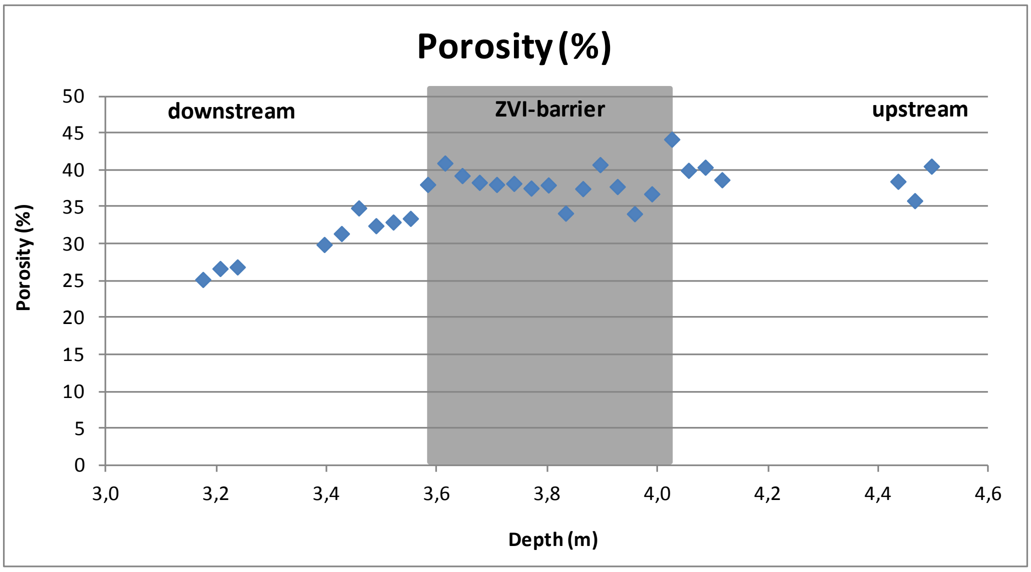

Figure 2: Overview of porosity from angled core sample taken from the ZVI-barrier at site A

Results: During core sampling, the aquifer material is being compressed somehow, which complicates the interpretation of the results. However, a porosity between 35% and 40% was still measured in the ZVI-barrier, indicating that the porosity in situ is at least this number. These results show that the ZVI barrier is still very permeable.

Characterisation of minerals

Method: The core samples were defrosted and homogenized. Two/three successive sections were mixed together to get sufficient sample to be pre-treated for microscopic analysis (SEM-EDX and EPMA). Approximately 10 g subsamples were taken from the mixed sections.

Results: During XRD analyses, the silica on the ZVI-particles did interfere with the XRD measurements, making identification of the minerals present difficult. Via SEM-analyses, elements could be identified and EPMA revealed a number of different phases mostly containing iron. However, without data on the present minerals, it is difficult to come to detailed conclusion related to clear profiles along the barrier. The higher amount of precipitates that can be expected at the entrance of the ZVI-barrier, were not confirmed by the results. Additional analyses are ongoing.

Characterisation of the microbial community in the ZVI-barrier

Method: Core sample number 2 (outside contamination plume) and 3 (inside contamination plume) were used for microbial analyses. Each frozen core was cut into small slices of 2 cm thickness. Out of each section 2 g sample was taken for DNA and 2 g for RNA. 2 ml RNA later was added to the RNA samples and all samples were stored again at -80°C. On a selection of the samples, DNA extraction was performed according to the protocol described by Hendrickx *et al* (2005). Further, also RNA was extracted. The extracted DNA and RNA samples were subsequently prepared for 16S-tag Pyrosequencing and quantitative PCR with specific primers.

Results: Via Quantitative PCR with specific primers, *Dehalococcoides* sp. were found present and active, and *vcr*A was identified as a dominant reductive dehalogenase. The first output of the DNA pyrosequencing data shows the presence of Proteobacteria, Chloroflexi, Acidobacteria and Actinobacteria as dominant organisms in most of the samples. Figure 4 gives more details on the composition within the Chloroflexi as detected in the different section from the angled core (upstream, within and downstream of the ZVI barrier). Within the ZVI-barrier and in the adjacent aquifer sections, a clear shift in microbial population is being observed. The Anaerolineae seem to be stimulated by the ZVI.

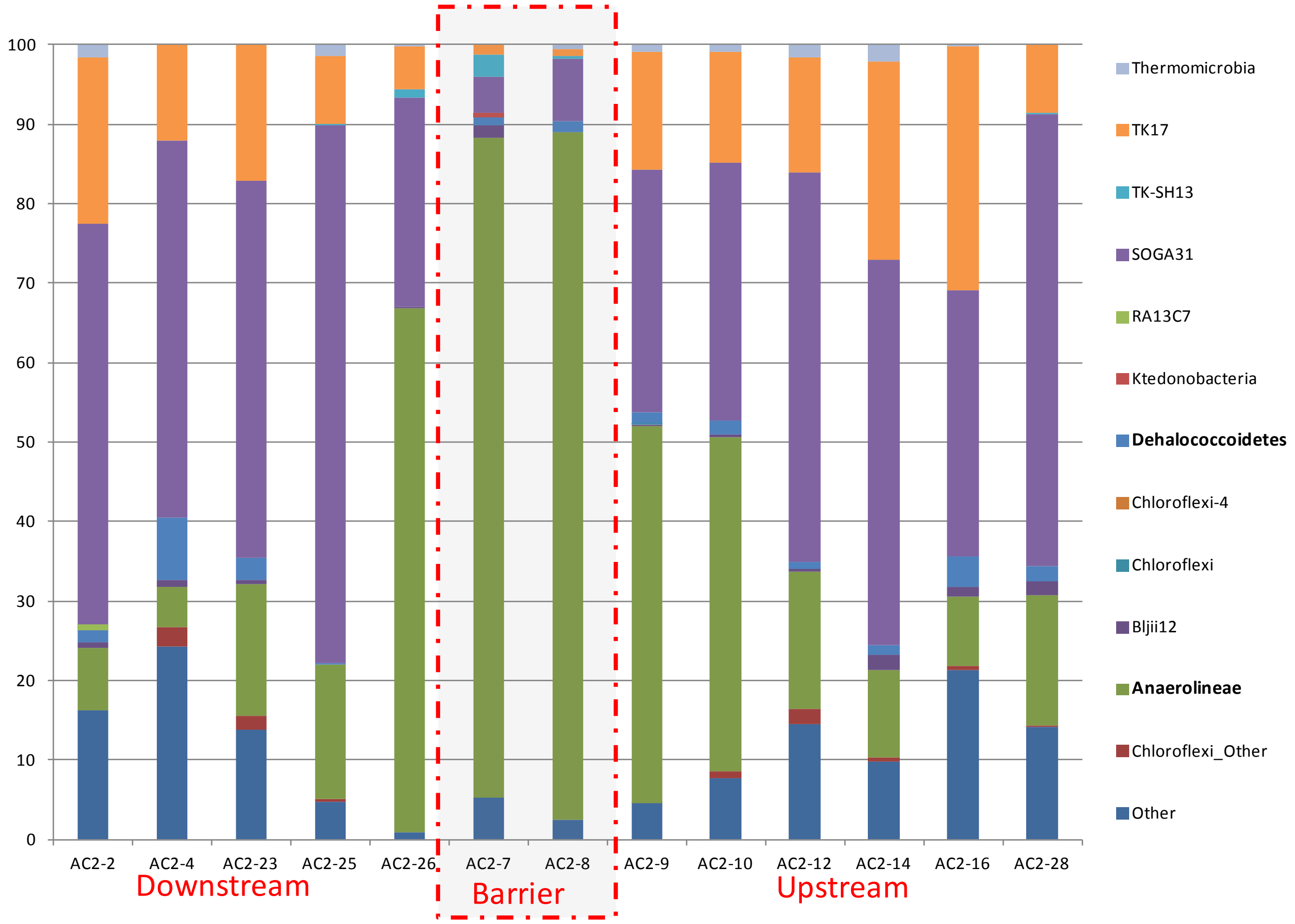

Figure 3: 16S tag-pyrosequencing results for composition of the Chloroflexi in the angled angled core sample taken from the ZVI-barrier at site A (core 2).

Degradation experiment

Method: The test was set up in 37 ml bottles with Teflon lined crimp-caps. Each bottle contained 2 g of ZVI (from several places in barrier), 20 ml simulated anaerobic groundwater spiked with 10 ppm TCE. The test was set up under anaerobic conditions and was incubated at 12°C (static). At several time points the remaining concentrations of CAHs in the bottles were measured by GC-FID with headspace injection. Two extra controls were set up to evaluate the effect of the freezing. Three fractions retrieved from within the ZVI-barrier were tested:

- Fraction 1: downstream part of ZVI-barrier
- Fraction 2: middle of ZVI barrier
- Fraction 3: upstream part of ZVI barrier

Results: The evolution of the TCE-concentration is given in figure 4. The following general conclusions were made:

- Freezing of the ZVI-samples has minor impact on the reactivity
- The samples from the ZVI-barrier at site A did not lose their reactivity as TCE was degraded completely in a similar way (or even better) than the ‘fresh’ sand/ZVI mixtures
- No clear difference was observed in the reactivity of the samples taken in the different parts of the ZVI-barrier (upstream part, middle part, downstream part)
- The iron-sand mixtures seem slightly less reactive than the iron without sand

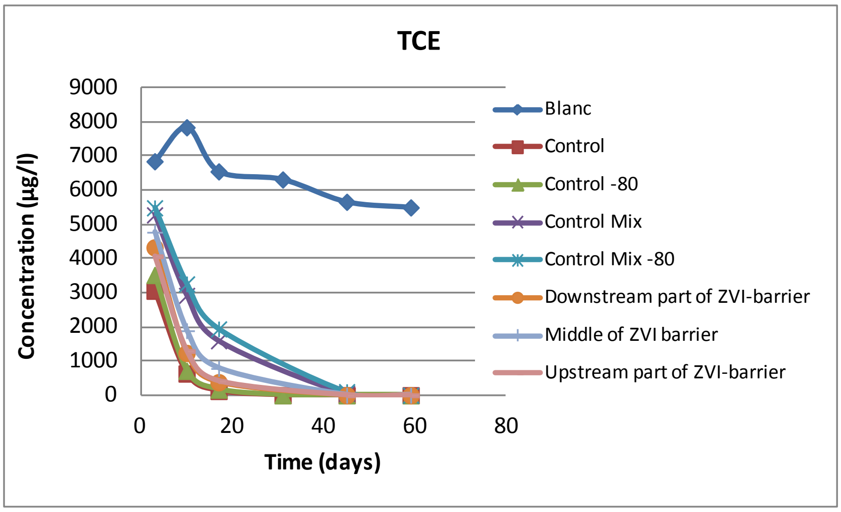

Figure 4: TCE degradation capacity of ZVI-iron mixtures taken from different parts from the ZVI barrier.

CONCLUSIONS

Results were described of angled core samples that were taken across a six year old full scale ZVI-barrier in Belgium and that were characterized. It was concluded that (1) the ZVI-barrier was still very permeable causing no decreased performance due to clogging problems; (2) The ZVI-barrier was still reactive – no decreased reactivity was observed in comparison with 'fresh' material, and (3) A diverse microbial population was present and active in the barrier – also Chloroflexi, which are known to comprise CAH-degraders.

ACKNOWLEDGEMENTS

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a NSR tecHnologY: ISTD trEATment of LNAPL layer contaminated with CVOC solvents

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Key words: NSR, LNAP, CVOC, ISTD, thermal treatment, thermal conduction, distillation, desorption.

INTRODUCTION

Ford First Aquitaine Industry called on TPS to use the NSR remediation technology on its Blanquefort's site near Bordeaux (France) to treat the LNAPL engine oil contaminated by CVOC, such as PCE and TCE products.
The NAPL is spread over more than 4000m^2. The area of the contaminated zone with the CVOC is 300m^2. The height of the LNAPL layer is 2m and the groundwater is located at 4.5m depth.
The CVOC contamination is coming from a cleaning operation and due to a leakage from a unit, which contained solvents. This unit was dismantled in 2005. The higher concentration of CVOC detected in the LNAPL layer is 145g/kg of oil.
The aim of the job is to tackle the source mainly represented by the floating phase containing CVOC. The full-scale treatment target is a 99% rate of CVOC reduction in oil. The works are planned during a long stoppage period of the plant's activity, required for maintenance and modernization purposes. The work comprises three phases:

- Laboratory treatment test;
- NSR Pilot test over 17m^2;
- Full-scale NSR-City© treatment over the total contaminated area (approx. 300m^2).

The whole treatment works are expected to take place between March and June 2012.

NSR PROCESS

NSR 'New Soil Remediation' is a new technology suitable for all materials and soils contaminated by various kinds of organic pollutants. This technology is based on a simultaneous application of heat by conduction and vacuum in the soil. The NSR process consists of installing stainless steel pipes in the soil, in which hot air is circulated. Each heating pipe is equipped with an individual gas burner and close to it a perforated tube is used to collect the contaminant vapour.

LAB TEST DESCRIPTION AND RESULTS

Approximately 250ml of polluted oil was poured in a round-bottom glass flask and heated by electric heater at different temperatures and times, and then gently stirred. Vapor produced in the flask was extracted by a vacuum pump and condensed.
The initial and final concentrations of CVOC were measured in the oil by AGROLAB's laboratory (Germany).
Due to the high affinity of CVOC and oil, a minimal temperature has to be reached to ensure the distillation of it out of oil. Undetectable low levels are reached rapidly under 24 hours at temperature equal or higher than 100°C.

PILOT AND FULL-SCALE DESCRIPTION AND RESULTS

The NSR pilot test was carried out in a hexagonal grid with six heating pipes (4.5m in length) and one extracting vapor tube in the center of hexagon. The distance between tubes is 1.8m. The target temperature in the LNAP layer was 100°C (see lab test results above). During the pilot test, off-gas was treated with a condensation VOC treatment system. The target temperature of 100°C was reached after 20 days of thermal conductive heating.

The analysis results of CVOC in oil show that more than 55% of CVOC was removed from oil after 20 days of heating. The distillation and desorption rates of CVOC were influenced by LNAP extraction and resultant recharges into the TTZ.

The NSR pilot test demonstrated that ISTD could meet all final remedial goals for the full- scale CVOC. The full-scale ISTD treatment will commence in June 2012

Session 8
Rehabilitation technologies for Metals

Oral presentations

Stability of metal precipitates formed after in situ bioprecipitation induced by sulfidogenesis

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The spreading of trace metals such as zinc (Zn) and cadmium (Cd) in groundwater as a result of mining and metal processing activities is a major problem, threatening drinking-water reserves, destroying ecosystems and adversely affecting many people's health in multiple ways. The treatment of strongly polluted contaminant plumes should generally be given high priority, especially in highly mobile groundwater systems, in order to limit the size of the affected regions and restrict the detrimental effects of these contaminants as much as possible. Traditional pump-and-treat approaches require long-term remediation which is economically not feasible. Moreover, this approach is not sustainable if the metals from the large amounts of toxic waste sludge are not recycled. A promising new alternative has been found in the in situ bioprecipitation (ISBP) process. While the ISBP process has been proven, the main question before implementing this technology in situ, in the field is whether the formed metalsulfide precipitates are stable under the environmental conditions after ISBP was successful and a few generations later. For two different sites, in situ precipitation by stimulating sulfate reducing bacteria was achieved both at lab scale and in the field for different metals (site 1: Zn, Cd; site 3: Co, Ni). The structure and stability of the formed metal precipitates was studied by a variety of methods both after inducing ISBP in batch tests and in column experiments. Moreover, mesocosm systems installed in the field have been harvested during successful ISBP and are studied for stability in terms of leaching behavior.

The stability of the metal precipitates formed during the batch tests was evaluated by four different methods. On the one hand two wet chemical analyses, i.e., sequential extraction and aquifer analyses by redox treatment under three different atmospheres were applied. Additionally bioavailability under aerobic conditions (BIOMET) was studied for the same aquifer. For site 1, the most appropriate e-donor was glycerol, although lactate-N/P also resulted in efficient metal removal after a longer lag period. Both wet chemical methods proved that ISBP with glycerol as electron donor for both sites formed the most stable precipitates. For site 3 the best results at lab scale in terms of metal removal from the groundwater were obtained when cheese whey or lactate-N/P were used as C-source and e-donor. These biologically induced conditions resulted in efficient removal of cobalt and sulphate. The stability tests, i.e., sequential extraction and the aquifer redox treatment method both indicated that these biotic conditions formed stable precipitates. SEM/EDX performed on the pink precipitates formed on the aquifer in the lactate-N/P condition of site 3 showed that the main elements of the precipitates were Co and S. Results obtained for the column leaching tests for 2 sites also showed stable metal immobilization since no increased metal concentration was found.
Finally, stability of the formed precipitates has been examined in the field by harvesting mesocosm systems containing the original aquifer. These mesocosm systems were installed before starting field tests and remained in situ during ISMP by either glycerol (site 1) or NaLactate injection (site 3) for about 6 months up to 1 year. Results for site 3 showed stable precipitates, in terms of leaching experiments carried out in the lab with 'natural' groundwater not containing any pollutant, although the amount of sorbed Co did result in increased Co concentrations in the effluent groundwater.

Field multi-step calcite and MgO passive system to treat acid mine drainage with high metal concentration

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The Iberian Pyrite Belt (SW Spain and Portugal) contains the highest reserves of pyrite in the world with mining activities dating back to prehistoric times. Once the mining activity is over, polluting discharges can remain for decades or even centuries with no specific responsible entity. In-situ passive remediation technologies are especially suitable for these orphan sites. Calcium carbonate pea-size gravel is the common alkalinity supplier to neutralize acidity and precipitate metals. These remediation systems have been traditionally implemented in coal mines. However, the acid drainages from the Iberian Pyrite Belt contain metal concentrations one to two orders of magnitude higher than those from coal mines and require special designs to avoid quick clogging or passivation (coating) of the grains of reactive material.

To overcome these problems, a Dispersed Alkaline Substrate (DAS) mixed from fine-grained calcite sand and a coarse inert matrix (e.g. wood chips) was developed. The small grains provide a large reactive surface and dissolve almost completely before the growing layer of precipitates passivates the substrate. The high porosity and the dispersion of nuclei for precipitation on the inert surfaces retard clogging. However, calcite dissolution only raises pH to values around 6.5, which is sufficient to precipitate the hydroxides of trivalent metals (Al, Fe), but it is not alkaline enough to remove divalent metals. Magnesium oxide, which hydrates to Mg hydroxide upon contact with water, buffers the solution pH between 8.5 and 10. A DAS system replacing calcite with caustic magnesium oxide has been tested to be very efficient to remove divalent metals (Zn, Cd, Mn, Cu, Co, Ni, Pb) from the water previously treated with calcite.

Heavy Metals Leachability and Associated Risks after ISCO Treatment

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ABSTRACT: With increasing application of in-situ chemical oxidation, it is important to understand how treatments can cause some side-effects deriving into potential damage on the soil properties and functionality. One of these effects is related to the potential leaching/dispersion or chemical modification of metals present in the site under treatment. Chemical treatment of real soil samples contaminated by diesel and chromium was conducted using different oxidants. The impact of ISCO treatment on the soil was tested using leaching tests particularly designed to this goal and sequential extraction tests (modified Tessier procedure) to understand heavy metal mobilization and ecotoxicity tests based on luminescence bacteria *Vibrio fischeri* concurrently. Results of performed experiments have demonstrated that, in some cases, significant concentrations of metals in the soil matrix can be mobilized by chemical treatment and also transformed into harmful species (by speciation analysis). This is particularly critical for chromium, which under oxidative conditions can be transformed into hexavalent species, a highly soluble and toxic species. Performed ecotoxicity tests indicated significant inhibition of luminescence after the ISCO treatment. Surprisingly, the increase of ecotoxicity was detected also in case of samples with low heavy metals content where no metal mobilization occurred. The effect of the increase of absolute concentration of bioavailable total petroleum hydrocarbons could stress bacteria with low heavy metals content. Furthermore, smart-coupling of chemical and biological treatments leads to the reduction of ecotoxicity probably due to further decrease of target contaminants concentrations and also due to the redevelopment of the initial conditions.

INTRODUCTION

Within the FP7 EU project UPSOIL, the mobilization of metals was investigated with a specific focus on understanding ecotoxicological risk.

The remediation is an action for risk reduction, i.e. the goal of remedial measures is to reduce the mass, mobility and/or toxicity of contamination. However, the conditions under which the risk resulted from could be modified by the application of remedial techniques (e.g. the precipitation of minerals could affect the soil permeability or change the chemical composition of groundwater, it could increase metals leachability and as a consequence their mobility and thus enlarging the source or plume zone, etc.). In-situ chemical oxidation (ISCO) could potentially lead to mobilization of toxic metals and thus the fundamental of remedial measures, i.e. reduction of toxicity, may not be reached even the target contamination will be reduced. Therefore, the goal of performed investigation is to incorporate a tool for modelling and predicting the risks for ecosystems and human health associated to the presence of mixed contaminants in the system before the active treatment takes place. Furthermore, as one of the goals within UPSOIL project is to improve smart-coupling of ISCO with in-situ bioremediation, it is especially important to understand this phenomenon and the related risks in coupling the chemical treatment with following bioremediation.

The work described in this document should be useful as part of the feasibility tests to be performed when designing or testing an oxidative remediation approach. Further than the main results or remedial efficiency of the technology (pollutants degradation), the metals mobilization analysis should be a supportive tool for the completion of a successful project design.

The effect of chemical agents at the end of the active treatment was assessed. Thus mobilized metals interaction with the environment can be critical into two different ways:

- Ecotoxicological impact on the soil, groundwater, fresh water, etc.
- Limit the effect of the second biological stage of the smart-coupling, reducing the abilities of microbes to biodegrade the remaining pollution.

EXPERIMENTAL SETUP

In order to verify the theoretical assumption of the metal leaching and/or soil ecotoxicity development after its chemical treatment, experiments comprised the chemical treatment and subsequent laboratory analyses of metals and ecotoxicity tests were performed.

Experimental setup for chemical treatment was based on results from another UPSOIL investigations, where the impact of treatment with a variety of chemical oxidants at a variety of concentrations on soil characteristics was investigated. Prior to and following chemical oxidation heavy metal analyses and ecotoxicity tests using luminescent bacteria *Vibrio fischeri* were conducted. Furthermore, ecotoxicity tests were also conducted following the additional soil treatment by biostimulation simulating the smart-coupling approach.

Chemical treatment tests

Following conditions were applied for chemical oxidation test:

- Liquid to soil ratio (leachant/soil): 5:1
- Duration: 40 days
- Atmospheric pressure
- Shaker table
- Darkness
- Tests performed in triplicates
- Temperature: 20°C
- Post-treatment by repeated centrifuging and washing with distilled water in order to remove remaining oxidant present in the supernatant

Two different oxidants, potassium permanganate and sodium persulfate were used for chemical treatment.

Metals leaching analyses

Total concentration of heavy metals were analysed submitting soil samples to aqua regia digestion. Extracts from this pre-treatment and water samples were analysed by means of ICP-OES.

In addition, sequential extraction has been studied pre- and post-treatment of the samples in order to analyse the changes in the chemical distribution of metals. The modified Tessier approach was used for sequential extraction. This consists of sequential extractions of the same soil sample using leachants of increasing aggressiveness towards the soil matrix, and then, to the metal bond with the soil. In that way it is possible to know how the different metals pools are released under different soil conditions: pH variations, changes in ionic strength, oxidative/reducing environment (e.g. presence of reagents), etc.

Ecotoxicity tests

Ecotoxicity test based on luminescent bacteria *Vibrio fischeri* was performed according to European Standard EN ISO 11348-3 *Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri*. A specific strain of marine bacteria *Vibrio fischeri* is used in this test to determine the toxicity of samples. This bacterium emits light as the result of normal metabolic processes, and light is measured with a standard photodetection device under specific conditions. Reduction of light at the given time (5, 15 and 30 minutes) is taken as a measure of ecotoxicity since it is presumed that any toxic action of substances present in the sample affect metabolic processes of bacteria, and luminescence is inhibited in proportion to the metabolic effect.

Relative inhibition of luminescence after 30 minutes (H30) was used as the appropriate parameter for the evaluation of the ecotoxicity tests performed within this study (higher H30, the higher ecotoxicity of the sample).

Researchers have reported the *Vibrio fischeri* bioluminescence assay as the most sensitive across a wide range of chemicals compared to other bacterial assays (Parvez et al., 2006). However, some studies point out lowered sensitivity to toxic metals (e.g. Fulladosa et al., 2006).

Samples

In order to study the release of heavy metals from soils under oxidative processes for organic compounds degradation, two different typologies were planned:

- *Samples with organic pollution and moderate contents of heavy metals* – two samples W2A and W2B from the demonstration site involved in UPSOIL project in Poland. Samples characterization is compiled in the table 1 below.
- *Samples with organic pollution and high contents of heavy metals* - sample J1 from Hradek (Czech Republic) was chosen attending to the high content of chromium, which under oxidative conditions could turned into hexavalent chromium with the corresponding environmental relevance of this transformation. Sensitivity of chromium in soils submitted to oxidation was key point to be addressed.

Following tables show results of metals analyses and ecotoxicity tests before chemical treatment.

Table 1: ***Characterization of samples W2A and W2B***

Conc. (mg/kg)	W2A	W2B
Sb	<2.0	1.7
As	55	45
Ba	430	320
Cd	1.1	0.33
Cu	31	30
Cr	28	19
Hg	0.12	<0.05
Mo	<1.0	1.1
Ni	17	20
Pb	140	62
Se	3	3
Zn	110	51
TPH	26,550	4,860
H30*	45.3	-0.5

* H30 –relative inhibition of luminescence after 30 minutes (unitless)

Table 2: ***Characterization of Czech sample J1***

Conc. (mg/kg)	J1
Sb	<10
As	<5
Ba	268
Be	1.0
Sn	<5
Cr total	4,770
Cr (VI)	<0.2
Cd	<0.5
Co	6.5
Cu	73.9
Mo	<5
Ni	22
Pb	154
Hg	<0.1
V	8.1
Zn	207
TOC	62.8
H30*	4.0

* H30 –relative inhibition of luminescence after 30 minutes (unitless)

Table 1 shows high contamination of sample W2A with TPH (diesel – the site is the railway depot with locomotive fuelling site) representing the source zone and moderate TPH level in sample W2B taken from the contamination plume area. Sample J1 from the Czech site Hradek is highly contaminated with total chromium up to 4,770 mg/kg but low Cr(VI) (site is a former chromite salts manufacture). Content of heavy metals in Polish samples is relatively low. The results presented in Tables 1 and 2 further indicate low ecotoxicity of samples W-2B and J-1 with relative inhibition of –0.5 % (the bacteria luminescence even slightly increased after 30 minutes of bacteria exposure) and 4.0, respectively. Sample W-2A representing the source zone of diesel contamination shows higher ecotoxicity reaching 45.3 %.

RESULTS

Regarding the oxidative treatments of persulfate and permanganate following results were obtained in the leached fraction at the end of the tests.

Table 3: ***Concentration of metals in leachates samples W2A and W2B (mg/kg) after treatment***

Parameter	W2A-PS	W2B-PS	W2A-PM	W2B-PM
pH	1,4	1,3	9,4	9,5
E^0 (mV)	673	660	209	198
As	68,33	49,17	1,47	1,10
Ba	0,85	0,80	0,67	0,79
Cd	3,00	1,167	0,009	<0,001
Cu	88,33	117,50	1,33	0,1358
Cr	30,00	21,67	0,82	18,67
Hg	0,0029	0,0019	0,001	0,0013
Ni	27,50	25,00	0,24	<0,05
Pb	9,42	16,58	<0,025	<0, 05
Zn	312,5	82,50	0,52	0,45

Main conclusion from these results is related to the acidic effect of the persulfate solution, causing high rates of mobilization in most of the metals. For permanganate, where pH is slightly above neutral values, the leaching ratio is significantly lower, or even, negligible. Thus, the potential side-effect associated to oxidative treatment in these cases are not related to changes in oxidation state of the metal, but in the existing species caused by the pH modification. As regards chromium with presumed ecological relevance due to expected transformation of chromium to hexavalent chromium species no detectable concentration of Cr(VI) were found, neither in water nor in soil. Therefore dominant species remained after treatment as Cr(III). Major content of trivalent chromium are in the soil, mainly as (highly) insoluble hydroxide ($Cr(OH)_3$). However, low pH in the persulfate treatment makes possible small fractions of soluble trivalent chromium species, as Cr^{3+}.

Tests with Czech soil sample J1 highly contaminated with total chromium showed that original Cr(III) in the soil is significantly affected by oxidative treatments, changing partially into Cr(VI). Approximately 50% of the total chromium mobilizes into water, appearing with an approximate ratio of 1:1 for Cr(III):Cr(VI). Generally Cr(III) species are highly insoluble, so they likely exist as Cr^{3+} at low pH for persulfate treatment and as soluble complexes with low molecular weight organic acids present in soil (citric and/or fulvic). Rest of the chromium (approx. 50%) remains in the soil, predominantly as insoluble Cr(III) species (probably most common and stable $Cr(OH)_3$). Low fractions of Cr(VI) can be found also in the soil, probably adsorbed to soil particles. Additionally other metals were also analyzed and assessed in sample J1. From tests results, it can be concluded that studied components are not significantly affected by permanganate treatment and concentrations remain similar to initial measures in the soil and no presence in supernatant water of the tests (mobile/leachable fraction). On the contrary, components with metallic behaviour (i.e., Cu, Ni, and Pb) seem to be affected by persulfate additions, mainly related to the acidified media associated to this reagent.

Ecotoxicity tests of the same samples after their chemical treatment showed that ISCO treatment leads to the significant increase of sample ecotoxicity up to 100 % inhibition of luminescence after 30 minutes. In case of persulfate that caused drop of pH to level between 2-3.2 the alternative tests with adjusted pH were performed. The effect of low pH on bacteria was thus eliminated, however high ecotoxicity remains, i.e. low pH is not the main stressor however pH contributes to the inhibition of bacteria luminescence 20-40 % (of H30; refer to Figure 1). This was also confirmed by ecotoxicity test of W2A sample treated by persulfate (100 g/L) buffered with sodium carbonate (pH of sample before ecotoxicity test was 8.5) when relative inhibition of luminescence after 30 minutes H30 was 98.5 % in average.

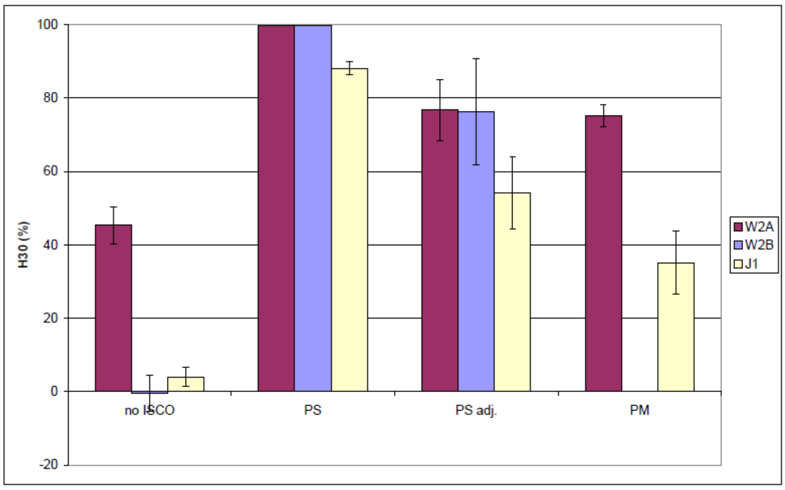

Figure 1: ***Results of ecotoxicity tests before (no ISCO) and after chemical treatment*** *(average values, PS=persulfate, PM=permanganate, "adj." indicates alternative test with adjusted pH; error bars refer to standard deviation – if no error bar then standard deviation smaller than 1; sample W2B not treated with PM)*

The following potential stressors inhibiting bacteria luminescence could be assumed:

- Mobilized heavy metals
- Increased bioavailable TPH
- Other aspects (e.g. various by-products of chemical treatment, ionic stress etc.).

However as showed by metal leaching tests a mobilization of heavy metals occurred only in case of the persulphate solution due to its acidic effect. For permanganate the metals mobilization was found negligible in both Polish samples. Considering the higher sensitivity of *Vibrio fischeri* bacteria to pH than to heavy metals (Fulladosa et al., 2006) it could be assumed that the mobilized heavy metals are not the main stressor. Another experiments performed within UPSOIL project indicated that absolute bioavailable TPH concentration increased due to chemical oxidation. By oxidizing soil organic matter, the chemical treatment releases TPH tightly bound to soil particles, thereby mobilizing the contamination. This phenomenon thus could be assumed as the potential stressor for bacteria used for ecotoxicity tests. In case of sample from the Czech site J1 the mobilization of hexavalent chromium was proved. Chromium VI could be thus considered as main stressor for bacteria. Surprisingly, the effect of hexavalent chromium on ecotoxicity of sample J-1 was lower than mobilized TPH effect on ecotoxicity of Polish samples. Nevertheless, the effect of other unidentified stressors cannot be excluded. In general, *Vibrio fischeri* bacteria are considered more sensitive to organic compounds than to heavy metals.

Smart coupling

UPSOIL project deals with the smart-coupling of remedial technologies. In respect to that, experiments were performed in which chemical and biological treatments were coupled. Such an experimental setup better simulates a field application, where a biological step would be initiated following chemical treatment. Thus, any ecological risks occurring during the chemical phase could be mitigated during the biological treatment.In this deliverable, additional ecotoxicity tests of samples after biostimulation following chemical treatment were performed (biostimulation run in Wageningen university).

The results of ecotoxicity tests indicate that biostimulation following the chemical treatment reduces the ecotoxicity of samples. Values of relative inhibition of luminescence were calculated to be approximately 52 to 54 % in case of persulfate treatment when persulfate chemical treatment (eliminated pH effect) without biostimulation showed average luminescence inhibition 76 % for both samples W2A and W2B (refer to Figure 1 - "*PS adj.*"). Relative inhibition of luminescence of samples treated by permanganate with following biostimulation varied between 21 (less contaminated sample W2A) and 67 % (sample W2B), respectively. Solely biostimulation reduced the ecotoxicity of sample W2A from H30 of 45 % with no treatment to 11 % after biostimulation. Low toxicity was confirmed in case of W2B sample (-0,5 % of H30 before treatment and 6 % inhibition after biostimulation).

CONCLUSIONS

The theoretical concept that chemical treatment could have the (eco)toxicological impact on soil at time point directly after treatment was confirmed. Performed metal leaching tests (combined basic batch leaching test and sequential extraction test) and ecotoxicity tests based on luminescent bacteria *Vibrio fischeri* showed metal leaching (caused by pH effect in case of persulfate and oxidation of trivalent chromium in case of high chromium content) and also significant inhibition of luminescence after the ISCO treatment. However, the increase of ecotoxicity was detected also in case of samples with low heavy metals content where limited metals mobilization occurred. The effect of the increase of absolute concentration of bioavailable total petroleum hydrocarbons could stress bacteria with low heavy metals content. Furthermore, smart-coupling of chemical and biological treatments leads to the reduction of ecotoxicity probably due to further decrease of target contaminants concentrations and also due to the redevelopment of the initial conditions. This result is especially important in application of smart-coupling techniques in field locations. The fact that short-term ecotoxicity due to chemical treatment is mitigated during a subsequent biological phase indicates the feasibility of coupling chemical oxidation with bioremediation.

ACKNOWLEDGEMENTS

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Poster Presentations

Design of a Permeable Reactive Barrier to retain Cs-137

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A Permeable Reactive Barrier has been designed to treat Cs-137 polluted groundwater. In order to check both reactivity and permeability, laboratory batch and column tests combined with reactive transport modeling have been performed. The trapping mechanism is based on the sorption of cesium on illite-containing clays. Batch experiments were conducted to obtain the partition coefficients (Kd) of different clay samples in solutions with different potassium concentration. The results were modeled with a cation-exchange model.

The permeability of the reactive material is provided by the dispersion of the clay on a matrix of wooden shavings. Constant head tests allowed obtaining permeability values. The mixture of wooden shavings and clay (2:1 by weight) is a material that has a hydraulic conductivity (10^{-4} m/s) high enough to ensure an adequate hydraulic performance for an eventual PRB excavated in many aquifers.

Several column experiments with different flow rates were conducted to confirm the Cs retention under different conditions. A blind 1D reactive transport model based on the cation-exchange model was able to predict reasonably well the results of column experiments.

The reactive transport model, validated with the column experiments, was used to investigate the performance and duration of 1m thick barrier under different scenarios (flow, clay proportion, Cs-137 and K concentration). As expected, the sensitivity tests proved that the retention capacity of dissolved Cs-137 in groundwater depends linearly on the amount of clay used in the filling material. As well, the operation time increases linearly when decreasing the flow rate. Finally, the concentration of potassium in inflow water has a remarkable and non-linear influence in the retention of Cs-137. Very high concentrations of potassium are the greatest threat and can lead to the infeasibility of the permeable reactive barrier. Due to the Cs-K competition, the barrier is comparatively more efficient to treat high concentrations of Cs-137.

The use permeable reactive barrier for treatment of groundwater contaminated with BTEX

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Throughout Europe, contamination of groundwater resources with heavy metals is perceived as a major problem among researchers due to the health threat posed to humans and other life forms. Biocides and other additives used in making antifouling paints for ships, boats and buildings; mine tailing wastes; fertilizers; and wastes emanating from the industries represent some of the main sources of soil and groundwater contamination with heavy metals. In situ remediation of groundwater using permeable reactive multi-barrier (PRmB) systems offers a potentially cheaper alternative to the existing conventional techniques for contaminated groundwater. The success of a PRmB depends, among other things, on the reactive materials used.

In Poland, previous sulphur mining activities have resulted in the quality of the soil and groundwater in Tuchepy being impacted. The groundwater which flows and feeds a river flowing through the site and to other places is acidic, and the soil is also contaminated with heavy metals. Treatment of soil and the groundwater before it exits the site is considered necessary. In this paper, a study of the test site to determine the possibility of using PRmB for the treatment of groundwater contaminated with multi-contaminants is presented. Results of different reactive materials intended to be used in the PRmB were tested in a batch experiment are also presented.

Laboratory study on permeable sorption barriers for treating of heavy metals contaminated groundwater

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Groundwater contamination with heavy metals caused by industrial waste storage and current and/or abandon mining activities is a widespread ecological problem. Toxic heavy metals (Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Zn(II)) have been penetrated to groundwater as a result of infiltration of contaminated rainwater. Permeable reactive barriers (PRBs) can be used for treatment of groundwater contaminated with heavy metals. A PRB is installed in a natural aquifer perpendicular to the groundwater flow direction. Heavy metals can be immobilized onto the reactive material contained in the treatment wall by e.g. sorption including adsorption, ion exchange and/or complexation processes.

In the present study, continuous-flow column experiments (using glass column, Tygon tubing, and peristaltic pump Manostat Carter) were conducted to investigate the performance of permeable sorption barriers for the removal of cadmium and zinc from synthetic groundwater. Zeolite, ion-exchange resin and activated carbon as reactive materials were used. The initial porosity of the PRB filling was between 0.4-0.5 depending on the used material. The upward flow of the synthetic groundwater was at a constant flow rate of 9.6 ml/h. The effectiveness and stability of reactive materials were studied by monitoring of changes of metal ions and selected background anions and cations concentration in groundwater during its flow through columns. Results showed that ion exchange resin was the most effective material of PRB. The percentage of metal ions removal was then above 99.5%. The high efficiency of ion-exchange resin in PRB for removal of heavy metals from groundwater was coupled with its reactivity and long barrier lifetime. The breakthroughs in the column tests on activated carbon and zeolite using synthetic groundwater occurred much earlier as compared to resin. Therefore, the system using resin requires smaller amount to treat a given volume of groundwater as compared to other materials. Moreover, the presence of other ions did not impact on activity and permeability of barrier filled with resin.

Session 9
Water management

Oral presentations

A dynamic evaluation of remediation measures at the river basin scale

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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. The nutrient discharge as well as the subsequent transport to water bodies is characterized by a large uncertainty impeding a straightforward calculation of the effect of a measure on the ecosystem 's status. 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.

The model explicitly describes the processes in the subsoil in order to be able to evaluate the dynamic effect of historical, current and future diffuse pollution on the aquatic ecosystem. It is exemplified by an evaluation of the nitrogen dynamics in the Scheldt basin. Scenarios were defined by a combination of predefined application percentages for waste water treatment, reduction of livestock and fertilizer and construction of wetlands and bufferstrips. The outcome of the scenario analysis is evaluated by cost-effect ratios, which are calculated on a subcatchment scale. The cost-effectiveness analysis is carried out at different points in time that correspond with the management cycles of the WFD to evaluate point source to diffuse source reduction measures.

The conceptual model framework proved valuable in the model calibration and yielded a hydrological model with a median Nash-Sutcliffe coefficient of 0.5 and an average normalised root mean square error of 1.0. The calibration highlighted the importance of a good definition of the model/study objectives and eventual penalty functions. Preliminary results of the scenario analysis indicate that measures influencing nitrogen in groundwater are indispensable to reach the WFD since it generally accounts for 25 to 35% of the nitrogen in the surface waters according to the model outcome. A further evaluation of the scenarios will be performed to evaluate the long-term cost-effectiveness.

Environmental Baseline and Sorption Studies for the Design of a Permeable Reactive Barrier

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ABSTRACT: An Environmental baseline study of surface and ground water was carried out in the former Uranium Mining Facility of Los Gigantes, Argentina, to evaluate the efficiency of future remedial actions in the site. Two million five hundred thousands tons of mineral, (0,15 ‰ U_3O_8 tcf, 0,239 ‰ U_3O_8 mean law, 0.123 ‰ U_3O_8 for maginal mineral), were processed between 1979 and 1990 to obtain 206 tons of concentrated uranium..

During the study, four monitoring campaigns of surface water (28 sampling stations) and two campaigns of ground water (11 sampling stations) were carried out on the site. Fifty eight physical, chemical and microbiological parameters have been measured in three different matrices: water, total suspended solids, and sediments. Additionally, field tests were carried out to determine the flow in creeks of the site by the velocity-area method. This information was then used to design and develop a salt tracer (NaCl) campaign to determine flow rate, water volume, and time of transport. This methodology contributed to the evaluation of the dispersion of different contaminants in the site. A Water Quality Index (WQI) was calculated using the measured values for the physicochemical parameters in order to assess the aptitude of use of the resource. The values of the WQI index show that: a) The water at the outlet of the site is safe according to aquatic life protection criteria; and, b) There are creeks impacted by acid drainage coming from the mineral tailings. In order to mitigate this impact, a permeable reactive barrier has been proposed as a remedial action for these water sources.

Biogenic hydroxiapatite ($Ca_5(PO_4)_3OH$), obtained from cow bones, through a process that includes calcination, grinding and sieving, has been chosen as the sorbent of this technological device, Sorption experiments of U, Mn, and F were carried out in order to characterize the efficiency of the material to immobilize these contaminants. Kinetic parameters were also determined in batch experiments by using 7 contact times, 3 concentrations for each contaminant and 3 particles sizes of the sorbent. At equilibrium time, between 2 and 48 hours U, Mn and F reached concentration values in solution lower than those proposed for aquatic life protection. Finally, hydraulic properties and the geochemical stability of HAPb were tested in packed bed, continuous flux experiments.

INTRODUCTION

Los Gigantes, Argentina, is a former Uranium Mining Facility that processed 2.500.000 tons (0,15 °/oo U_3O_8 tcf, 0,239 ‰ U_3O_8 mean law, 0.123 ‰ U_3O_8 for marginal mineral) between 1979 and 1990 to obtain 206 tons of concentrated uranium (PRAMU 2005). Uranium mines generate environmental impacts such as acid drainage. Permeable Reactive Barriers (PRB) have been suggested as a suitable method to remediate acid drainage (Gavaskar et al., 2000). Among the reactive materials used in PRBs, Hydroxyapatite (HAP) was studied for the removal of As, Cd, Co, F, Mn, Ni, Pb, Sb, U, Zn (Leiva et al., 2001; Seaman et al, 2001; Fuller et al., 2002; Mavropoulos et al., 2002; Gómez del Río et al., 2004; Czerniczyniec et al., 2005; Medellin-Castillo et al., 2007; Oliva et al., 2010).

In order to assess a PRB project a characterization of the site is needed an environmental baseline, (Gavaskar et al., 2000).

MATERIALS AND METHODS

Environmental baseline

A Water Quality Index (WQI) was calculated from the data collected through several monitoring campaigns of the study site, in order to assess the potential use of the water resource. For this purpose, it was used the index agreed for the Latin American and Caribbean region in the frame of the project ARCAL RLA/1/010 "Improved Regional Management of Water Bodies that are Contaminated with Metals" (Ávila-Perez et al, 2011). The data set used came from 4 surface water and 2 groundwater campaigns on monitoring network of 28 and 11 sampling stations respectively. A maximum of 58 physical, chemical and microbiological parameters have been measured in samples of water, total suspended solids, and sediments for each campaign.

Flow rate measurement

In a first field campaign, the creeks flow rates were determined by the velocity-area method. Depending on the flow velocities and depths of streams, either a current meter or floating debris was used to measure the flow velocity and therefore calculate total flow rates. These data was then used to design and implement a tracer campaign (injection of NaCl) to determine flow rates, water volumes, and mean residence time of the system (Leibundgut et al, 2009).

Reactive material

Biogenic hydroxyapatite was obtained after calcination of dry cow bones at 500 ºC for 3 hours. The resulting mineral was then grinded and sieved through analytic sieves (4, 10, 14 and 20 mesh) in order to obtain fractions of HAPb of different particle size (Figure 1).

Figure 1 ***Left: HAPb fractions, size l: 2-4 mm (top left), m: 0.85-2 mm (middle left) and s: 0.105-0.85 mm (bottom left). Right: SEM image of HAPb particles.***

Batch tests

Batch reactors were prepared by mixing an aqueous solution containing 200 mg L^{-1} of calcium and 400 mg L^{-1} of sulphate; to which 5 g L^{-1} of HAPb were added. Each reactor was shaken for approximately 15 days until pH was equilibrated at room temperature. After the reactors attained pH equilibrium, sorbates were added in three different concentrations, C_1 (0.4 mg Mn L^{-1}, 0.025 mg U L^{-1}, 1.25 mg F L^{-1}); C_2 (1.6 mg Mn L^{-1}, 0.050 mg U L^{-1}, 5.0 mg F L^{-1}) and C_3 (4.0 mg Mn L^{-1}, 0.100 mg U L^{-1}, 12.5 mg F L^{-1}). Samples were taken at 0, 15, 30, 60, 120, 2880 and 10080 min and filtered through 0.45 µm filters for the analysis of U (KPA), Mn (ICP-MS) and F (Ion Selective electrode). This procedure was repeated for each of the three HAPb particle diameter ranges tested (s: 0.105-0.85 mm, m: 0.85-2 mm and l: 2-4 mm).

Column studies

In order to investigate the effective porosity of the biogenic hydroxiapatite and to verify the uniformity of flow through the packed sorbent, a bromide tracer column experiment was performed. Constant flow conditions were chosen similar to those expected in the *in situ* full-scale PRB. A 14 cm-long, 2 cm-diameter column was filled with medium size HAPb particles (diameter: 0.85-2 mm); previously equilibrated for 15 days in deionized water. An inflowing KBr 0.1 M solution was administered continuously at a rate 1±0.1 mL min^{-1}, through a clean plastic tube connected to a high precision piston pump. Samples were taken on a minute basis and filtered through 0.45 µm filters for the analysis of Br (ISE) until breakthrough was observed.

Modelling

Reactive transport modelling in porous media was performed using the program PHREEQC 2.18.3 (USG S). This algorithm used a thermodynamic database to evaluate the stability and reactivity of the sorbent material. The mass balance equation for a chemical compound that is transported and immobilized in the column is described by the advection-reaction-dispersion (ARD), equation 1, (Parkhurst 1999)

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D_L\frac{\partial^2 C}{\partial x^2} - \frac{\partial q}{\partial t} \qquad \text{Equation 1}$$

Where C is concentration in water, t is time, v is pore water flow velocity, x is distance, D_L is the hydrodynamic dispersion coefficient and q is the concentration in the solid phase. Modelling runs were performed to simulate both Mn removal using preliminary data from batch tests and the behaviour of bromide tracer.

RESULTS

Environmental baseline

The WQI index (Figure 2) shows that the water at the outlet of the studied system is excellent according to aquatic life protection criteria. Some of the creeks (Figure 3) are impacted by acid drainage coming from the mineral tailings. The specific site for the installation of the PRB has been chosen taking into account the former results and the accessibility and proximity to the contamination source (white circle in Figure 2).

In the creek, where the barrier will be placed, the elements that are above the reference values are manganese, fluorine and uranium (Decreto 831/93).

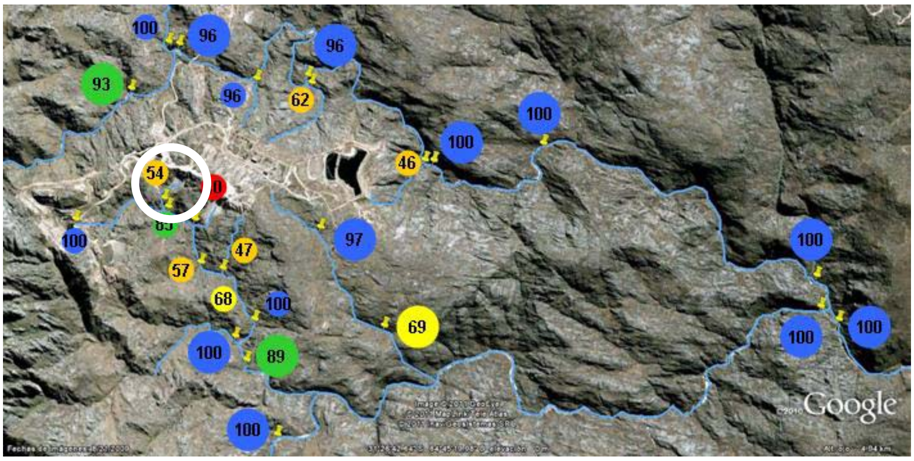

Figure 2: Results of the WQI using the environmental objective of aquatic life protection. Large circles indicate that flow rates of creeks are higher than 10 L/s; and small circles, flow rates lower than 10L/s. The colour code is: blue for excellent (95-100), green for good (80-94), yellow for fair (65-79), orange for marginal (45-64), and red for poor (0-44). Satellite Image from Google Earth (09/20/2011)

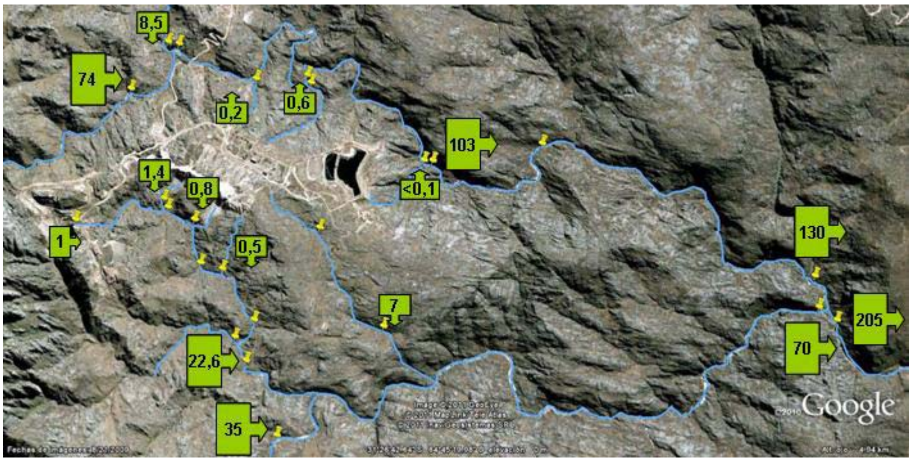

Figure 3: Flows of creeks in L/s. Satellite image from Google Earth (09/20/2011)

Batch tests

Batch experiments results show that Mn is the solute that would be less retained in HAPb compared to the other elements tested (Figure 4). The Mn equilibrium constant (K_{ads} = 6650 L mol^{-1}) and its adsorption capacity (Γ_{max} = 2.65 x 10^{-4} mol g^{-1}) were obtained by linearizing the Langmuir equation (Equation 2) and plotting Γ^{-1} versus the reciprocal concentration of the adsorbate (Figure 5).

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} \times K_{Lang} \times [Mn]} \qquad \text{Equation 2}$$

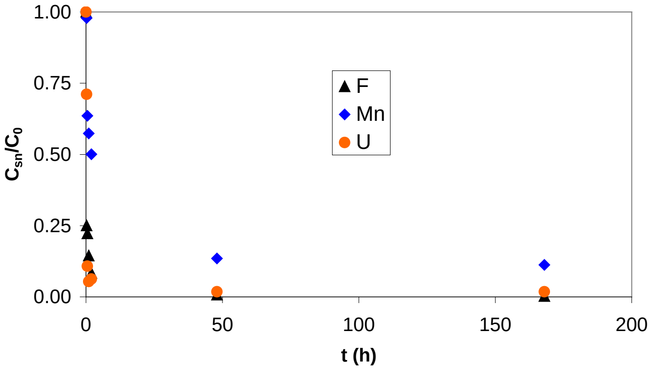

Figure 4: Fraction of the initial concentration remaining in the solution after 0, 15, 30, 60, 120 minutes for U, Mn and F.

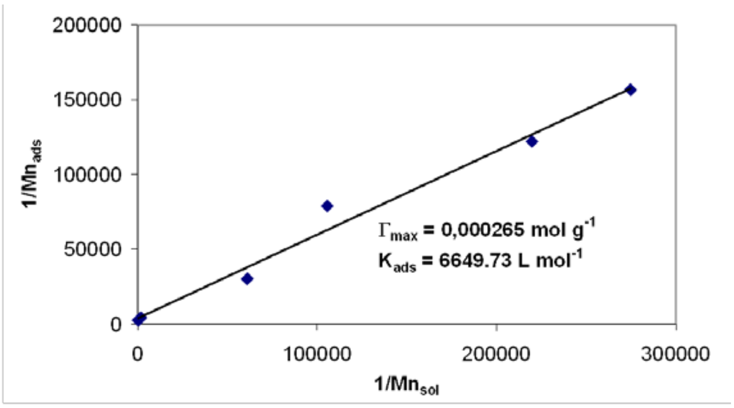

Figure 5: Inverse of Mn concentration in the solution versus inverse of the manganese adsorbed in the solid.

Column test

The longitudinal dispersivity coefficient ($\alpha_l = 0.08$ cm) and, average residence time (t = 32 min) were obtained by fitting the tracer experiment results using the ARD equation (equation 1 and Figure 6). The porosity of the material (0.84) was calculated from the breakthrough curve presented in Figure 6. The longitudinal dispersivity coefficient, average residence time, and equilibrium constant; plus the adsorption capacity presented in the previous section, allowed the simulation of the transport of Mn through a full-scale PRB (lineal velocity, 0.24 cm min^{-1}; 10 m length). Figure 7 shows the metal concentration in water inside the PRB as function of the time and length.

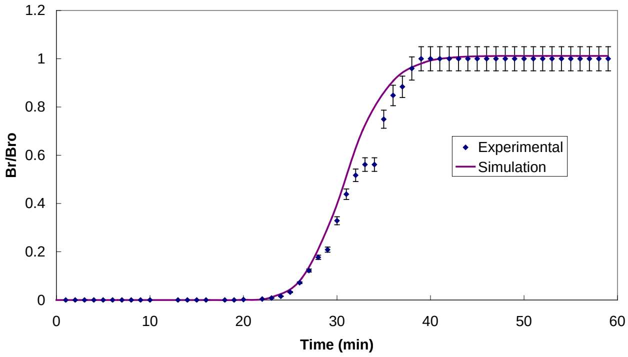

Figure 6: Breakthrough curve of KBr. Blue dots are experimental measurements; while the solid line correspond to the simulated data. Concentration is expressed in relation to the initial concentration of bromide.

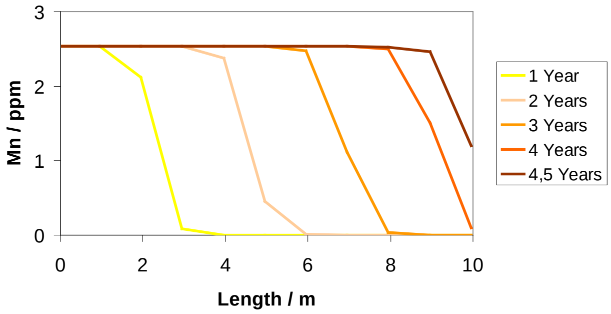

Figure 7: Simulation of the concentration of Mn in the solution along the length of the PRB calculated at different times (Mn_0 = 2,6 ppm).

CONCLUSIONS

The environmental baseline data, WQI and flows of the creeks, identified places where to take remedial actions. These data together with accessibility and proximity to the source of contamination leaded to the selection of the stream where to place the PRB. Manganese, fluorine, and uranium where identified as the elements that are above the reference values. It was found that biogenic hydroxyapatite, the selected sorbent material of the barrier, was able to immobilize the three contaminants. Batch experiment results show that Mn is the controlling element of the efficiency of the barrier. This is due to its higher concentration in the acid drainage effluent to be treated and its slower sorption onto biogenic hydroxiapatite, compared to fluorine and uranium.
Column experiments proved that HAPb is hydraulically and chemically stable. The hydrodynamic constants calculated from these results, allowed to simulate the transport of Mn through a full-scale PRB; thus, the performance of the device along time.

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Evaluation of different model structures for flow and nitrate simulation in a tile-drained river basin

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Abstract: With the need of managing pollution problems at river basin scale, hydrological modeling tools are promising tools to support the quantification of the pollution loads originating from different sources. So far, a very limited number of studies have reported on the use of these models to predict the pollution fluxes in tile drained watersheds. This study aims at evaluating different model structures in representing the hydrological and nitrogen processes using the Soil and Water Assessment Tool (SWAT) model in a tile drained watershed named Odense River basin in Denmark. There are three different versions of the Odense watershed built on SWAT with different structures: (i) without tile drains, (ii) tile drains are applied in specific parts of agriculture areas that have gentle slope and (iii) the river basin is subdivided in different landscape units and tile drains are applied differently in each unit. Model (i) is manually calibrated for flow and the best parameter set was used to apply for the other two models to test the model performances when tile drain and landscape are respectively included. The results show that the performance improved considerably with the inclusion of tile drainage component while little improvement was seen with the subsequent inclusion of landscape units. The three models were then calibrated using auto-calibration tool. It can be concluded that calibration could help to give reasonable total discharge but could not identify the correct flow and nitrate flux division through different flow paths.

INTRODUCTION

With the need of managing pollution problems at river basin scale, hydrological modeling tools are promising tools to support the quantification of the pollution loads originating from different sources. So far, a very limited number of studies have reported on the use of these models to predict the pollution fluxes in tile drained river basins. The case study in this paper is Odense river basin, Denmark which are a densely tile drained basin, thus, it is an ideal study area for tile drainage simulation. The Soil and Water Assessment Tool (SWAT, version 2005) which is a world-wide used model at river basin scale is applied in this study.

Odense river basin is a lowland river basin with intensively drained agriculture areas. Therefore, tile drainage is assumed to have a strong impact on lowland hydrology. The inclusion of tile drainage in the model is supposed to obtain a better representation of hydrological processes in the case study. As mentioned above, the present approach of SWAT does not consider the reference between HRU position to landscape location, i.e two HRUs with the same soil, landuse and slope characteristics are simulated similarly although they may locate in different landscapes. The incorporation of landscape division (floodplain and hillslope in this case study) with tile drainage simulation allows to separate tile flow modelling in different landscape units by giving different values for tile drainage parameters. The landscape approach is more realistic than the present approach because it considers the possible effect of difference in landscape characteristics on tile flow simulation. Therefore, this approach is assumed to give better simulation of tile drainage. Previous studies show that many different parameter sets can give almost identical fits to the measured data (the equifinality problems). The study aims at testing: (i) the effect of tile drainage inclusion in the flow simulation, (ii) the effect of landscape variability inclusion in the flow simulation and (iii) model performance in different structures with the help of auto-calibration.

MATERIALS AND METHODS

Study area: Odense river basin, Denmark

The Odense river basin which is located on the island of Funen in Denmark comprises an area of approximately 622 km^2 and is part of the Odense Fjord Basin encompassing 1046km^2 (figure 1). The Odense floodplain was formed by a melt-water river during the last glacial period 11,500 to 100,000 years ago (Fyns county, 2003). Clay soil types are slightly dominant and encompass approximately 51% of the basin, while sandy soil types cover about 49% of the basin area (Fyns county, 2003). The land use in Odense River Basin is dominated by agricultural exploitation and over 50% of the agricultural areas are drained by subsurface tile drains.

Different set-ups and auto-calibration description of the SWAT model for Odense river basin

Three different model set-ups were carried out to test the role of tile drainage in the simulation of hydrological balance and the effect of incorporating landscape units in the improvement of tile drainage as well as discharge simulation:

- Setup (1): tile drainage is not included
- Setup (2): with tile drains applied in the gentle slope agricultural areas (slope: 0 - 2%)
- Setup (3): incorporating landscape division with tile drainage simulation

In these three models, the differences are mostly on land use and tile drainage components (table 1). The steps for building the SWAT model are explained in details for setup (1). For the other set-ups, only the differences compared to setup (1) are mentioned.

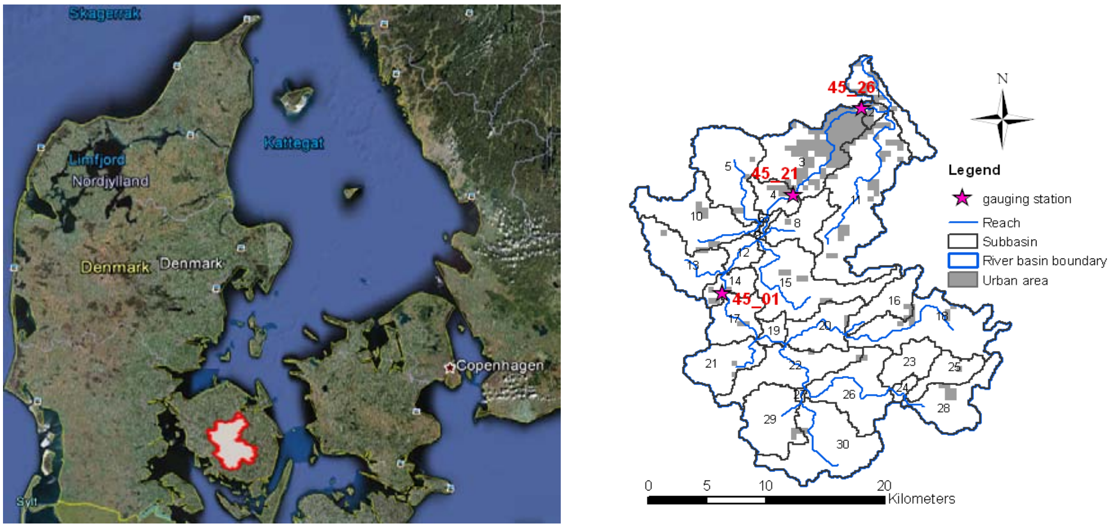

Figure 1: Study area - Odense river basin, Denmark

Setup (1) _ without tile drainage

- River basin delineation

The ArcSWAT interface delineated the river basin into 30 sub-basins based on the available DEM grid map with a spatial resolution of 100 meters and user-defined stream networks. Three out of 30 outlets of sub-basins were manually added at the locations of three gauging stations (45_01, 45_21 and 45_26) which were then used for model calibration (figure 1). These subbasins were then further subdivided into HRUs.

- HRU definition

The Hydrological Response Units (HRUs) are defined by overlaying soil map, landuse map and slope classification map. Each HRU is a unique combination of soil, landuse and slope within a subbasin.

Soil: The soil profile in the Odense river basin was divided into three horizons: A (0-30cm), B (30-70cm) and C (70-150cm). There were seven soil types distributed in the SWAT model: JB1 coarse sand (0.9%), JB3 coarse clayey sand (31.6%), JB4 fine clayey sand (20.5%), JB5 coarse sandy clay (26.6%) and JB6 fine sandy clay (19.4%), JB7 clay (1%) and JB11 organic (0.03%).

Land use: The area was divided into 6 types of land use: cattle farms, plant production, pig farms, grass, coniferous forest and deciduous forest. In each of the four agricultural groups, one crop rotation was applied.

Slope: The area was divided in 2 slope classes: (i) from 0% to 2% which is considered as gentle slope and suitable for agriculture activities and (ii) higher than 2%.

- Climate

Daily precipitation in the area of the Odense river basin is available in the forms of 11 interpolated 10km x 10km precipitation grids from the Danish Meteorological Institute. The data were included in the SWAT model by creating 11 rainfall stations located at the centroid of each precipitation grid. The temperature was based on 20km x 20km grid values which were applied in the model by 4 temperature stations. Solar radiation, relative humidity and wind speed data were taken from a single weather station for the whole area.

Table 1: Descriptions and differences of four SWAT model set-ups for Odense river basin

	Setup (1)	Setup (2)	Setup (3)
Basin delineation			
Number of subbasins	30	Same as (1)	Same as (1)
HRU definition			
Soil types	7	Same as (1)	Same as (1)
Land use types	7	Same as (1)	12 (Incorporating landscape characteristic in landuse)
Slope classes	2	Same as (1)	Same as (1)
Number of HRUs	654	Same as (1)	771
Climate		Same as (1)	Same as (1)
Precipitation	10km x 10km grid	Same as (1)	Same as (1)
Temperature	20km x 20km grid	Same as (1)	Same as (1)
Solar radiation, humidity, wind speed	1 weather station	Same as (1)	Same as (1)
Tile drainage	No tile drains	- tile drains applied in the areas with slope 0-2% - same value of *dep_imp* for the whole basin *ddrain* = 1m *dep_imp*=3.2m	-tile drains applied in the areas with slope 0-2% -different values of *dep_imp* for different landscape units *ddrain* = 1m $dep\_imp_{hillslope}$=3.2m $dep\_imp_{floodplain}$=1.5m

Setup (2) _ with tile drains applied in the gentle slope agricultural areas (slope: 0 - 2%)

Compared to setup (1), tile drainage component was added in this setup. Tile drainage was applied in the agricultural areas that have gentle slope from 0 – 2%. Tile drainage is handled by the tile drainage option in the management files in SWAT. The parameters related to tile drainage simulation consist of *ddrain* (depth from soil surface to tile drains), *dep_imp* (depth to impervious layer), *tdrain* and *gdrain* (drain tile lag time).

Setup (3): incorporating landscape division with tile drainage simulation

The incorporation of landscape division with tile drainage simulation was conducted in two steps. First, the landscape characteristics were incorporated with soil characteristics by overlaying landscape and soil maps of the case study. Based on DEM, the Odense river basin was delineated into two landscape units (floodplain and hillslope) using slope position method (USDA Forest Service, 1999) and own modifications of the algorithms. Because the Odense river basin is relatively flat, hillslope and divide units are not expected to have very different processes. Secondly, the new landscape map was overlaid with the soil map to create a new soil map in which each soil type is defined to locate in hillslope or floodplain units. This new soil map was used to overlay with soil and slope maps to create the HRUs. With this incorporation, it is easily known which landscape unit that each HRU locates in.

With the incorporation of landscape location in each HRU, it is allowed to implement different tile drainage simulation in two landscape units by providing different values for tile drainage parameters. In this setup, the *dep_imp* was set at higher value for hillslope than for floodplain units (table 1), which implies the hillslope areas have deeper groundwater table than floodplain areas. This setup takes into account the effect of landscape on groundwater depth and tile drainage generation.

SWAT run, calibration and validation

The three SWAT setups were run with a daily time-step in the 14-year period of 1990-2003. The first three years were used as warming-up period. For flow simulation, calibration was carried out for the period of 1993-1998 while 1999-2003 was the validation period. Sensitivity analysis was implemented using the sensitivity analysis tool LH-OAT in SWAT and then the most sensitive parameters were included in the calibration.

Three gauging stations 45_26, 45_21 and 45_01 which correspond to the outlet of subbasin 3, 4 and 17, respectively are available for flow calibration. The station 45_26 is nearest to the outlet of the river basin, however, the measured discharge is strongly affected by discharge from the concentrated urban area which covers most of the area of subbasin 3 (figure 1). Odense river basin is dominated by agricultural areas, urban area only cover a small part of the basin. Therefore, this station is not suitable to be chosen for calibration since the optimal parameters may not correctly represent the river basin characteristics due to the strong effect of urban discharge. Consequently, the station 45_21 which locates upstream of the concentrated urban area (figure 1) and is mostly affected from discharges from agricultural fields was chosen for calibration and validation.

To evaluate the SWAT performance for the simulated discharge and nitrogen flux, the following criteria were used:

- $NSE_{Q,\ daily\ or\ monthly}$: the model efficiency calculated on the basis of observed and simulated daily or monthly discharge values (Nash and Sutcliffe, 1970).

- $r_{Q,\ daily\ or\ monthly}$: the correlation coefficient between simulated and observed daily or monthly discharge values.

Comparison between different setups

The comparisons between different setups were conducted to reach the three objectives of this paper. Figure 2 illustrates the methodology of these comparisons and their objectives.

(i) To test the influence of tile drainage inclusion to the SWAT model, setup (1) without tile drainage was used as a reference model to compare with setup (2) in which this component was added. Sensitivity analysis and manual calibration were carried out for setup (1) to get an optimized parameter set. This parameter set was applied for setup (2) to ensure that two models are comparable. Setup (2) was then compared with setup (1) to study the difference that the tile drainage component caused in flow and nitrate simulations.

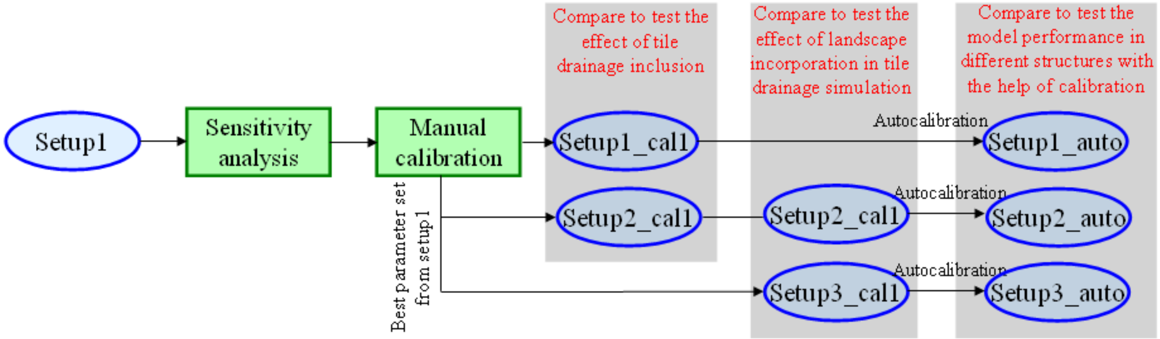

Figure 2: Methodology of comparing different SWAT setups

Note: Setup()_cal1: SWAT setup that uses the best parameter set from setup (1)

Setup()_auto: SWAT setup that uses the best parameter set from autocalibration procedure

(ii) To test the effect of landscape incorporation in tile drainage simulation, setup (2) and setup (3) were compared. The obtained parameter set from the manual calibration of setup (1) is still used in this comparison to ensure the equivalence between the two models.

(ii) To test the model performance in different structures with the help of auto-calibration, all three models were calibrated with the same parameter list (table…). It is assumed that the auto-calibration tries to help the model to compensate the lacking processes by increasing or decreasing the effect of other processes.

RESULTS

Setup (1) without tile drainage inclusion was calibrated manually to get the reasonable trend and magnitude compared to measurements (figure 4a). NSE_Q and r_Q for setup (1) after manual calibration is 0.62 and 0.82, respectively. The results are considered satisfactory according to Moriasi et al. (2007). The parameter set from manual calibration for setup (1) was also applied in other setups to ensure a fair comparison among the three models and an accurate assessment on the effect of tile drainage and landscape on the SWAT model for Odense river basin.

The effect of tile drainage inclusion

From figure 4a and b, it is clearly observed that setup (2) fitted better to measurement than setup (1). According to performance criteria, NSE_Q and r_Q also increased respectively to 0.79 and 0.90 in setup (2) (table 2). The difference between the two models is clearer in high flow periods (November to March) than low flow periods (April to October). In high flow periods, the inclusion of tile drain parameters improves the SWAT model performance by producing higher peak flows and steeper hydrograph recession (figure 4d). In setup (1), groundwater contributes the most significant flow while groundwater and tile flow share flow contribution in setup (2). Tile flow is a fast flow component which has a shorter lag time while groundwater flow is considered as a slow flow component. The contribution of tile drainage as a fast flow component in the high flow periods result in higher and more dynamic flows in setup (2). In low flow periods, there is not significant difference between the two setups because flow in both setups is mostly contributed by groundwater. Tile drainage was only generated in the high flow periods, not low flow periods. The reason is that evapotranspiration is high in low flow periods (summer); thus, SWAT predicted less water percolation out of the soil profile and in turn the water table rarely reaches the tile drain level.

Figure 3 show the change of groundwater flow and tile flow when tile drain parameters were added in setup (2). It can be seen that the decrease of groundwater always come along with the increase of tile flow. This is reasonable because the source of tile flow is from groundwater from aquifers. It can be noticed in figure 3 that the decrease of groundwater is always higher than increase of tile flow. The reason is that not all groundwater loss become tile flow, some contributes to the change of soil moisture which results in small change in surface runoff and lateral flow

The effect of landscape inclusion

The inclusion of landscape variability in setup (3) is implemented by setting different values for the parameter DEP_IMP. This parameter reflects the groundwater table at which water stops infiltrating and starts to build up the groundwater height. It is assumed that the groundwater table is nearer to the ground surface in floodplain than in hillslope area. Therefore, DEP_IMP in floodplain was set smaller (1500mm) than DEP_IMP in hillslope (3200mm). Figure 4c shows the relatively good fit of setup (3) to measured data both in trend and magnitude. The NSE_Q and r_Q reached 0.8 and 0.91, respectively which are considered very good results according to the guidelines of Moriasi et al. (2007). However, compared to setup (2), the results from setup (3) has improvement, but not significant. Therefore, it is concluded that in this tile drained basin, the effect of tile drainage is more significant than the effect of landscape variability on groundwater height. However, in this study, the landscape variability is only reflected by the difference in initial groundwater height. It is possible that the landscape variability will have larger effect if all the differences in landscapes (for eg: topography, soil, land use, transport processes etc) are considered in the model.

Table 2: Performance criteria for different SWAT setups at the gauging station 45_21 using parameter set from manual calibration of setup (1)

Performance Criteria	Setup (1)		Setup (2)		Setup (3)	
	Calibration	Validation	Calibration	Validation	Calibration	Validation
NSE_{Qdaily}	0.62	0.59	0.79	0.75	0.80	0.77
r_{Qdaily}	0.82	0.83	0.90	0.90	0.91	0.91

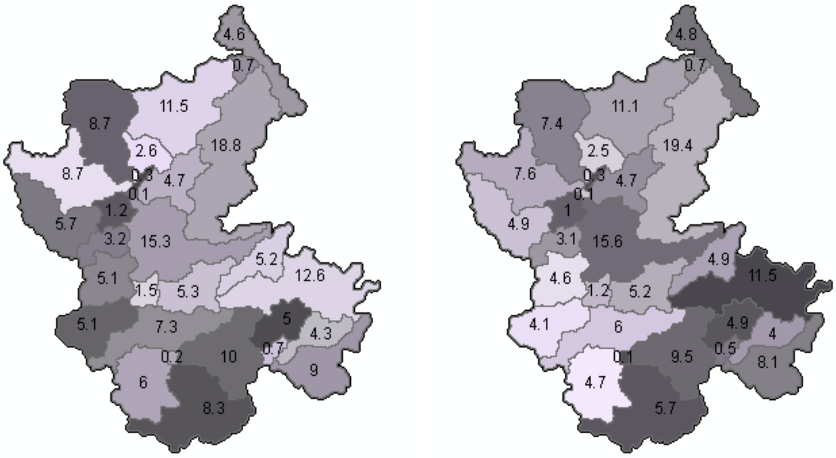

Figure 3: (a) Decrease in average annual groundwater flow in each subbasin from setup1 to setup 2; and (b) Increase in average annual tile flow in each subbasin from setup 1 to setup 2 (b)

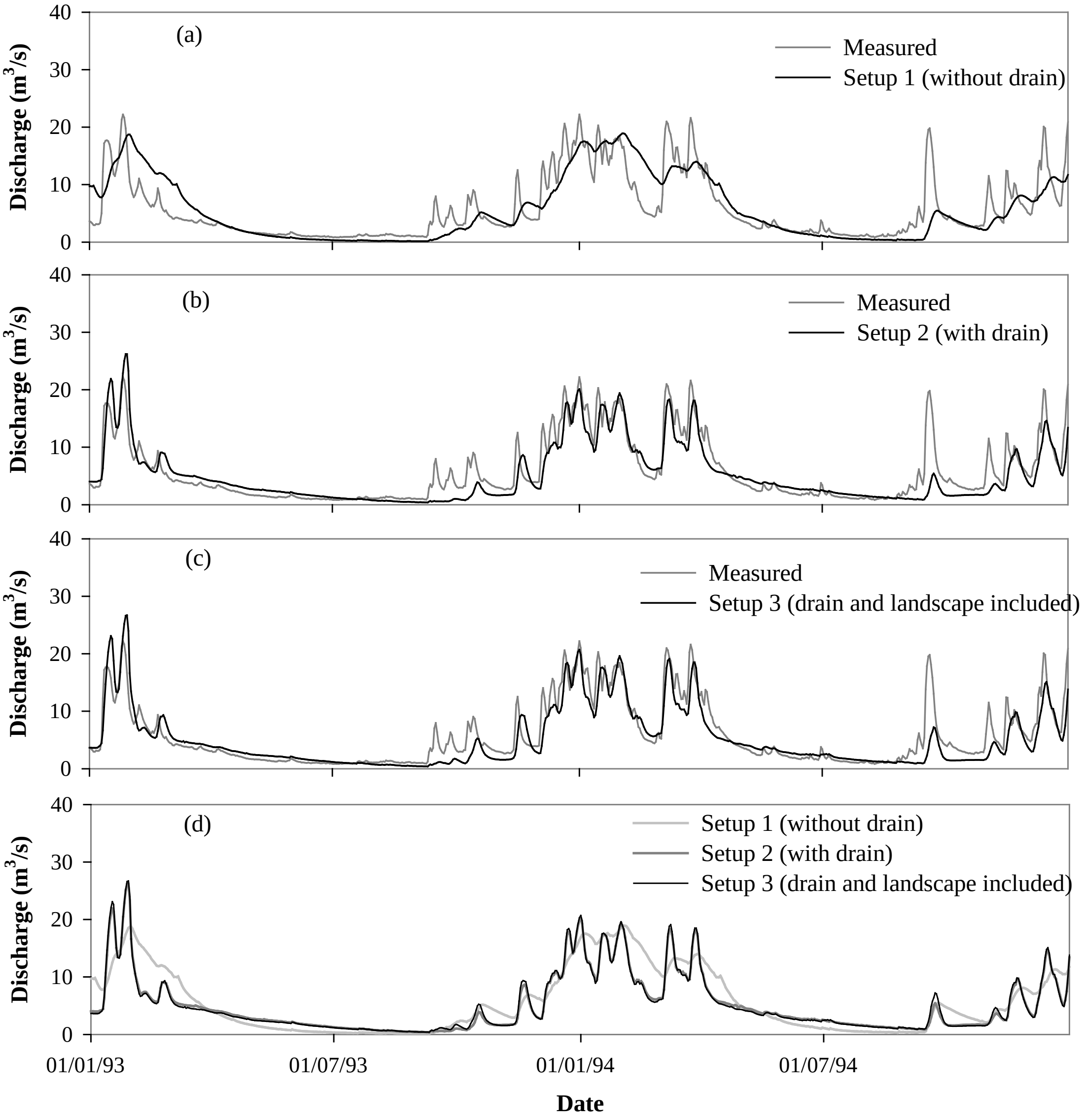

Figure 4: Comparison of measured and simulated discharges from different SWAT setups at the gauging station 45_21

Model performance in different structures with the help of auto-calibration

The three setups were calibrated by auto-calibration tool of SWAT at the station 45_21. The most sensitive parameters were taken into account in the auto-calibration. Table 4 presents the value of model performance criteria in daily time step of the three setups. The results show that with the help of auto-calibration the three model all give very good fit to measurements (NSE = 0.83 – 0.85). Setup (1) which does not include tile drain simulation gave better fit than the other setups in which tile drainage parameters are considered. We also check the result at station 45_26 which locates downstream of the calibrated station 45_26. Compared to the station 45_21, the result at the station 45_26 is a bit better in setup (1) but has more significant improvement in setup (2) and (3). Looking at the water balance in 3 setups, we can see the difference in the contribution of flow components. In setup (1), surface runoff is dominant flow component while tile flow and groundwater flow are both dominant contributions in setup (2) and (3). Because of high contribution of surface runoff which has shorter lag time, flow result in setup (1) is more dynamic and thus easily fit to the variation of measured flow. Setup (2) and (3) has less dynamic flow result because they are dominated by subsurface flows which have longer lag time. It can be noticed that the result at the station 45_26 is better than at the station 45_21 which is calibrated station. Compared to station 45_21, 45_26 is strongly affected by urban flow which creates small variations in the hydrograph both in high flow and low flow periods, which gave a better fit to observations.

Table 3: Values of daily NSE$_Q$ at the gauging station 45_21 (calibrated station) and 45_26 for different SWAT setups after auto-calibration

Station	Setup (1)		Setup (2)		Setup (3)	
	Calibration	Validation	Calibration	Validation	Calibration	Validation
45_21 (calibrated station)	0.85	0.81	0.83	0.79	0.83	0.79
45_26	0.86	0.84	0.86	0.84	0.86	0.84

Table 4: Annual water balance for different SWAT setups after auto-calibration (1993-1998)

Water balance components	**Setup (1)**	**Setup (2)**	**Setup (3)**
Precipitation	855	855	855
Surface runoff	244	45	52
Lateral soil	1	14	16
Tile flow	0	180	185
Groundwater flow	119	161	148
Evapotranspiration	488	446	446

CONCLUSIONS

From the results of the study, three main conclusion were brought out

(i) The inclusion of tile drainage simulation contributes a significant improvement in the model performance. That is a reasonable result because the case study is a densely drained agricultural area.

(ii) The inclusion landscape variability is small and does not make a significant improvement for the model performance compared to the effect of the inclusion of tile drainage simulation. However, the landscape variability is only shown by the difference in initial groundwater height. The effect can be much higher if all the differences in landscape characteristics (for eg: topography, soil, land use, transport processes etc) are considered.

(iii) Different setups can all get good performance with the help of autocalibration. It is still possible for an unrealistic setup to get good fit to observations. However, the breakdown of flow components is very different in different setups.

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REACHER: a Decision Support Tool to evaluate impacts of remediation measures on pollution fluxes towards the receiving water bodies

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ABSTRACT

The complicated nature of simulation models and the large computation time they need hamper the use of these tools in the decision making process. Stakeholders lack the detailed domain knowledge to judge processes included in the models. They need decision support systems (DSS) with an intuitive user interface (UI) design simplifying the interaction with models and the visualization of the produced results. In this study, we present a WebDSS prototype named REACHER that is fully based on Free and Open Source Software (FOSS). A Bayesian Brief Network (BBN) model is chosen as the decision model to generate the probabilities of future scenarios. The advantages of using BBN are: its graphic structure is ideal to link the upstream-downstream topology, it is efficient and it can combine different measures at the same time. A REACHER implementation has been done for the Odense river basin in order to allow users to evaluate in real time the effects of remediation measures on the nitrate fluxes towards the groundwater bodies and the river reaches.

Using a decision support tool to set up cost effective programs of measures as required by the Water Framework Directive

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The Water Framework Directive (WFD) sets ambitious objectives to ensure that all waters meet 'good status' by 2015. Member states have to publish river basin management plans that include programs of cost-effective measures. VITO supported the policy makers in Flanders (Belgium) with the preparation of the first generation of river basin management plans and more specifically with the assessment of the costs and effects of programs of measures. The environmental costing model was used to select cost effective measures to improve surface water quality (Cools et al, 2011; Broekx et al, in press). The public consultation process of the river basin management plans and a user requirements analysis resulted in recommendations for further development involving a more extensive analysis covering multiple water aspects as water quality, hydromorphology and sediments, a more transparent structure reporting information on different scales and for different scenarios. Consequently, a web-based decision support tool is being implemented in preparation of the next generation of river basin management plans that focuses on:

- Functionalities: information about status, pressure, costs and effects of measures and assessment of costs, effects, benefits and affordability of packages of measures.
- Scales: information retrieval and simulation results that can vary from individual water bodies to regional level.
- Water aspects: surface water quality, sediments, hydromorphology, floods.
- Interactive: users can built up draft packages of measures (scenarios), assess their costs and effects and share these scenarios with other users (e.g. users building scenarios for other aspects or for other water bodies).

The tool can be consulted on http://rma.vito.be/mkm.

The Use of WFD Tools to Assess the Effects of Remediation Technologies

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The objectives of Work Packages 1 and 3 of the AQUAREHAB project were to study the effects of remediation technologies in the Odense and Zenne Rivers respectively. In order to study the ecological effects of wetland construction (WP1), degradation of Chlorinated Aliphatic Hydrocarbons (WP3) and reduction of municipal sewage discharges (WP3), existing WFD tools for ecological status assessments were used.

Within WP1, a comprehensive study was carried out on the changes in the indicative ecological status of the Odense River (Fyn Island, Denmark) as a response to wetland construction in the riparian zone. In WP3, the effects of the combination of an in situ biological reactive zone near the river bank and a permeable capping of the river sediment were studied in the Zenne River at Vilvoorde in Belgium.

To this end, five surveys of the Odense and Zenne River were performed in September/October 2009, May 2010, September 2010, May 2011 and September 2011 to characterise the ecological and chemical situation and its changes. The goal of the surveys was the determination of relevant Biological Quality Elements (BQEs; macrozoobenthos, phytobenthos, phytoplankton and macrophytes) at species level. The presence of all WFD priority substances (PS) was investigated as well in order to obtain an indication of the river's chemical status. A general GC-MS screening of organic compounds was performed to identify site-specific pollutants that could be included in programmes for future monitoring. The requirements of the WFD were followed as closely as possible, although a full chemical and ecological status assessment was not the goal of this study. Indications of ecological and chemical status were determined for each sampling site (3 per river) for each year.

The results showed that, although the conditions in the Odense and Zenne Rivers are very different, indicative ecological and chemical status assessments are a helpful tool when studying the effects of remediation measures.

Poster Presentations

Modeling the reactive transport of chlorinated solvents in the groundwater towards the Zenne River

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Abstract

Groundwater pollution incidents from major industrial complexes are becoming more common and are often the subject of major, expensive investigations and clean-up activities. Chlorinated solvents contamination of groundwater resources has been widely reported. Such contamination reduces the amount of water available for use, as well as posing risks to human health. Field investigations in the Vilvoorde – Machelen site located 10 km north-east of Brussels indicated that chlorinated aliphatic compounds (CAHs) are the major contaminant of concern. At this site, due to more than a century of industrialization a plume containing mainly CAHs is flowing towards the Zenne River.

The objective of this study is therefore to develop a natural attenuation model for evaluating the fate and transport of CAHs in saturated groundwater system towards the Zenne River. We used MODFLOW, and RT3D, a three-dimensional multi-species reactive transport model to simulate the degradation and advective-dispersive transport of tetrachloroethylene (PCE), trichloroethylene (TCE), cis-dichloroethylene (DCE) and vinylchoride (VC). A steady state flow model was calibrated. First order degradation rate constants compiled from literature were modified during model calibration to recreate the contaminant distribution patterns currently observed at the site. Scenario analysis was also performed by applying an increased degradation rate, to reflect different degradation conditions.

INTRODUCTION

The long industrial history of the Vilvoorde – Mechelen area has lead to complex patterns of pollution from multiple sources. Due to more than a century of industrialisation the site has been polluted to the extent that individual plumes are not definable any more (Dujardin et al., 2009). The groundwater of the study area is highly contaminated with contaminant from different sources. Bronders et al (2007) identified four major sources zones of groundwater contaminants shown in figure 1. The present study focuses on source area 3 (car manufactory), which is characterized by the presence of pure product of both LNAPL, BTEX (benzene, toluene, ethylene, and xylene) and DNAPL (dense non-aqueous phase liquid).

Chlorinated solvents and their natural transformation products represent the most prevalent organic ground-water contaminant in the area. These solvents primarily consist of CAHs. There is a growing concern about these compounds, because they are known to persist in the environment over a long period of time, and because they are suspected carcinogens, even at low concentrations. Concern about the contamination with PCE or TCE has become more acute, because certain anaerobic bacteria in groundwater transform these compounds to c-DCE and VC. The latter compound is known to be a potent mutagen and carcinogen in humans (Schaerlaekens et al., 1999). Because of their relative solubility in water and their somehow poor sorption to soils, they tend to migrate downward through soils, contaminating water with which they come into contact. Being denser than water, their downward movement is not impeded when they reach the water table, so they can penetrate deeply beneath the water table and continue to sink within the aquifer until an impermeable layer is reached. Hence, CAHs contamination particularly, in heterogeneous subsurface environments is difficult to both indentify and remediate. Therefore, the conventional pump and treat method for these contaminants can be very expensive and in some cases ineffective (Shoemaker et al., 2003). On the other hand, the use of natural attenuation not only saves cost compared to more conventional remedial alternatives but also lessen the problem of dealing with the complexities of subsurface systems such as complex geochemical, bio-chemical, and hydro geological uncertainties which are dominant in most sites (Azadpour-Keeley et al., 2001). Previously published natural attenuation studies indicate that the biological activity required for degrading many chlorinated organic compounds are present in most anaerobic aquifers (Clement et al., 2000; Semprini et al., 1995).

The objective of this study is therefore, to develop a natural attenuation model for better understanding of the fate and transport of chlorinated solvent and their degradation products in the subsurface and to assess the sensitivity of the result to degradation rates. Inverse modeling was performed to estimate the unknown contaminant transport model parameters while simultaneously characterizing the contaminant sources.

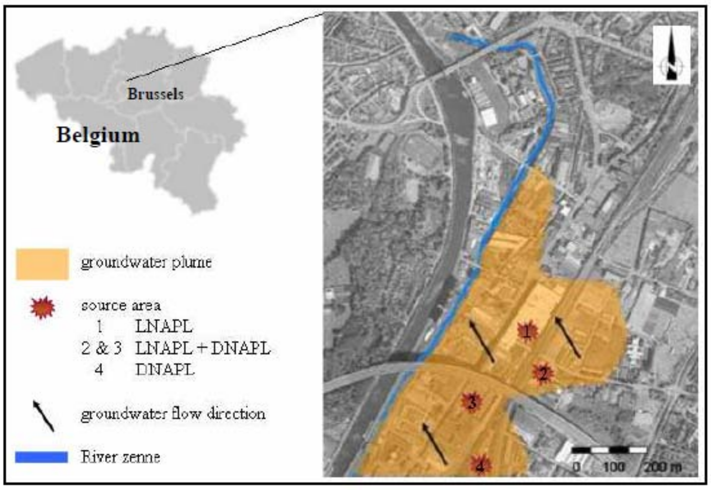

Figure1: Location of the industrial area of Vilvoorde- Machelen (near Brussels), indication of the groundwater plume and the major known source area (source: Bronders et al. (2007))

METHODOLOGY

SITE DESCRIPTION

The industrial area of Vilvoorde – Machelen, is located about 10 km north-east of Brussels, Belgium and comprises 10 km^2 in size. It is located in the Zenne catchment along the Zenne River. The site lies between the Brussels-Scheldt Maritime Canal and the Zenne River on the west, the R22 road on the east and Trawool River on the north. The topography ranges from 10 to 50 m a.s.l., with an average value of 16 m a.s.l. and mean slope of 1.3 %. The dominant soil type is silty loam, while in the north-eastern part clay-loam occurs (Dujardin et al., 2009). Figure 1 shows all know or suspected sources. Geologically, the study area is formed by an accumulation of several marine sand deposits. The aquifer system is composed of silty eolian sands, upper layer of the formation; sediments deposit consisting of gravel in a silty sand matrix, with clay –containing organic base, second layer of the formation, the wedge-shaped Ghent formation consisting of densely packed sand (the third layer), clay-containing silty sand (fourth layer), and the lower layer is characterized by a 25 m thick deposit of silty,glauconite-contaning fine sands known as the Tielt formaiton.

GROUNDWATER FLOW MODEL

The groundwater flow system was modeled using the MODFLOW code in Processing MODFLOW modeling environment assuming steady-state conditions. The model domain covers an area of 10 km^2. The conceptual setup of the model, boundary conditions, geologic formations, hydraulic parameters, pumping wells and drainage data were used from previous study (Boel, 2008). The finite-difference mesh consists of 60 rows and 52 columns with a uniform grid size of 50 m x50 m. In the vertical directions, the model consists of five layers with variable layer thickness. In order to orient the model rows along the flow lines the model grid was rotated at an angle of 30^0.

The following boundaries were assigned along the perimeter of the active model domain: In the western side the navigation canal Brussels –Scheldt was used as the general head boundary, in the southern side, as there are no well-defined hydrologic or physical boundary conditions no flow boundary was assumed, in the eastern side prescribed head boundary condition was used, and in the northern side, Traweol River for some part and no-flow boundaries in the other part were used. In the vertical direction, the model is bounded by a recharge flux at the top and by impermeable layer at the bottom. The recharge fluxes used in the modeling are from the WetSpa model developed for the study area (Dujardin et al., 2011). The groundwater model was calibrated using observed head data from 26 monitoring wells measured from 1999 till 2005.

CONTAMINAT TRANSPORT MODEL

The purpose of the contaminant transport model is to compute the concentration of dissolved CAHs in an aquifer at any specified space and time. Modeling the fate and transport of contaminants in the aquifer requires not only the rate and direction of water movement in the aquifer, but also the transformation of contaminants and other chemical species that might influence contaminant degradation or transport. The rate of contaminant transport in groundwater is governed by many factors including advection, dispersion, diffusion, dilution, retardation and decay. Advection is the most important process that causes the dissolved contaminant to be transported along the flow path. The heterogeneities and non-uniformity of the aquifer matrix cause micro-scale spreading, commonly referred to as dispersion. Dispersion is a process that describes the spread of contaminants along and perpendicular to the flow direction. Diffusion is a very slow process that occurs along a concentration gradient. The combination of advection, dispersion, and diffusion results in dilution of the contaminant. On the other hand, contaminant such as chlorinated solvents can attach (partition or sorb) to the organic fraction of the aquifer matrix, thus slowing their transport in the dissolved phase. This effect is commonly referred as retardation. Contaminant type, aquifer mineralogy, and organic matter in the aquifer matrix are the main factors that affect sorption.

For this study, RT3D (Reactive Transport in Three Dimensions, Clement, (1997)) was used to model the reactive transport of chlorinated solvent in the aquifer. The RT3D code used in this study is a part of highly integrated simulation system called Processing MODFLOW. It utilizes the same finite-difference grid as of the MODFLOW model.

SOURCE INFORMAITON AND INITIAL CONDITONDS

Information related to source is one of the key inputs to any transport model. Similar to other contaminant transport modeling case studies the historical release of contaminant at the site is poorly known. The location of the source, the time period over which the source was active, and the magnitude of the source are all important characteristics which need to be known. Lack of information on contaminant sources may influence the selection and design of a remedial technology (Wiedemeier et al., 1996).

In this study, the infiltration of PCE and TCE into the underground is assumed to occur in the period between 1950 and 1990. Simulation was performed to predict the contaminant plume observed during the 2005-2007 monitoring effort completed at the study site. Therefore, the total duration for all the transport simulation was assumed to be 58 years. This period was divided into five stress periods to reflect the temporal change in contaminant mass release rates (Table 1). Hypothetical wells, which discharge the primary contaminants PCE and TCE, were used to simulate the sources. The locations of the wells correspond to the source locations are shown in figure 2a. The injection flow rates at all the source grids were maintained at relatively low levels so that the added flow did not affect the groundwater head contours. To define initial conditions, we assumed the presence of a pristine aquifer before the contamination period. To circumvent the limitations associated with the source uncertainties, the contaminant sources were quantified through model calibration.

REACTION PROCESSES AND KINETICS

Geochemical data are necessary to assess what types of reaction processes may occur at a site. Previous study conducted at the study site by Hamonts et al. (2012) indicated that the geochemical conditions at the site are appropriate to support reductive dechlorination processes. PCE and TCE are assumed to be the primary contaminants that were originally disposed at the site. Sequential dechlorination of chlorinated ethenes was used to simulate the degradation of PCE to TCE, TCE to DCE, and DCE to VC.

Determining the degradation rates are complex and might depend on several biogeochemical and environmental factors such as type and amount of dechlorinating bacteria present in the aquifer and availability of electron donors (Semprini et al., 1995). Therefore, for practical field scale applications chlorinated solvents degradation reaction are often hypothesized first-order decay reactions (Clement et al., 2000; Wiedemeier et al., 1996). In this study the rate of all the degradation reactions are assumed as first-order with respect to the respective contaminant concentration. The use of first –order degradation rates are justified when the microbial mass is not increasing or decreasing over time within the region of interest and for biodegradation at low-pollutant concentration levels (Schmidt et al., 1985).

DISPERSIVITY

To compute directional values of the hydrodynamic dispersion coefficients, RT3D model requires the cell by cell or layer by layer assignment of effective molecular diffusion coefficients, longitudinal dispersivity, and the ratio of transverse and vertical dispersivity. In this study we used the guidelines presented in Gelhar et al.(1992) and estimated the field scale dispersivity value for our problem as 10 m. The horizontal transverse dispersivity was assumed to be one order of magnitude smaller than longitudinal dispersivity (i.e. 0.1), while vertical transverse dispersivity was assumed to be two orders of magnitude smaller (i.e. 0.01).

SORPTION CONTSTANTS

We used an assumption of linear equilibrium to describe partioning process between the fluid phase and solid phase. Linear isotherm has been applied far more widely than nonlinear equilibrium isotherm for contaminant adsorption processes, because it is simpler and more convenient to use in practice (Zheng and Bennett, 1995). The linear isotherm uses a single distribution coefficient, kd, to define the relation between the concentration in the dissolved phase and concentration aqueous phase in the porous matrix (kd = mass concentration in the sorbed phase/ mass concentration sorbed in the solid phase). It greatly influenced by the fraction of organic matter in the porous media. Site-specific kd values can be calculated multiplying the octanol-water portioning coefficient of the contaminant with the fraction of organic carbon of the soil. The resulting estimates of kd values then used to compute the retardation coefficient using Equation 1.

—— (1)

Where R= coefficient of retardation (dimensionless), ρb= bulk density of aquifer (M/L^3), kd = distribution coefficient (L^3/M), n=porosity

Representative values of porosity were determined from Morris et al.(1966). Accordingly, an effective porosity of 15 % is initially assigned to all model layers. Bulk density of the aquifer material was assumed to be 1.7 kg/L.

RESULT AND DISCUSSIONS

The dimensions of the flow model are usually much larger than the dimensions of the polluted aquifer part. Further, transport modeling requires a considerable fine grid than pure flow modeling for numerical reasons. Therefore, the flow model discussed in the previous section was refined with telescopic mesh in to a fine grid around the polluted source area. Stream line was used as impervious boundary during singling out the flow model. Figure 2a shows the simulated steady state head contours and Figure 2b shows back ward particle tracking. Back ward particle tracking was performed to identify contaminant sources by introducing particles in SB1 and SB2 wells where contaminants have been detected.

Simultaneous calibration of source strength and degradation rates constant was performed with the available field data. The reaction rates constants assumed in the model were bounded by the literature given in Wiedemeier et al. (1996). The calibration was performed using the automated parameter estimation code PEST (Doherty et al., 2000) and parameters were varied to minimize the sum square error to match the observed concentration to the simulated concentration at the three monitoring wells during the period 2005 till 2007. The calibrated degradation rate constants for PCE, TCE, cis-DCE and VC respectively are 2.0×10^{-3}, 1.7×10^{-3}, 6.9×10^{-4} and 1.5×10^{-4} day^{-1}. The calibrated concentration release rates from the assumed sources are tabulated in Table 1.

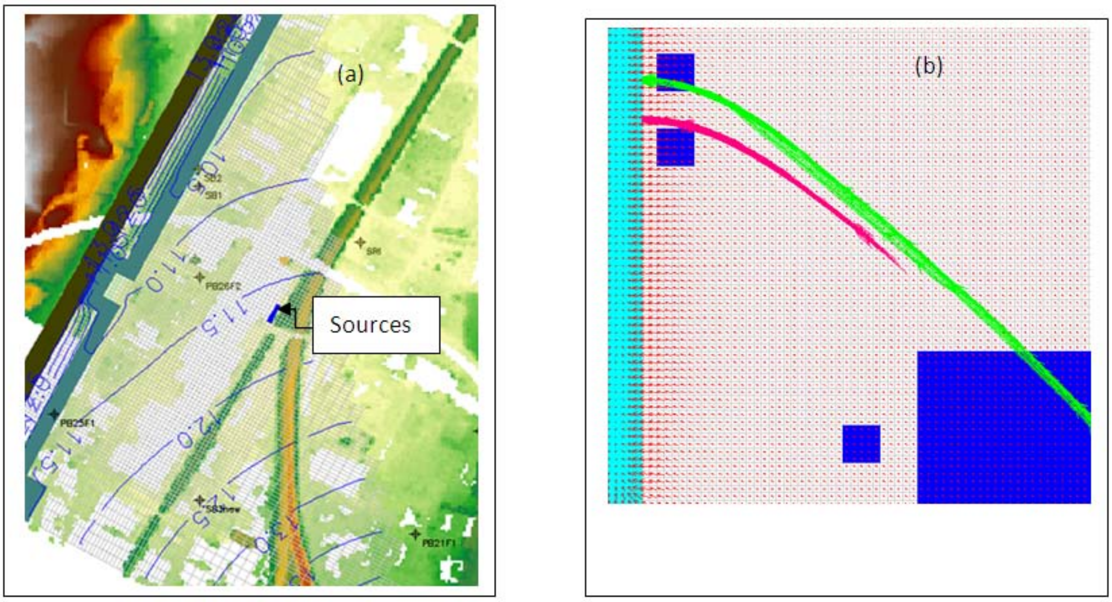

Figure 2: simulated groundwater heads (a) and backward particle tracking from the monitoring well SB1 and SB2

Table 1: Estimated contaminant release concentration.

Stress period	PCE (µg/L)	TCE (µg/L)	Period (years)
#1	44,845	23,687	1950 - 1960
#2	204,693	5000	1960 - 1970
#3	163,745	81,650	1970 - 1980
#4	5000	65,379	1980 - 1990
#5	0	0	1990 - 2007
Five injection wells with rates of 2 m^3/d was used in each stress period			

Sensitivity analysis

Sensitivity analysis is used to quantify the impact of input parameter variation on the model results. This analysis helps to quantify the uncertainties in the model, identify the model parameter that exerts the strongest influence on the model result, and provides an indication of the level of confidence that can be placed in the model results. The process involves a systematic variation of the parameter while noting the impact on simulated result. Parameter variation is expressed as a percentage change from the calibrated model value.

A sensitivity analysis was performed to investigate the influence of the reaction rate constants on the calibrated model. The reaction rates were perturbed 50% above and below the calibrated values (i.e. the baseline), and the resulting plume at 21137 days (November 2007) were shown in Figures 3. Results of the analysis showed that the plume extent is very sensitive to the degradation rates. When the degradation rate is increased the plume of PCE, TCE and cis-DCE is significantly distorted but VC didn't show significant change

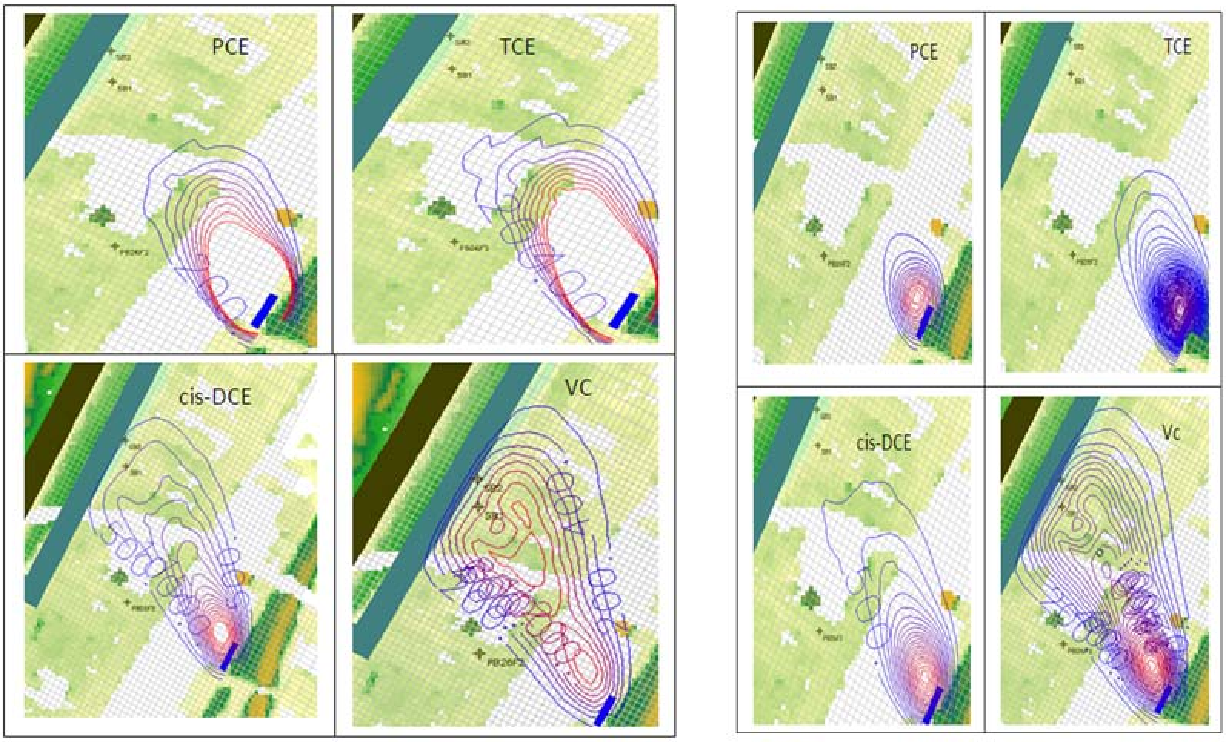

Figure 3: Simulated PCE, TCE, cis-DCE and VC for scenario 1(right) and scenario 2 (left) after 21137 days

CONCLUSIONS

A multi-species reactive transport model was applied at chlorinated solvent natural attenuation study site in Vilvoorde-Machelen. The flow and transport models were calibrated to reflect the field conditions observed at the site. In this study simultaneous calibration of the source strength and degradation rates were performed. The calibrated degradation constants are within the range of values reported in literatures. However, due to data deficiency, the calibrated parameters are by no means unique solutions.

Sensitivity analysis was also completed to understand the sensitivity of model parameter. Detail analyses were restricted to degradation rates, which are assumed to control the fate and transport of chlorinated solvents at the site. The result of the analysis also confirmed that the plume is most sensitive to degradation rates.

ACKNOWLEDGEMENT

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A semi-stochastic approach for pesticide risk assessment for the Odense river basin

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Pesticides application provides benefits as well as considerable toxicological risks to human society and environment, both in short and long term. Approximately 5.2 billion pounds (2.6 million tons) of pesticides were used worldwide in 2007, of which 40% was herbicides. The quantification of pesticide fluxes towards river systems at catchment scale remains a complicated issue due to the gaps in knowledge about the application rates of pesticides, application dates, and the high retention times of pesticides. Often, less then 1 % of the applied pesticides reach the aquatic environment, however, in absolute terms this is still a huge amount.

For this reason, a semi-stochastic approach is presented. A dynamic spatially distributed catchment model is used to quantify the total fluxes at river basin scale, with the aim to describe the overall mass balances properly. The total fluxes are then converted to probabilistic concentrations (cumulative distributions) on the basis of obtained stochastic flow-concentration relationships in observations. The ecotoxicological effects are assessed by computing the single substance PAF and msPAF (multi-substances Potentially Affected Fraction) of species in the aquatic community. The overall procedure is validated with biological data in the field.

Winterbeek:
a complex contamination requires an integrated remediation

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The Winterbeek is a seemingly untainted stream of 17 km in the Scheldt Basin District and its floodplain is a component of European as well as national ecological networks.
Due to years of industrial discharges of a phosphoric ore plant, this stream is heavily contaminated: In the past (up till 1990) large quantities of heavy metals (Cd, As,...) and radioactive substances (Ra) were discharged in this stream. Nowadays the wastewater discharge still contains large quantities of calcium chloride. Soil investigations demonstrated the occurence of contamination in the sediment, the banks and the flooding area (toplayer, which is mapped out thanks to dose rate measurements). Remediation of this contaminated area is needed. This poses challenges on different levels.

Environmental-technical challenge The presence of contamination in different compartments shows the first challenge : pollutants can spread within a particular compartment, but may also spread to another. Knowledge of the global water and soil system is the basis for the determination of remediation actions. After all, an intervention in one compartment may affect another compartment.

Legal challenge The second challenge is therefore evenly important: soil, surface water, ecology, radioactivity - each discipline has a separate jurisdiction and different authorities, each with their own interests and perspectives. This fragmented vision gives rise to a complex problem and requires an integrated approach.

Organizational challenge The actual remediation actions require a exhaustive preparation.

Integrated solution The remediation requires an integrated approach: integral consultation can align the objectives for a coherent vision in order to achieve a win-win story. In this case, the discharge permit of the phosphoric ore plant was recently renewed, which triggered the cooperation of the different authorities. In 2014 the concentration of $CaCl_2$ in surface water will be decreased with 90%, which makes the start of a sustainable remediation feasible. Therefore OVAM (Flemish Waste Agency) and VMM (Flemish Environmental Agency) started the remediation plan, in cooperation with the other stakeholders.

Development of Rehabilitation Technologies and Approaches for Multipressured Degraded Waters and the Integration of their Impact on River Basin Management – FP7 AQUAREHAB project

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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 are being developed to cope with a number of priority contaminants (nitrates, pesticides, chlorinated compounds, aromatic compounds, mixed pollutions…) within heavily degraded water systems. Methods are being developed 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 are made to connect the innovative technologies and river basin management. One of the outcomes of the project will be a generic river basin management tool that integrates multiple measures with ecological and economic impact assessments of the whole water system. The project will aid in underpinning river basin management plans being developed in EU Member States, and will demonstrate cost effective technologies that can provide technical options for national and local water managers, planners and other stakeholders (drinking water companies, industry, agriculture, recreation and nature conservation) to revive highly polluted areas.

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).

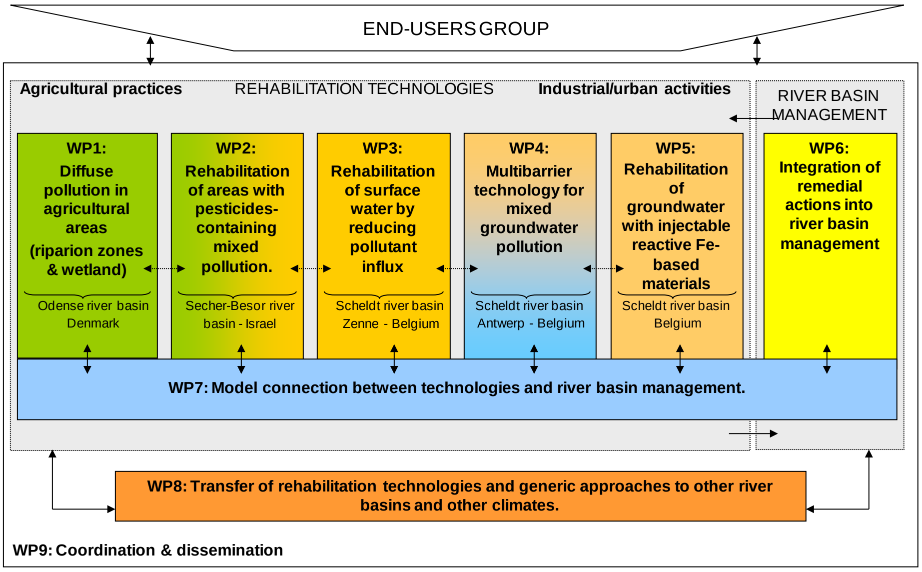

Figure 1: ***Schematic overview of the AQAUREHAB project structure***

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

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, additional river basins are being included. This paper summarises some activities and results obtained within AQUAREHAB.

RESULTS

Rehabilitation technology 1 – Activated riparian zone (WP1)

The installation of wetlands in the riparian zone is considered as a very promising approach for mitigating the diffuse pollution of agricultural pollutants. In this part of the AQUAREHAB project, we study and quantify how wetland zones mitigate pesticide and nitrate diffuse pollution into surface water and how this can be possibly activated and maximized. The processes contributing to nitrate and pesticide removal in wetlands are therefore being studied at the field and at lab scale and these data are being used for modelling the fate of nitrate and pesticides in wetland riparian zones. Two wetland field sites within the Odense River Basin District (Denmark) are being studied: (1) the "Brynemade" site, as a model of a well-established wetland, and (2) the "Skallebanke" site, a freshly restored wetland. Both sites were equipped for field monitoring earlier in the project.

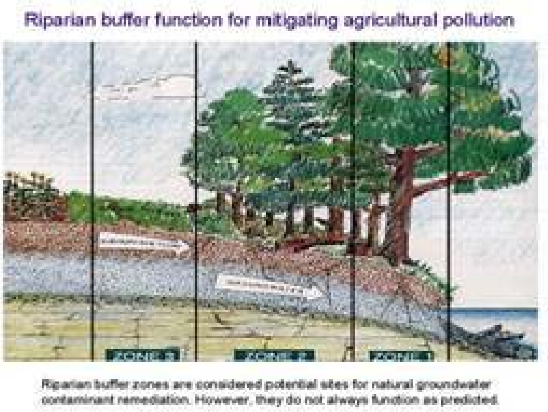

Figure 2: Riparian zone

Monitoring campaigns were performed at the two wetland field sites in order to built their respective hydrogeological models and to acquire information about the groundwater chemistry. Based on these measurements, a final 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. The hydrogeological model and the data on nitrate distribution are used for reactive transport modelling in WP7. As previously observed with the Brynemade site, the site at Skallebanke showed clear pesticide mineralization capacities in the subsurface despite the apparent lack of pesticides. Bromoxynil was degraded with oxygen, nitrate and ferrihydrite as electron acceptors. Prosulfocarb was only degraded with oxygen as electron acceptor. Moreover, top samples showed a denitrification capacity. A fourth and last ecological survey was performed and results from all survey campaigns are being compiled and analyzed.
Lab experiments further showed the capacity to degrade/mineralize the pesticides isoproturon (IPU) and MCPA in the above surface compartment of a wetland. 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 at different time points over a winter period did not give indications for seasonal changes. Continuous experiments were performed to explore denitrification activities in subsurface environments. 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.

Rehabilitation technology 2 – Drain with smart carrier materials (WP2)

The overall objective of this work package is to develop a tailored carrier/bacteria material that can be implemented in an open or closed drain, to remediate polluted water flowing through the drain. The field site considered as example within AQUAREHAB for this technology is an industrial site within the Secher-Besor river basin in Israel. The water at the site is brackish and is polluted with an extended mixture of pollutants. The focus in AQUAREHAB is on pesticide removal.

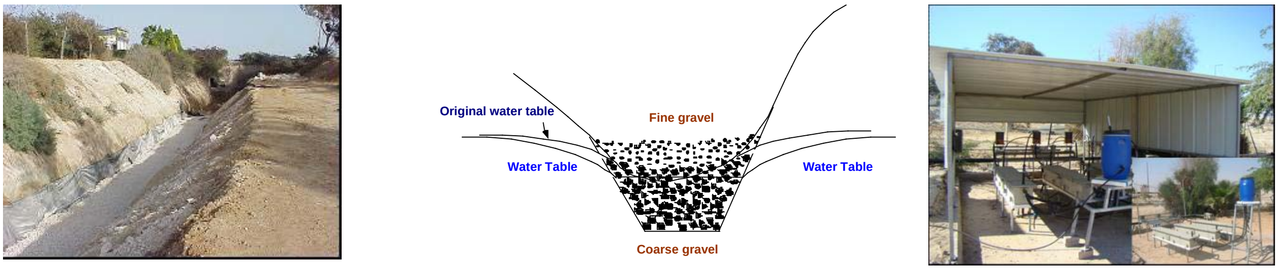

Figure 3: Open trench where tailored bacteria/carrier materials will be introduced for semi-passive treatment of drained pesticide-containing water.

A first part of the study is dedicated to the design of tailored carrier-bacteria mixtures. So far, a combination of experiments and tests were performed in order to find the best arrangement of bacteria and carriers. Natural carriers (chalk, sand, gravel) were tested with indigenous microbial population under both natural and lab conditions. Another line of experiments dealt with the combination of “synthetic” carriers available on the marked (GAC, biosep beads, ...) in combination of selected herbicides degrading strains. Finally a new carrier based on calcite was developed and its properties were evaluated. These carriers were tested in regard to their herbicide sorption/desorption capacity, biofilm formation, compatibility with herbicide degrading bacteria. The results suggested that combinations of native microflora with natural carriers was effective in degrading the dissolved organic compounds of the contaminated site water but not the target herbicides. The selected degrading strains (like atrazine-degrading Pseudomonas sp. Strain ADP, carbofuran-degrading *Sphingomonas* KN65.2) were able to degrade the selected compounds at high salinity and thus may be applied to the field as necessary inoculums. In respect to the synthetic carrier, it was decided to focus on XAD-7HP. An atrazine degrading culture was isolated from the high salinity groundwater from the site in Israel.

In a second part, the technology is being demonstrated at pilot scale at the Israeli site. A pilot system that was earlier design and compiled, has been tested and optimised hydraulically. Three parallel artificial drains filled with chalk, are being fed with real groundwater amended with carbofuran. Without inoculation, no removal of carbofuran was observed, indicating that inoculation with specialised bacterial strains can have added value. An inoculum of *Sphingomonas* sp. KN65.2 is being prepared.

Rehabilitation technology 3 – Stimulated sediment biobarriers (WP3)

For WP3 the main aim was to develop techniques to prevent the influx of CAHs from a groundwater plume into a river. As a test case, the Zenne site in Vilvoorde Machelen (Belgium) was selected. The techniques considered are (1) stimulation of the biodegradation just upstream of the sediment zone in the aquifer, and (2) capping of the sediment with a permeable biodegradation stimulating material.

Tests performed at batch scale indicated that vinyl chloride (VC), cis-dichloroethene (cDCE) and trichloroethene (TCE) degradation occurred in the aquifer compartment only when external carbon sources were added to aquifer microcosms. In situ injection of glycerol close to the CAH-plume source, resulted in a stimulated degradation of cDCE as the main pollutant with concomitant increase in the community size of *Dehalococcoides* spp. and their reductive dechlorination genes. Sediment capping technology was chosen as the rehabilitation technology for the sediment zone.

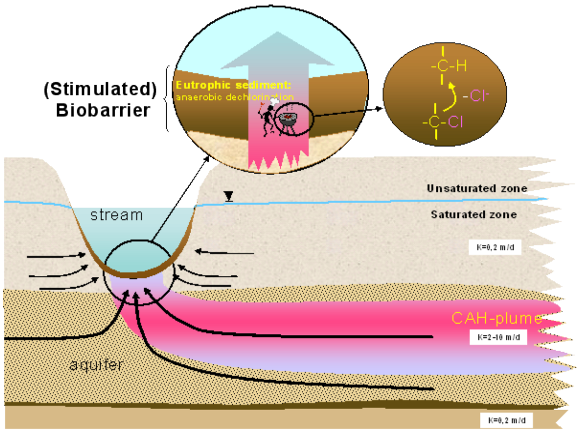

Figure 4: stimulated sediment/aquifer biobarrier technology to inhibit the influx of pollutants from the groundwater into the surface water.

Batch scale screening of 5 different solid organic materials (SOMs) as potential capping materials that can be adapted as the reaction media in a bioreactive cap showed enhanced and long-term reductive dechlorination of VC/cDCE. Of all SOMs, tree bark showed the most promising results with the highest stimulation effect on the dechlorination community and the lowest channeling of the released carbon/electron to methanogenic population. The adaptation of tree bark into a bioreactive cap is currently being studied under dynamic conditions in small columns.

Since 2007, a wastewater treatment plant (WWTP) has been in operation in Vilvoorde Machelen, resulting in an increased oxygen concentration in the surface water. The infiltration of oxygenated surface water into the sediments can stimulate the aerobic biodegradation of VC. This concept was proved in river-bed sediment microcosms showing co-occurrence of anaerobic and aerobic VC degradation potential and further verified by monitoring the changes in abundances of biomarkers associated with known microbial guilds and functional catabolic genes involved in anaerobic and aerobic VC degradation. Although an increased oxygen and decreased dissolved organic carbon (DOC) concentration was observed in the Zenne surface water, ecological surveys between 2009 and 2011 indicated that the ecological status of the Zenne site is not promising and has not improved during this time period. Currently, samples from sediment cores are being analysed by pyrosequencing to investigate the effect of these changed physicochemical conditions on the structure of the microbial community. Since 2010, no CAH pollution has been detected in the sediments of the Zenne River. Therefore, it is not possible to perform in situ rehabilitation technologies. However, based on current data obtained from lab experiments and field monitoring in the past, different scenarios to stimulate the CAH degradation will be modelled and will provide the best approach to prevent the influx of CAHs from a groundwater plume into a river.

Rehabilitation technology 4 - Multibarrier technology (WP4)

The multibarrier technology is an innovative in-situ technology to improve the quality of groundwater. It consists of a combination of permeable reactive barriers (PRBs) and reactive zones (RZ), in which different pollutant removal processes are combined. The multibarrier considered within AQUAREHAB comprises 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. This multibarrier concept is being studied for an industrial site in Belgium (Scheldt river basin).

Via lab scale experiments, corrosion rates of the zerovalent iron were determined and a numerical model (describing CAH-degradation, precipitation and corrosion) has been developed and is being used to predict the lifetime of the ZVI-barrier. Lab scale experiments were also used to determine CAH-biodegradation potentials and rates. The degradation rates are being compared with the number of specific gene & transcript copies that were detected via q-PCR, to find correlations. Stable Isotope Fractionation factors during CAH-degradation by ZVI have been determined, and a new approach to use the data to predict the occurrence of CAH-degradation at a site is being evaluated. At the studied site, additional site characterizations and monitoring campaigns were performed, and revealed among others a temporally reversed groundwater flow across the ZVI-barrier after a rain event. All gathered data is input for a numerical model (developed within WP7), which allows evaluating the impact of the multibarrrier technology on the water quality in time and in space. The aim of the model is to realise a more accurate design of PRBs and RZ, including information on the longevity of the technology. Angled core samples were taken across the ZVI-barrier and adjacent aquifer, and showed that (1) the barrier was still very porous, (2) that the iron was still reactive, and that (3) a microbial population was present in the ZVI-barrier that differs from the one observed in the adjacent aquifer (pyrosequencing).

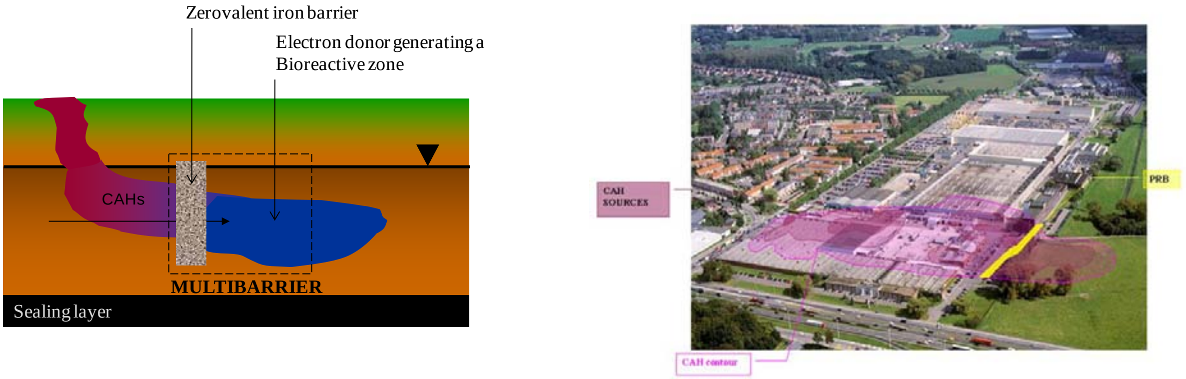

Figure 5: Studied multibarrier concept & visualisation of the plume at siteA.

Rehabilitation technology 5 – Injectable Fe-based materials (WP5)

Zerovalent iron filings are being used throughout the western hemisphere for in-situ remediation of groundwater contaminated with chlorinated compounds. Conventionally, these particles are installed as a permeable reactive barrier (PRB) intercepting a contaminant plume. This application has two important drawbacks: Since only the plume is being treated, no source depletion occurs and therefore no shortening of remediation time is to be expected. The second drawback is that the emplacement of PRB is costly and restricted to areas that can be accessed easily. Injection of micro- and nano-scale particle will overcome these obstacles. The particles may be injected directly into the source, thus depleting it efficiently and they may be injected underneath buildings as long as a limited access to drilling equipment may be assured. Besides ZVI, also injectable iron-oxides are studied for stimulating BTEX-biodegradation.

During the first phase of AQUAREHAB WP5 the reactivity and transport characteristics of different injectable particles were screened in the laboratory, first steps towards a measuring technology were taken and possible field sites were screened for a pilot application. In the second phase this research was intensified. While additional particles were developed and tested to ensure maximum reaction efficiency, it was evident that the transport of the particles could be a major challenge. Therefore the suspension fluid had to be improved (viscosity control by guar gum). A large number of experiments had to be conducted to test the rheology and the corresponding transport properties of the new suspension but also the influence of the new suspension design on reactivity toward the target contaminants. The measuring device based on magnetic susceptibility, envisioned in phase one, was improved upon, built and tested in the laboratory.

A monitoring concept for a field site was developed and the necessary hardware was assembled. For the selected site in Belgium, a pilot test site was designed taking into account the low groundwater flow velocity at the site. Different injection technologies were investigated and evaluated in view of their applicability at the pilot site. Based on the relatively low permeability, injection via fracturing with direct push was selected. October 2011 the monitoring equipment was installed at the site and November 2011 100 kg of guar gum stabilised micro-scale ZVI was injected. Monitoring campaigns are ongoing to reveal the fate of the ZVI in the subsurface and its effect on the CAH-concentrations.

Figure 6: Pilot test with Injectable Fe-based particles to create reactive zones for groundwater treatment.

Numerical models describing the technologies (WP7)

The objectives of this task are (1) to develop reactive transport codes and hydrological models for simulating pollutant removal in riparian zones, river beds and groundwater, (2) to design experimental work related to the technologies, (3) to evaluate models on various cases and to generalize the model results, and (4) to develop a common modelling framework for incorporating model results in catchment models. Since the start of the project, a 2D field model for pesticide and nitrate removal in riparian zones and wetlands, a model for biodegradation of chlorinated compounds in river beds, a model for degradation of chlorinated compounds in a zerovalent Fe multibarrier and an hydrological model for source detection at a industrial site were developed and calibrated. The modelling results were used to improve the design and interpretation of feasibility tests for the various technologies. Subsequently, the developed models were evaluated using monitored field data from various project sites, including; a wetland receiving water that has passed through agricultural soils containing nitrates in the Odense catchment (DK), a drained area in an industrial site contaminated with a mixture of pollutants in the Sechor Besor basin (IL), a CAH contaminated groundwater-surface water interaction zone in the Zenne subbasin (BE) and a CAH contaminated site treated with a Fe-PRB in Antwerp (BE). The models being thoroughly evaluated through laboratory and field experiments are intended to simulate the effects of management scenarios at the regional or river basin scale.

Integration of rehabilitation technologies impact into river basin management (WP6)

The objective of WP6 is to develop a generic collaborative management tool 'REACH-ER' that 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. A great deal of effort has been put into the development of fate models for the Odense and Scheldt River Pilot Areas. Refinements in the fate models have been made with the purpose to better represent the processes behind the pollutant fluxes that are of concern in the AQUAREHAB project. In the Scheldt river (PCRaster fate model), work has been done on the fluxes of nitrogen through the groundwater while in the Odense river (SWAT fate model) a better representation of the fluxes (nitrogen & pesticides) through tiles/lateral/groundwater flow is aimed for. In addition, a separate fate model for contaminated sites, called COMFRACS (COnceptual Model FRAmework for a regional assessment of Contaminated Sites), is developed to assess the effects of regionally distributed contaminated sites on groundwater quality at the groundwater body scale. The model is demonstrated for chlorinated aliphatic hydrocarbons (CAH) for a 1 km grid. In terms of assessing the eco-toxicological effect of chemicals in rivers new approaches have been developed to provide better information with respect to (a) sensitivity of individual species towards specific chemical contamination and (b) recovery potential of respective species. Both are included in the SPEAR concept (SPEcies at Risk - http://www.systemecology.eu/SPEAR/index.php), which is currently being validated within AQUAREHAB. For the economical analyses of water quality remediation measures, a database structure has been worked out and data on a number conventional remediation measures was inserted in the database. The development of the DSS REACH-ER has followed two major lines: 1. a light-weight, probabilistic alternative to complicated, process-based fate models, based on the Bayesian Belief Network (BBN) approach. This approach represents model results in a comprehensive and probabilistic way without having the same (high) computing demand of many process-based models, and can therefore be used as a management tool. 2. A WEB-based front end version of REACHER that can be used to present scenario-based model results and interact with stakeholders, so as to build and analyse scenarios with different rehabilitation measures. This is an on-going process in AQUAREHAB involving active collaborations with other partners of the project. In summary, progress has been made within the different modules, while the linking of the different parts remains a challenge for the next period.

CONCLUSIONS

The first phase of the AQUAREHAB project is being finalised. The outcomes generated so far are products (improved reactive particles), numerical models describing the remediation technologies (to estimate impact in time & space), fate models at river basin scale, a concept for a water management tool (REACHER), and generic guidelines supporting potential users of the technologies, the models and the tool.

Within AQUAREHAB it became clear that integration of surface water as well as groundwater in river basin management is challenging. Up to now river basin management is mainly focussed on surface water and less on groundwater. Groundwater and surface water do interact, but were found to be different since (1) river water is much more dynamic than groundwater, where flow velocity can be as low as some meter per year do occur; (2) the type of pollutants that are of concern in surface water and groundwater are different. The WFD lists mainly pollutants relevant for surface water; (3) The procedures elaborated to evaluate good quality of surface water are only partially applicable for groundwater. For the latter, hydro-morphology and the ecological evaluation elaborated so far are not relevant. Groundwater may require a different approach in river basin management in comparison with surface water for these reasons. Time steps in the fate models for groundwater can be bigger for groundwater, while smaller grids may be needed.

In the second phase of AQUAREHAB, a number of the approaches and guidelines developed within the first phase will be extrapolated to other cases and/or other river basin systems. The generic character will be tested as such. Potential extrapolation cases have been identified and proposals are being worked out more in detail. The practical start of this phase is envisioned for summer 2012. This effort will results in improved generic guidelines which will be public documents.

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Tailored Management of Hazardous Substances Diffuse Sources in River Basins

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ABSTRACT: Hazardous substances are the subject of various policies in Europe and European Union Directives. Appropriate requirements are defined for example by the Water Framework Directive. Diffuse sources become the more important as the active sources are successfully dealt with by phasing out the use of these substances in economy and society and mitigating the industrial emissions. Persistent organic pollutants and metals are of special concern in that matter. Contaminated soil and groundwater are potential emission sources predominantly on local scale in the catchments being under long term anthropogenic stress. This situation is usually related to contaminated sites, sediments, landfills of hazardous wastes and residual wastes in the environment. Soil and groundwater as sources of hazardous substances are in most of cases difficult to be controlled, and require good recognition and characterization of the problem and wholistic risk management approaches. Analysis of cost-efficiency of mitigating identified problems with technical approaches shows that in many cases it is low. In other complex situations such as industrial landfills they can be overshadowed by other environmental problems and related decisions. The situation is even more complex on catchment scale. In other cases, although, the most contaminated areas can be identified, but technical mitigation measures can be of low feasibility, high costs and low potential efficiency. The current experience shows that combination of technical and none technical; short and long term approaches has to be recognised in tailored management of diffuse pollution with hazardous substances.

INTRODUCTION

Hazardous substances are the subject of various policies in Europe and European Union Directives. Appropriate requirements are defined for example by the Water Framework Directive. Diffuse sources become the more important as the active sources are successfully dealt with by phasing out use of these substances in economy and society and mitigating the industrial emissions. Persistent organic pollutants and metals are od special concern in that matter. Contaminated soil and groundwater are potential emission sources predominantly on local scale in the catchments being under long term anthropogenic stress. This situation is usually related to contaminated sites, sediments, landfills of hazardous wastes and residual wastes in the environment.

Soil and groundwater as sources of hazardous substances are in most of cases difficult to be controlled, and require good recognition and characterization of the problem and wholistic risk management approaches. Analysis of cost-efficiency of mitigating identified problems with technical approaches shows that in many cases it is low. Furthermore, as in an example of a pesticide landfill in Jaworzno (Poland) technical options can lead to temporary elevated impact (emissions) and risk for local community. In other complex situations such as industrial landfills they can be overshadowed by other environmental problems and related decisions. In another case studied in UPSOIL project the railway area contaminated with diesel oil, being the source of continuous pollution to a nearby river, a combined short and long term technical approach can be the sustainable solution.

The situation is even more complex on catchment scale. In a study done in Poland within SOCOPSE project a Kłodnica river catchment located in a highly industrialized area was researched for contamination of mercury, cadmium and polycyclic aromatic hydrocarbons. The performed study showed that especially for mercury the diffuse pollution, including the sediments, industrial and municipal landfills and postindustrial areas, is the essential source of contamination but at the same time none of those is a dominating source category. In this situation appropriate catchment scale risk management is the best solution. In other cases, although, the most contaminated areas can be identified, but technical mitigation measures can be of low feasibility, high costs and low potential efficiency. Such situation was identified for example in COHIBA project concerning the Baltic Sea basin where dioxins, tributyltin compounds and cadmium were identified in relation to previous industrial activities and soil sediments contamination.
The experience shows that combination of technical and none technical; short and long term approaches has to be recognised in tailored management of diffuse pollution with hazardous substances.

THE SOURCES

Hazardous substances are emitted at various sources related to industrial activities, use of industrial and commercial products, waste and wastewater management and as a result of land contamination. Lately diffuse pollution is considered as remaining important source for many substances which were used in the past (Krupanek, 2011). One of the reasons is the declining role of industrial and product related emissions resulting from implementation of industrial and product policies. At the same time there is visible change in the impact on water resources, with improvements in environmental management of point sources (the e.g 7 FTP EU project SOCOPSE – see www.socopce.se).

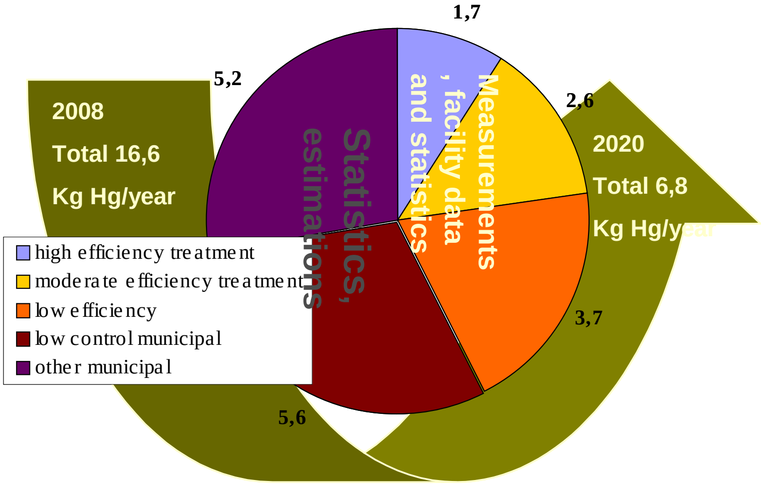

Figure 1: industrial sites and landfills in Kłodnica catchment

In the case example from SOCOPSE project of Upper Silesia region, mercury, cadmium and polychlorinated hydrocarbons emission from diffuse sources are important sources of surface water contamination. Graph present (Figure 1) prognosis of mercury load in Upper Silesia Kłodnica river catchment which is located in highly industrialized region. Diffuse pollution sources include contaminated sediments, soil and groundwater, run off, residual wastes, landfills. Soil contamination is one of the essential source of hazardous substances. It is connected with post-military sites, airfields, terminals, distribution network and fuel depots Industrial facilities, landfills, and port areas which are the These sources are frequently contaminated with hydrocarbons, polycyclic aromatic hydrocarbons and chlorinated compounds and metals which are the most common pollutants and in many case with leas but more hazardous substances. Some of the hazardous substances such as dioxins and furans, trbutyltin, endosulfan, Cadmium and mercury are accumulated in sediments, soils or other “historical” deposits in long-life products. For many substances, waste is an important pathway for emission of hazardous substances (brominated flame retardants, short and medium chain chlorinated paraffins and endosulfan). It should be stated that the relative emissions from diffuse sources are much lower then the emissions from active sources which mean that the risk control is the most efficient measure.

CATCHEMENT AND RIVER BASIN PERSPECTIVE

Problem definition on catchment of river basin perspective depends highly on the quality of accessible information concerning water bodies their chemical and ecological status. For problem identification at catchment or river basin scale the Material Flow Analysis (MFA) tool is used with emission inventory, estimation of emission loads and further modelling of substance distribution in environmental media. Uncertainty of evaluation is important. Accepted level of data reliability should be clearly defined in that aspect. MFA assessment can allow for determining relative importance of the identified emission sources.

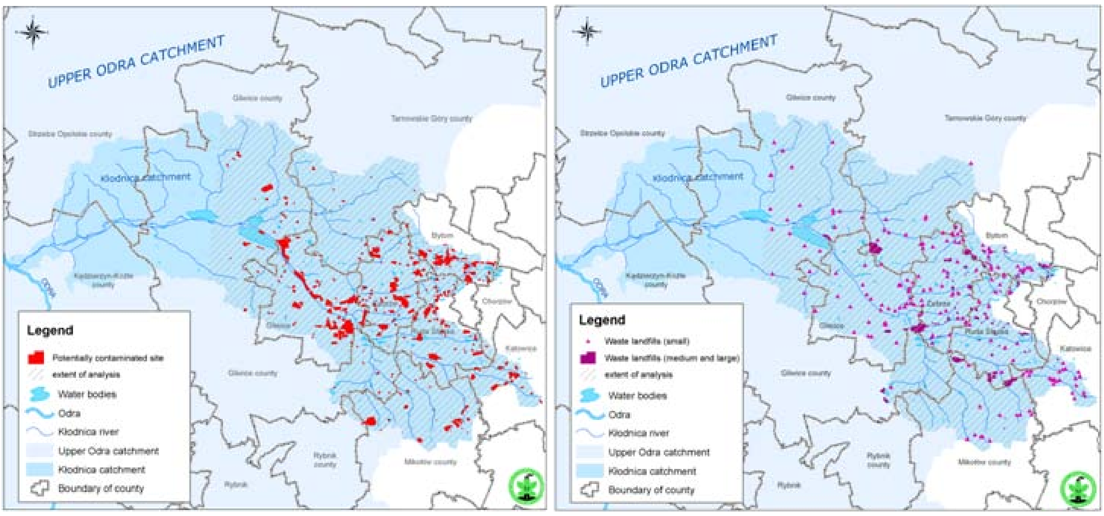

Figure 2: industrial sites and landfills in Kłodnica catchment

Internal and external factors of catchment or river basin management have to be taken into account. Contaminated sites are frequent at areas with highly modified water bodies located in urbanized and industrialised region. Another issue is the time lag that can be observed for many substances between awareness of harmful characteristics) and corresponding regulations as well as decreasing trends in the environment. It is also relevant for contaminated sites where the relative impact can be low in comparison to other emissions. Frequently the active sources in the area overshadow the impacts of diffuse sources. Buffering capacity of environmental and degradation potential e.g natural attenuation should be recognized in relation to human health and environmental risks. Unlike the site scale, on catchment scale many factors can influence the risks for surface water or groundwater resources The possibility to assess the changes in the water quality in the catchment often is very limited. From the results of COHIBA project (www.cohiba-project.eu) it is observed that in some cases the hazardous substances are products of other substances degradation, like e.g. octylphenols and nonylphenols and their etoxylates or perfluorooctanes from precursors. Municipal landfills with poor protection are a source of emissions of these substances to water environment.

MEASURES

Measures for reduction of emissions should be selected on the basis of their technological feasibility, cost efficiency and the highest reduction potential. They should be risk oriented and be related to water bodies as defined in Water Basin Management Plans. For management of diffuse sources of hazardous substances there should be distinguished:

- technical measures (remediation techniques of contaminated sites, risk oriented measures e.g reactive or hydrolic barriers, phytoremediation)
- risk management oriented measures e.g. monitoring, land cultivation practices

Sustainability of remediation is underlined as the key direction of improving soil and groundwater management (Ellis, Hadley, 2009; NICOLE 2010). For this reason it is important to take into account co-benefits and multi goal approaches related to various basic actions and policies undertaken or planned in the catchment. Remediation techniques can be very specific to a given substance or can tackle a set of hazardous substances. For substance oriented measures, the cost benefit ratio can be expected much higher. Environmental impacts of pollutants releases or degradation processes has to be taken into account along with structural economical and social aspects. Technological risks can be connected with emissions to air and to water during excavations of contaminated material and its transport. Measures applied at a given site should meet conditions and requirements which are defined in management according to land uses: urban areas, industrialised areas. From catchment perspective emissions for persistent pollutants on large scale e.g contamination of sediments or soil can be relatively more important than selected hots spots. For those large scale measures has to be applied eg contaminated soils like phytoremediation or point scale measures can be distinguished.

For different regions efficiency of the techniques may greatly vary due to region-specific conditions. There are differences in using in-situ technologies in particular countries with preferences to use ex-situ methods on the basis of strict regulations e.g. waste management (7 FTP EU project UPSOIL, see: www.upsoil.eu). Green remediation concepts are not recognized sufficiently by the practitioners. Long term solutions are also avoided. The merits of combining technologies are not recognized as well.

STRATEGIES

The management cycle as defined in Water Framework Directive is very important allowing for step by step approach in complex situations and gradual improvement of the river quality and its catchment. The catchment or river basin oriented solutions can be tailored according to specific situation in a given case with regard to identified concrete contaminated sites and areas. Apart from the hot spots requiring immediate intervention because of the risks or the legal requirements, for the most of the potential diffuse sources a long term scenario of continuous improvement has to be considered with appropriate definition of long term and short term measures (remediation activities). This should be analysed in the context of driving forces of socio-economic development, environmental policy impacts and natural environmental changes are identified. Good example was provided in SOCPSE project for Kłodnica river case study.

There are many aspects and factors which has to be taken into account. Baseline scenario for changes in source categories has to be determined on the basis of analysis of already implemented or proposed investment projects, plans and programs. High importance of autonomous developments ensuing from ongoing socio-economical activities and changes, undertaken and planned investments in water protection infrastructure, impact of EU policies and opportunities arising. It concerns the diffuse pollution as well. For example the industrial policy helps in improving the soil management in existing facilities. The environmental liability full implementation will also have a great impact on the practices of land management with better characterization of problems and selection of measures. The baseline scenario should be well documented and assessed as to the changes in the impacts of emission sources (Figure 3).

The basic question is whether the baseline scenarios can be sufficient for achieving good chemical and biological status and if not, whether additional measures will be needed in the context of hazardous substances. The need for additional measures cannot be evaluated without good knowledge of the river system and better emission assessment, especially for the diffuse sources. For this the gradual improvement of understanding of the problems has to be incorporated into management with the focus on the existing potential for improvement (technological, organizational) in many of the sources.

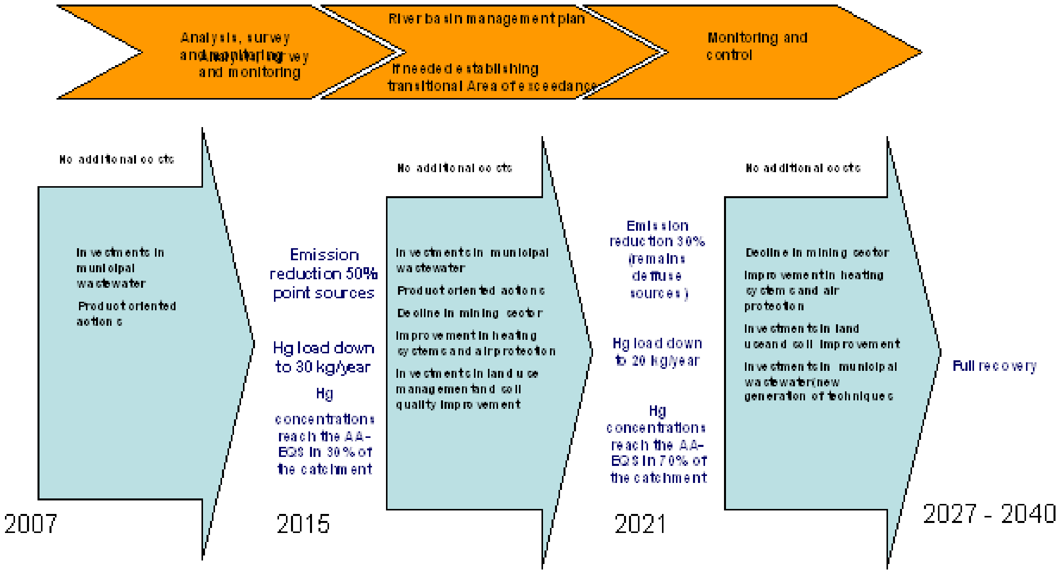

Figure 3: Role of diffuse pollution sources in long term perspective of river catchment improvement (Mercury reduction in Kłodnica case study – project SOCOPSE)

Institutional aspect is very important and has to be included in the decision making process along with technical and socio-economic aspects. It concerns the decision making process, the level of decision, the division of competences and responsibilities between local, regional and national administration. In the management the following issues has to be taken into account:

- Complex management pattern and decision making process,
- Data provision on the environmental quality and integration of monitoring efforts,
- Efficiency of law execution e.g. not controlled emissions,
- The political issue: low policy relevance of hazardous substances,
- Public awareness, interest and perception.

It should be underlined that strong interaction with stakeholders helps in better understanding of the existing and future problems and to define the main challenges for the catchment and tailor the approaches.

CONCLUSIONS

Tailored management of hazardous substances diffuse emissions on catchment and river basin scale can be beneficial from the perspective of cost efficiency and sustainability of the solutions. The following recommendations for improvement of management can be drawn out from the current experiences:

- Development of the diffuse component in water management system as essential factor of achieving improvement in the catchment with competences and responsibilities and decision making processes
- Verification of stakeholders involvement and socio-economic tools application
- Handling the situation with dynamic processes in the catchment, policy impacts, socio-economic and environmental changes
- Application of tools for assessing relevance of diffuse sources on catchment and site scale with the focus on risks,
- Definition of the quality of information on each level of assessment sufficient for decision making and appropriate handling uncertainty in available data evaluation,
- Securing data quality, recognition of monitoring requirements, and modeling of the river quality.

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SWAT model as a first step in the assessment of surface-groundwater interactions and remediation needs

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Waterborne pollutants transport is a multifactor dependent process, which is difficult to be monitored and simulated. The reactive transport of pollutants depends on natural factors (e.g. meteorology, geology, soil, morphology, vegetation) and anthropogenic factors (among others: land morphology changes, agriculture, intensive exploitation of minerals and groundwater, wastewater discharges, landfills). Remedial or preventive actions can be taken basing on the information about interactions between human activities and the response of environment only. This is an issue of great importance to densely populated and industrialised areas.

This presentation includes results of the first stage of project aimed at development of complex surface water and groundwater model simulating the reactive transport in a highly urbanised and industrialised river basin. The case study area for this project is the Nacyna River basin in the southern Poland. This basin of appr. 70 km^2 is covered by mixed landuse including: residential areas, agriculture, industry (coal mines), and less than 15% of natural green areas. The surface water quality in the study area is affected mainly by mines' water discharges and industrial run-offs resulting in the extreme salt concentration~~s~~ (exceeding even those in the Baltic Sea). Groundwater is also of poor quality with high concentration~~s~~ of nitrogen compounds (result of agricultural activities, wastewater discharges or natural processes in the aquifer). In order to assess the impact of human activities and natural processes on the: 1) quality of surface water, 2) rate of infiltration into the shallow aquifer and 3) infiltrating pollutants load, the SWAT (Soil and Water Assessment Tool) model was used. The first model outcome – relation of human activities and surface water quality – can be used directly by decision makers responsible for water resources management. The second one – quantitative and qualitative assessment of the infiltration – may be used after the further processing by more detailed groundwater reactive transport model such as PHT3D.

The presented work shows high seasonal variations in the water balance and water quality, and confirms significance of dynamic approach in the assessment of factors affecting water quality and needs for remediation actions.

Validation of SSD in retrospective risk assessment of herbicides – the Scheldt river basin case study

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Species sensitivity distribution (SSD) is commonly used in prospective risk assessment to derive predicted no effect concentrations (PNEC) or environmental quality standards (EQS) for individual chemicals such as pesticides. The application of SSD in the retrospective risk assessment of chemical mixtures at the river basin scale (i.e. the estimation of 'multiple substance potentially affected fractions' - msPAFs) has been suggested but detailed critical assessment of such an application is missing. The present study investigated the impact of different data validation approaches in a retrospective model case study focused on seven major herbicides monitored at the Scheldt river basin (Belgium) between 1998 and 2009. The study demonstrated successful application of the SSD approach. Relatively high impacts of herbicides on aquatic primary producers were predicted (up to 40% of the primary producers were potentially affected, as predicted by chronic msPAF). The risks of the studied herbicides decreased during the 1998-2009 period, along with decreasing concentrations of toxic pesticides like simazine or isoproturon. Various data validation approaches (removing of duplicate values and outliers, testing different exposure durations and purities of studied herbicides, etc.) substantially affected SSD at the level of individual studied compounds. However, the time-consuming validation procedures had only a minor impact on the outcomes of the retrospective risk assessment of herbicide mixtures at the river basin scale. Selection of the appropriate taxonomic group for the SSD calculation and selection of the species-specific endpoint (i.e. the most sensitive or average value per species) were the most critical steps affecting the final risk values predicted. The present validation study provides methodological contribution for the practical use of SSD in the retrospective risk assessment of chemical mixtures. [Supported by the EU FP7 project AQUAREHAB and by the project CETOCOEN (no. CZ.1.05/2.1.00/01.0001) from the European Regional Development Fund.]

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

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Various methods to evaluate impacts of contamination of aquatic ecosystems have been suggested including specific bioindices such as saprobic index or SPEAR_pesticides index, which has been shown to reflect pesticide pollution. The SPEAR index uses biomonitoring data on invertebrates and classifies different species as “at risk” or “not at risk” according to their ecological traits. On the other side, Species Sensitivity Distribution (SSD) is a statistical method, which uses toxicity data of different species or taxons (e.g. EC50 or NOEC), and it can be used for prediction of the "potentially affected" fraction (PAF) of the aquatic community exposed to a certain concentration of specific compound. It can also be used to predict PAF of mixtures, i.e. multisubstance PAF (msPAF). In the present study we compare msPAF values for 25 pesticides measured at localities in France, Germany and Finland (1988-2000), and compared the results with the bioindicaton (SPEARpesticides index). Our objective was to compare performance of both approaches in the retrospective site-specific risk assessment of pesticides Concordance between the predictive ecotoxicological approach (SSD) and field bioindication (SPEAR) was observed - SSD (based on a broad range of ecotoxicity values for different taxa) was well correlated with SPEAR. SSD might provide more reliable outcomes than alternative “toxic unit” TU approach, which is based on ecotoxicity values from a single species (D. magna). Although agreements have been found, further validation of SSD and SPEAR in other retrospective risk assessment field studies is needed. [Supported by the EU FP7 project AQUAREHAB and by the project CETOCOEN (no. CZ.1.05/2.1.00/01.0001) from the European Regional Development Fund.]

Integration of rehabilitation technologies impact into river basin management – Collaborative management tool REACHER

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One of the objectives of FP7 AQUAREHAB is to develop a generic collaborative management tool 'REACH-ER' that 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 eco-toxicological 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.

Fate models were developed for the Odense (SWAT, nitrogen & pesticides) and Scheldt River Pilot (Python/PCRaster, nitrogen) with focus on the processes behind the pollutant fluxes. In addition, a separate fate model for contaminated site (COMFRACS, TCE) is developed to assess the effects of regionally distributed contaminated sites on groundwater quality at the groundwater body scale.

For assessing the eco-toxicological effect of chemicals in rivers new approaches (integrated in SPEAR concept, SPEcies at Risk - http://www.systemecology.eu/SPEAR/index.php) have been developed to provide better information with respect to (a) sensitivity of individual species towards specific chemical contamination and (b) recovery potential of respective species.

For the economical analyses of water quality remediation measures, a database structure has been worked out and data on a number conventional remediation measures was inserted in the database.

The development of the DSS REACH-ER has followed two major lines: 1). a light-weight, probabilistic alternative to complicated, process-based fate models, based on the Bayesian Belief Network (BBN) approach. 2). A WEB-based front end version of REACH-ER that can be used to present scenario-based model results and interact with stakeholders, so as to build and analyse scenarios with different rehabilitation measures.

An overview of the concept that is being worked out as a prototype, will be presented.

Session 10
New developments

Oral presentations

Smart injection technology for efficient *in situ* remediation: demonstration at a contaminated site in the port of Antwerp

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ABSTRACT: Contact between injected reagents and pollutants is crucial for efficient *in situ* remediation of soil and groundwater. The innovative detection-injection technology presented here is based on the MIP-IN device, which combines detection of pollutants by a membrane interface probe (MIP) and a simultaneous correlated injection (IN) during direct push of the device using a Geoprobe®. The main advantage of the new technology is the nearly simultaneous coupling of detection of pollutants at a certain depth and injection of the reactive agent. In this way, the injected reagent is more targeted towards the real location of the pollution with reduced remediation time and cost. In addition, non-contaminated aquifer is not exposed to the reagents resulting in less impact on the soil matrix. The injection technology was demonstrated at pilot scale during a field test at a site in the port of Antwerp, Belgium. The site has a heterogeneous geology (dredged sand and alluvial deposits of loamy sand) and a heterogeneous distribution of BTEX (especially ethylbenzene and toluene) and chlorinated solvents (especially dichloromethane and cis-1,2-dichloroethene). Sodium permanganate for *in situ* chemical oxidation was selected as the reagent for this specific site.

INTRODUCTION

During the last decade, the focus of *in situ* remediation shifted from physical, chemical and microbiological treatment mechanisms to a renewed interest in hydrogeology. The need to achieve contact between injected reagents and target pollutants has been one of the main driving forces for the development of remediation hydraulics (Payne et al. 2008). To build a site conceptual model, MIP drillings are often used to delineate the horizontal and vertical distribution of the pollution. Based on the MIP logs, filter depth of the monitoring filters is chosen. The information of the site characterization is used to make a soil remediation plan with injection depth. Even after a thorough site characterization, the distribution of the pollution in a heterogeneous geology often remains difficult to predict with a limited number of MIP drillings and monitoring wells. Therefore, an innovative detection-injection technology, called MIP-IN, is presented. If pollution is detected with the MIP at a certain depth, reagent is almost simultaneously injected during the same direct push at the same depth. This targeted injection, leading to improved contact between reagent and pollutants, will lead to a more efficient remediation. In combination with the flexibility of the injection approach, total remediation time and costs will be significantly reduced. During the MIP-IN operation, a large density of contamination data (from the MIP) are obtained resulting in improved understanding of the contaminant distribution giving the possibility to detect all important contamination branches of the contamination source or plume.

The MIP-IN is a combination of pollutant detection with a membrane interface probe (MIP) and a simultaneous direct push injection (IN) with a Geoprobe®. The membrane interface probe (MIP) is a semi-quantitative direct push tool used to log the relative concentration of volatile organic compounds (VOCs) with depth in soil. If the probe is advanced into the subsurface, VOCs in soil and groundwater migrate across the membrane into the probe and are transported to an analytical detector above ground.

Direct push injection is often used as reagent delivery method. Krembs et al. (2010) concluded that in 23% of the 181 sites where in-situ chemical oxidation (ISCO) has been applied, direct push was the oxidant delivery method. Other methods of reagent delivery are injection wells (with or without recirculation), mechanical mixing and infiltration at the ground surface (Huling and Pivetz, 2006). Christiansen et al. (2010) concluded that the direct-push delivery method was a robust and efficient delivery method at a clay till site with a good vertical distribution of injected reagent.

The MIP-IN technology was demonstrated during a field test at an industrial site in the Port of Antwerp, Belgium. The MIP-IN device was tested for detection of pollution and simultaneous injection of reagent at the exact location of pollution. The site has a heterogeneous distribution of BTEX (especially ethylbenzene and toluene) and chlorinated solvents (especially dichloromethane and cis-1,2-dichloroethene). Sodium permanganate for *in situ* chemical oxidation was selected as the reagent for this specific site.

MATERIALS AND METHODS

Field site

The site is located in an industrial area in the port of Antwerp, Belgium. The geology is heterogeneous and can be summarized as follows: 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. The groundwater flow direction is south to the docks.

The main contaminants in the groundwater are ethylbenzene (210 to 39951 µg/L), toluene (34 to 4300 µg/L), dichloromethane (<10 to 540000 µg/L) and cis-1,2-dichloroethene (41 to 18000 µg/L).

Pilot test site

An area of 10 m by 10 m at the field site was selected for the pilot test. A scheme of the pilot test site is shown in figure 1.

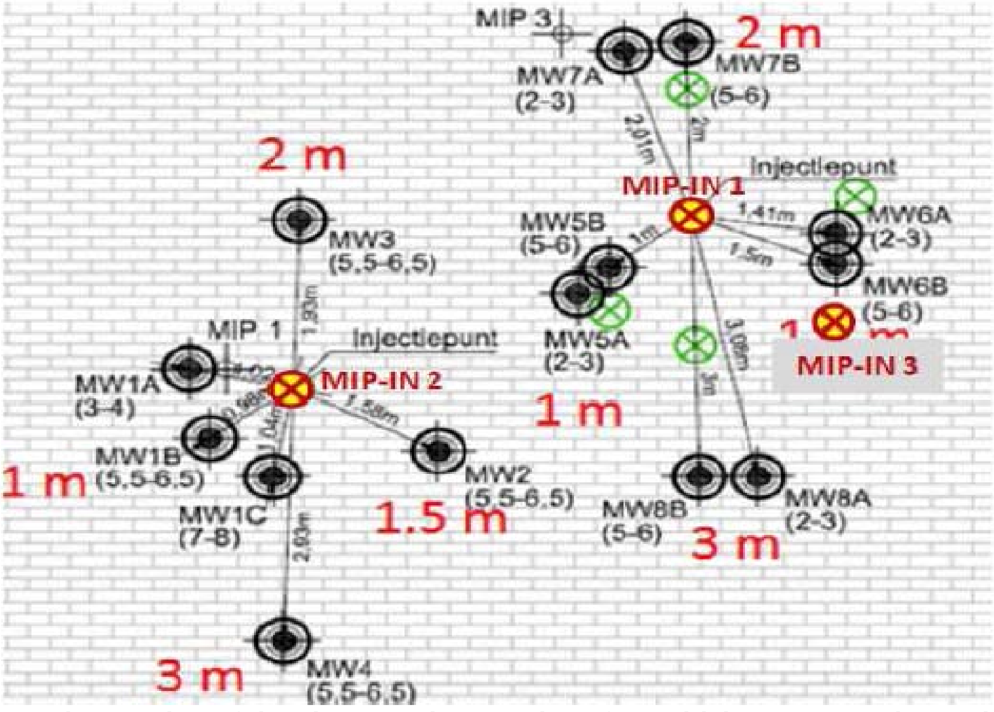

Figure 1: Schematic overview of the pilot test site: location of MIP drillings MIP1 and MIP3 (MIP2 is out of range), location of monitoring wells MW1, MW2, MW3, MW4, MW5, MW6, MW7, MW8 (filter depth in m bgl) and location of MIP-IN drillings MIP-IN1, MIP-IN2 and MIP-IN3. The distance between monitoring wells MW1, MW2, MW3, MW4 and MIP-IN2 and between MW5, MW6, MW7, MW8 and MIP-IN1 is shown in red.

In a first phase, three conventional MIP-drillings (MIP1, MIP2 and MIP3) were performed on site to evaluate the distribution of the pollution. Two drillings with a Geoprobe® were performed and soil was sampled with Geoprobe® liners. One drilling was located close to MIP1, the other close to MIP3.

In a second phase, 14 monitoring wells were installed on site with different filter depths. Based on the MIP1 and MIP3 logs, the filter depth of the monitoring filters was chosen. An overview of the monitoring wells with filter depth and location is given in table 1.

In a third phase, three MIP-IN injections were performed. MIP-IN1 was located close to MW5, MW6, MW7 and MW8. MIP-IN2 was located close to MW1, MW2, MW3 and MW4. MIP-IN3 was located at 0.66 m from MW6b.

In a fourth phase, two drillings with a Geoprobe® up to 8 m bgl were performed and soil was sampled with Geoprobe® liners. One drilling was located close to MIP-IN3, the other close to MIP-IN2.

Table 1: Overview of monitoring wells for pilot test.

Location	Monitoring well	Filter depth (m bgl)	Distance from MIP-IN (m)
MIP-IN2 area	MW1a	3-4	1.02
	MW1b	5.5-6.5	0.98
	MW1c	7-8	1.04
	MW2	5.5-6.5	1.58
	MW3	5.5-6.5	1.93
	MW4	5.5-6.5	2.93
MIP-IN1 area	MW5a	2-3	1.43
	MW5b	5-6	1.00
	MW6a	2-3	1.41
	MW6b	5-6	1.50
	MW7a	2-3	2.01
	MW7b	5-6	2.00
	MW8a	2-3	3.08
	MW8b	5-6	3.00

Membrane interface probe (MIP)

The MIP drillings were performed up to a depth of 19 m bgl. Data were analyzed with three serially used detectors: the photoionization detector (PID) for detection of aromatic compounds, the flame ionization detector (FID) for detection of hydrocarbons, and the halogen specific detector (XSD) for detection of halogenated compounds. The electrical conductivity (EC) is logged to have an indication of the soil lithology.

Soil sampling and analysis of volatile organic compounds and manganese

Soil was sampled with Geoprobe® liners. The liners were opened under anaerobic conditions (N_2 gas) in the lab and subsamples were taken for analysis of volatile organic compounds and manganese.

A 10 g soil sample was extracted with 10 g methanol during 30 minutes of ultrasonic treatment. The methanol extract was analyzed for volatile organic compounds by gas chromatography and mass spectroscopy (GC-MS). The manganese in the soil was measured after total soil destruction with $HNO_3/HCl/HBF_4$ and analysis with inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Groundwater sampling and analysis of volatile organic compounds

Groundwater was sampled from monitoring wells by low-flow pumping with a peristaltic pump. BTEX and chlorinated solvents in the groundwater were analyzed by GC-MS.

MIP-IN technology

Figure 2 illustrates the principle of the MIP-IN technology. The MIP-IN probe is a combination of membrane interface probe (MIP) and an injection probe (IN). The probe diameter is 2.5 inch. During the top-down penetration of the MIP-IN probe in the soil, 25 MIP measurements are collected for each 0.3 m depth interval, giving a very high data resolution for detecting volatile organic compounds. For each 0.3 m depth interval, the reagent volume can be adjusted to the amount of pollutants detected by the MIP. Injection volume, flow rate and pressure are logged for each 0.3 m. The injection probe contains two reagent tubes and a mixing chamber for the injection of two reagents (for example chemical oxidant and activator, organic carbon substrate and bacteria, dilution of reagent with water).

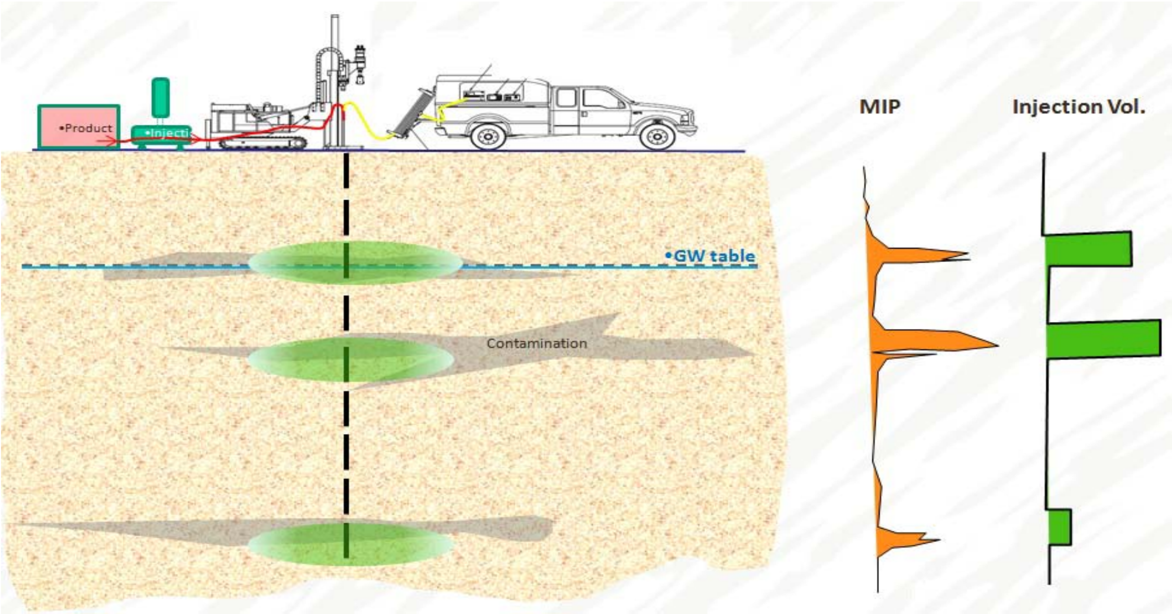

Figure 2: Principle of the combined detection-injection technology (MIP-IN).

In situ chemical oxidation

To evaluate the MIP-IN technology, a chemical oxidant was injected at the field site. To select the chemical oxidant, a matrix demand test and a degradation test were performed in the lab with contaminated soil and groundwater from the site. The matrix demand is the background oxidant demand for oxidation of organic matter and reduced inorganic species in soil. For the matrix demand, lab tests were conducted with permanganate, persulphate and persulphate activated with Fe(II)citrate. A very high matrix demand of about 20 g oxidant per kg wet soil was obtained for both permanganate and (activated) persulphate. Based on this very high matrix demand, *in situ* chemical oxidation is normally not selected as *in situ* soil remediation technology. However, the Antwerp site was used as test location for the injection technology since remediation of the site was no objective of the injection test.
The degradation test was performed with permanganate, persulphate, persulphate activated with Fe(II)citrate, with NaOH and with heat (50 °C). Permanganate showed complete degradation of the major pollutants (ethylbenzene, toluene and cis-1,2-dichloroethene), except dichloromethane (no degradation). Therefore, sodium permanganate ($NaMnO_4$, RemOx® L ISCO Reagent, Carus) was selected as chemical oxidant for the pilot test.
Based on a worst-case calculation of pollutant concentrations in soil and groundwater with a safety factor of 1.5, an injection concentration of 164 to 221 kg m^{-3} $NaMnO_4$ was calculated. This very high injection concentration was mainly due to the very high matrix demand. A lower injection concentration of 83 kg m^{-3} $NaMnO_4$ was used in the pilot test based on health and safety considerations. Furthermore, a high injection concentration will result into vertical density-driven transport of the injection fluid and subsequent loss of the injection fluid into a deeper zone.

The goal of this paper is to present the innovative detection-injection technology. Therefore, the effect of the chemical oxidation on the pollutant concentrations was not described in this paper.

RESULTS

The results of the MIP drillings (data not shown) indicate the presence of a pollution with aromatics especially at 2 m bgl and a pollution with chlorinated compounds especially at 4 to 6 m bgl. Furthermore, the three MIP logs show different profiles, indicating a heterogeneous distribution of the pollution on site.

The results of the GC-MS soil analysis (data not shown) for soil samples close to MIP3 show a large ethylbenzene concentration (480 mg kg^{-1}) at 1.8 m bgl, while 71 mg kg^{-1} dichloromethane was present at 3.4 m bgl, confirming the data of the MIP drillings.

MIP-IN

Based on the MIP logs, the injected reagent volume can be immediately adapted on site. In the example for MIP-IN1 (data not shown), a volume of 300 L was injected between 4.8 and 5.1 m bgl since a relatively large pollutant concentration was present. The MIP-IN1 injection was interrupted at 5.4 m bgl due to surfacing of the chemical oxidant.

Manganese distribution

After injection, Geoprobe® drillings for manganese analysis in soil were performed to check the distribution of the injected permanganate. The drillings were performed next to MIP-IN2 and next to MIP-IN3. The results of the manganese concentrations with depth are shown in figure 3.

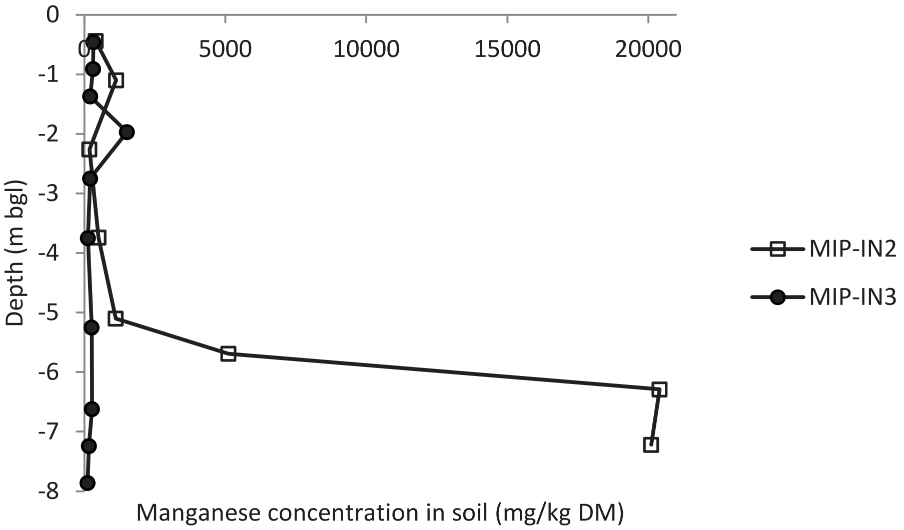

Figure 3: Manganese concentration profile in soil (DM: dry matter) for samples next to MIP-IN2 and next to MIP-IN3.

For MIP-IN2, elevated manganese concentrations (5 to 20 g kg^{-1}) are shown from 5.7 to 7.2 m bgl indicating the presence of permanganate. This correlates well with the injection of permanganate from 5.4 to 6.9 m bgl at this location. For MIP-IN3, no elevated manganese concentrations were found in the soil samples, indicating no presence of permanganate in the soil samples, although permanganate was injected between 5.1 and 6.0 m bgl. These results indicate a heterogeneous distribution of the injected permanganate.

CONCLUSION

This pilot test demonstrated the possibilities of the innovative detection-injection technology. The main advantage of the new technology is the coupling of detection and immediate injection so the injection will be targeted towards the real location of the pollution. Also the significantly improved understanding of the contaminant distribution and the flexible injection approach will lead to a more efficient use of reagent and overall reduced remediation time and costs.

The MIP-IN technology is a one-step alternative for the time (and money) consuming process of contaminant delineation (for example by MIP), installation of injection wells and injection of reagent. Furthermore, the MIP-IN is a flexible injection system. Sites with a heterogeneous geology or heterogeneous pollutant distribution can benefit from its flexibility. During the MIP-IN remediation, detailed information of the pollutant distribution is collected so the injection location can be changed.

In this paper, the injection was performed with a chemical oxidant as example, but the technology can also be used for zero-valent iron slurries, biostimulation substrates or bacterial inocula for bioaugmentation.

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Detection of ZVI in Aquifers – development of field equipment

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Monitoring a successful remediation using zero-valent iron (ZVI) faces two major challenges:

- The distribution of the iron in the aquifer in the vicinity of the injection well during and right after injection has to be ascertained
- The longevity of ZVI in the aquifer and therefore the frequency of reinjection after reaction of the particles need to be determined.
-

During the last several years, sensor arrays have been developed in VEGAS within the AQUAREHAB project which can detect zero valent iron specifically in the subsurface without being influenced by the geogenic iron present ubiquitous. These arrays are based on the magnetic susceptibility which is specifically high for the ferromagnetic Fe(0).In addition, the sensor arrays are equipped with special temperature sensors and sampling ports that enable measurements with a high temporal and spatial resolution of different parameters in the subsurface. These relatively inexpensive systems can be emplaced by direct push techniques and can detect the distribution of the iron during an injection and the decrease of the iron concentration in the course of the reaction.
The development of the field arrays starting from the first laboratory prototypes based on commercially available mine detectors to the field ready sensor arrays will be presented and future possibilities will be illustrated.

Removing organic micro pollutants by means a reactive layer in an artificial recharge system.

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The demand for quality water increases with time. Artificial recharge of aquifers is a useful technique whereby it is possible to improve not only the quality of water resources, but also increase them.
Emerging contaminants including pharmaceutically active compounds (PhACs), personal care products (PCPs) and pesticides show low concentration in the environment (ng/L), but the effects of the mixtures and indeed the lifelong exposure to humans are currently unknown. Given that several of these micro pollutants are not eliminated from the wastewater by conventional treatment processes, they and their metabolites reach river waters, aquifers and aquatic environment. Several lab studies show that the behaviour of many of these micro pollutants is affected by the dominant redox conditions.

In this study we propose to improve and/or increase the removal of these emerging contaminants by installing a reactive layer in an infiltration basin. This layer is a mixture of compost, aquifer material, clay and iron oxide. It is intended to provide an extra amount of DOC to the recharge water and to promote biodegradation by means of the development of different redox zones along the travel path through the unsaturated zone and within the aquifer. Moreover, compost, clay and iron oxide in the layer are believed to increase sorption surfaces for neutral, cationic and anionic compounds, respectively.

The infiltration system is located at Sant Vicenç dels Horts (Barcelona, Spain). Llobregat raw water, highly affected from treatment plant effluents, is driven first to a decantation basin, and then to an infiltration basin. The system is equipped with a network of piezometres, suction cups and tensiometers. Two different infiltration tests have been performed, one prior to the installation of the reactive layer on the bottom of the infiltration basin, and another one afterwards. Several sampling campaigns were carried out in order to:

- Monitor infiltration water evolution and its seasonal variations.
- Test the efficiency of the reactive layer to remove micro pollutants
  (46 micro pollutants were analysed).

Background concentrations in the aquifer were analysed with no artificial recharge.
The results show the effectiveness of the reactive layer in removing micro pollutants from the infiltration water and thus improving the water quality.

Enhanced Physical Recovery of Petroleum Hydrocarbons from Groundwater – a new reagent for increasing Pump-and-Treat efficacy

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In situ Pump and Treat (P&T) systems are widely used for the remediation of hydrocarbon contaminated soil and groundwater. Whilst the initial phase of a P&T operation will typically achieve a rapid reduction in groundwater hydrocarbon concentration, on-going effectiveness may diminish over time with the recovery trend commonly approaching an asymptote above the desired clean-up concentration. When this occurs, the implication can be costly extended operation with little incremental benefit, negatively impacting both project costs and time.

This phenomenon typically arises as a result of hydrocarbon distribution through zones of differential matrix permeability, the presence of slowly dissolving smeared or sorbed hydrocarbon contamination, or a combination of both of these factors. Whilst slow-release oxygen substrates may be used with good effect to address modest contamination in zones of differential permeability, the presence of smear can present a greater challenge owing to the greater total hydrocarbon mass that may be involved, presenting a consequential oxygen demand which increases both the cost and time required for biological treatment.

The use of surfactants to enhance recovery of sorbed-phase or smeared hydrocarbon present problems of cost, pore-blockage, trapping of residual hydrocarbons by sub-CMC residual surfactant and high residual surfactant biological oxygen demand (BOD) inhibiting follow-on biodegradation or natural / enhanced attenuation of residual hydrocarbon.

This paper presents information of a new reagent designed to address the above issues in order to increase the efficiency and expedite the closure of physical extraction-based clean-up installations (P&T etc) and at the same time support the integrated use of follow-on technologies in a 'treatment-train' approach should this be necessary - for example, to secure more stringent clean-up objectives in complex formations. The new reagent is entirely inorganic presenting no BOD, and may be used in combination with existing P&T installations or in simpler, rapid-application fast mass-removal campaigns that may not require equipment installations on site.

An overview of the results from laboratory and Mediterranean field studies will be presented, and the potential modes of usage and anticipated benefit to common remediation projects explored. Recommendations for a best-practice approach and for use in combination with P&T systems, ISCO and enhanced bioremediation technologies will also be made.

Complete Dehalogenation of Chlorinated Ethenes Quantified by Repeated Isotope Monitoring at a Complex Contaminated Site

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ABSTRACT: Isotope monitoring of chlorinated ethenes is a major tool in remediation strategies, which rely on natural attenuation processes. In particular, the proof of total dehalogenation (i.e. biodegradation of vinylchloride) is of high relevance, which can be discerned from the enrichment of heavy isotopes in the bulk of chlorinated ethenes (CE). Suitable isotope enrichment factors describe the proportionality of isotope enrichment and concentration decrease, and thus enable the calculation of biodegradation parameters. Generally, one isotope monitoring campaign is performed to assess biodegradation quantitatively, but the validity of a single survey for overall conclusions is arguable. In AQUAREHAB WP4 (an EU-FP7 project) we performed six isotope monitoring campaigns to check the variability of isotope data and related biodegradation parameters at a complex contaminated site. We investigated a parcel in Belgium, where a zero valent iron barrier had been installed and natural attenuation processes should be evaluated. Calculated from weighted average isotope enrichment of bulk chloroethenes and lumped fractionation factors, the percentual degradation of total CE along potential flow paths was in the range of 5 to 50 %. Accordant halflife distance was inbetween 70 m and 700 m, which is typical for most contaminated sites. On the other hand, the halflife period was generally much longer than 100 years (as a consequence of minimal flow velocity at the site). Isotope values at most monitoring wells were remarkably constant in time, so that reliable conclusions on biodegradation can be attained also by minor efforts. Isotope investigations indicated that complete dechlorination of CE at the site is prevalent, but apparently too weak for notable retardation of the contaminant plume. Therefore, active remediation technologies such as ZVI barriers are recommended to achieve a more effective removal of contaminants.

INTRODUCTION

Within the frame of natural attenuation strategies for groundwater remediation the exploration of contaminated sites generally follows several objectives:

- qualitative and quantitative assessment of biodegradation
- description of the spatial and temporal variability of biodegradation
- conclusions on the dynamics of hydraulic conditions
- demonstration of the efficacy of enhanced vs natural attenuation processes
- exploration of secondary contaminant sources.

Isotope monitoring of contaminants can provide substantial information on these demands. Its application is based on two principles:

1 - The biodegradation of molecules containing heavy isotopes (e.g. ^{13}C) is less pronounced than that of molecules with light isotopes. Therefore, the molecules with heavy isotopes are getting enriched, and the isotope signature of degraded contaminants is more positive/heavier.The quantification of biodegradation can then be provided, if a substance-specific isotope enrichment factor is available. This factor ε describes the proportionality between concentration and isotope values of specific substances and for specific degradation processes. δ_0 is the primary isotope value of the contaminant (at the source) and δ_t is the isotope signature measured at downstream wells, where biodegradation along the flow path had reached a certain time t (according to flow velocity). Just three parameters allow the calculation of percentual biodegradation along flow paths and of 1st order degradation rates (per meter or per day) by a so-called Rayleigh equation.At sites contaminated with chloroethenes (CE) it is specifically important to assess the degradation of VC (vinylchloride), i.e. to prove and quantify complete dechlorination by isotope monitoring. For this purpose, the isotope values of all CEs are summarized in a weighted

Table 1: Weighted average isotope values (δ^{13}C‰; upper table) and concentrations (µM/L; lower table) of bulk chlorinated ethenes during six monitoring campaigns (single values, means, standard deviations). Colours are related to qualitative evaluation (see below).

characteristics	well	Feb. 10	Jul. 10	Nov. 10	Apr. 11	Jul. 11	Nov. 11	mean	sd
primary source	**PB104**	**-24.9**	**-24.6**	**-23.8**	**-24.1**	**-23.7**	**-23.7**	**-24.1**	0.5
biodegradation	**B4**	-20.3	-21.9	-21.7	-21.4	-22.4	-23.3	**-21.8**	1.0
neglectable contamination	**B6**		-19.0				-18.5	**-18.8**	0.4
neglectable secondary source	**PB505**	-25.6						**-25.6**	
minor secondary source	**PB603**	-26.2	-23.9			-24.8	-23.0	**-24.5**	1.4
biodegradation	**PB305**	-17.6	-17.9	-17.1	-15.4	-16.9	-15.4	**-16.7**	1.1
variable flow, biodegradation	**PB401**	-13.5	-18.1	-5.5	-10.0	-21.3	-18.9	**-14.6**	6.0
close to major source	**PB402**	-20.5	-24.9	-24.1	-24.5	-24.9	-25.0	**-24.0**	1.7
major source, biodegraded	**PB405**	-22.3	-21.1	-19.9	-18.9	-21.5	-19.4	**-20.5**	1.3
minor biodegradation	**PB501**	-22.4		-18.8		-23.1	-23.0	**-21.8**	2.0
variable biodegradation	**PB404**	-15.9	-15.8	-20.2	-11.8	-21.9	-21.7	**-17.9**	4.0
major/variable biodegradation	**PB504**	-16.8	-9.9	-13.8	-10.3	-5.7	-8.7	**-10.9**	3.9
upstream ZVI barrier	**PB104**	34.4	12.5	30.9	25.0	15.1	27.7	**24.3**	8.7
just downstream	**B4**	5.5	8.5	4.9	3.9	12.0	9.5	**7.4**	3.1
just below ZVI barrier	**B6**		3.8				2.5	**3.1**	0.9
close downstream ZVI	**PB505**	0.2	0.1						
close downstream ZVI	**PB603**	0.1	0.5			0.1	0.3	**0.2**	0.2
downstream	**PB305**	10.1	16.1	29.3	10.0	9.9	9.4	**14.1**	7.8
more downstream east	**PB401**	0.2	1.3	0.2	0.2	5.1	5.0	**2.0**	2.4
more downstream west	**PB402**	9.2	6.9	6.5	2.2	7.5	10.4	**7.1**	2.8
far downstream east	**PB405**	20.9	50.9	57.8	27.8	31.1	74.1	**43.7**	20.5
far downstream east	**PB501**	0.2	0.1	0.3		0.2	0.7	**0.3**	0.2
farer downstream west	**PB404**	6.0	6.9	14.1	8.5	33.5	23.1	**15.4**	10.9
farest downstream west	**PB504**	48.7	33.8	47.3	25.5	16.9	44.2	**36.1**	12.9

red = contaminant sources (i.e. most negative isotope signatures)
green = evidence for biodegradation
blue = high variation of values
yellow = highest concentrations

average isotope value ($^{13}C_{\Sigma CE}$). The intensity of complete dechlorination is reflected in the isotope enrichment of this value and can be quantified by a lumped isotope enrichment factor (Aeppli et al. 2010).

2 - The primary isotope signature of contaminants depends on production process and the isotope ratio of the raw materials. Various manufacturers of PCE (tetrachloroethene) and TCE (trichloroethene) can be identified because of a fingerprint of $^{13}C/^{12}C$ primary isotope signatures, which vary between -36 ‰ and -22 ‰. Due to this wide range of potential isotope values, the opportunity for source identification is given for different events of contamination.

The feasibility of isotope monitoring to develop effective groundwater remediation strategies has been demonstrated in numerous case studies and is described in several guidelines (US EPA 2005, 2008; Aelion et al. 2010; Eisenmann and Fischer 2010). However, the advantages of repeated isotope monitoring campaigns have rarely been reported. It is arguable, how far the temporal dynamics of hydraulic changes and and biological activities can be traced by the variation of isotope signatures. Here, we show the results of a 2-year study, where six monitoring campaigns were performed at a complex site contaminated with chloroethenes.

SITE DESCRIPTION AND SCHEDULE OF MONITORING

We investigated the area of an industrial field site in Belgium (site A), where chlorinated ethenes had been detected in quaternary sediments close to a lowland river. A zerovalent iron (ZVI) barrier is installed downstream from a major contaminant source (PB104). Groundwater flow velocity is slow at the site (around 2-5 m/year). The estimated age of the pollution is about 55 years, which would theoretically result in a 110 m to 275 m impact zone. Recent results from groundwater flow modeling was used to specify the flow velocities at specific flow paths, where carbon isotope values of CE were determined.

Six monitoring campaigns for carbon isotopes of chlorinated ethenes (Feb 2010, Jul 2010, Nov 2010, Apr 2011, Jul 2011, Nov 2011) were performed at least at 12 wells in parallel with a survey of contaminant concentrations and environmental parameters. Compound-specific isotope values of CE were summarized in a weighted average isotope value (according to Aeppli et al. 2010) and related to total CE concentration (Tab. 1). Complete dechlorination of CE was indicated by a significant increase (≥ 2 ‰ according to US -EPA 2008) of bulk isotope values downstream from the primary source.

RESULTS

INTENSITY OF COMPLETE DECHLORINATION AND DISCRIMINATION OF CONTAMINANT SOURCES

The results provide qualitative and quantitative insights on site dynamics regarding contaminant sources, biodegradation and groundwater flow paths that were used to state a conceptual site model (Fig. 1). In most monitoring wells, bulk isotope values showed a significant enrichment compared to the primary source PB104. This proves *widespread biological degradation of CE* at the site including complete dehalogenation of contaminants. The consecutive pattern of isotope enrichment downstream from the primary source points to the following flow paths: PB104 - PB305 - P401; PB104 - PB404 - PB405 - PB501 (or PB504); PB104 - PB404 - PB504 (Fig. 1). Even at the highly contaminated well PB405 the isotope value is considerably enriched compared to the upstream well PB402 (+3,5 ‰). Therefore we conclude that P402 is touching a major contaminant source, which is going to be slightly degraded in PB405. High contaminant concentrations in PB404 and PB504 can be explained by downstream flow from this source, but strong isotope enrichment at these wells show a remarkable biodegradation along these flow paths.

For quantification of complete biological dehalogenation of CE by Rayleigh calculations average isotope fractionation factors and small-scale flow velocities derived from a preliminary flow model (TUD) were used. It has to be regarded that this approach has a considerable uncertainty with respect to the range of lumped isotope enrichment factors (see related poster). Percentual degradation of total CE along potential flow paths was in the range of 5 to 50 % (Fig. 1). The consequential spatial and temporal first-order rates for complete dechlorination of CE offer quite different perspectives for interpretation. The halflife *distance* of the considered flow paths was inbetween 70 m and 700 m, which is typical for most contaminated sites (Fig. 2). On the other hand, the halflife *period* was generally much longer than 100 years (due to minimal flow velocity at the site). Both parameters suggest that biodegradation at the site is actually too weak to effect a retardation of the contaminant plume.

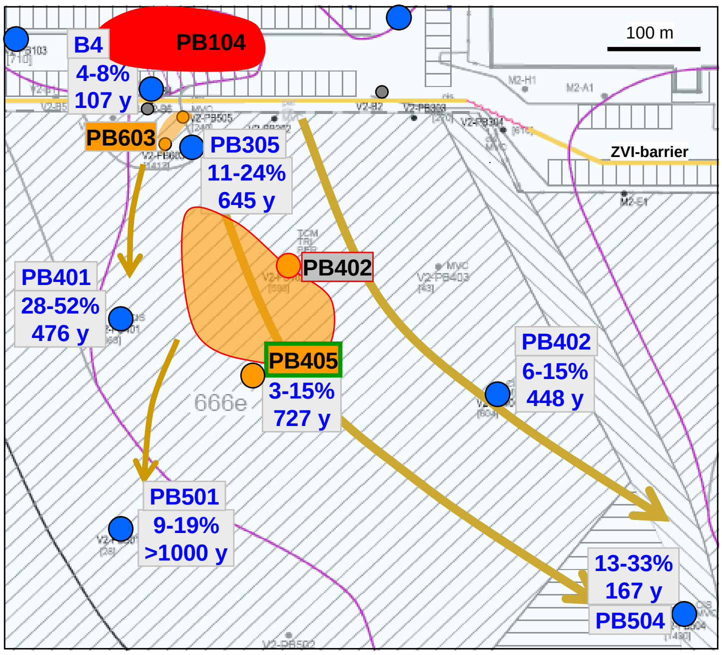

Figure 1: Conceptual site model derived from isotope values and concentrations of CE showing primary (red) and secondary source (amber), zones exhibiting complete dehalogenation (blue), and major direction of groundwater flow.Moreover, percentual biodegradation and halflife periods of degradation were calculated for selected flow paths downstream from the primary source (PB104).

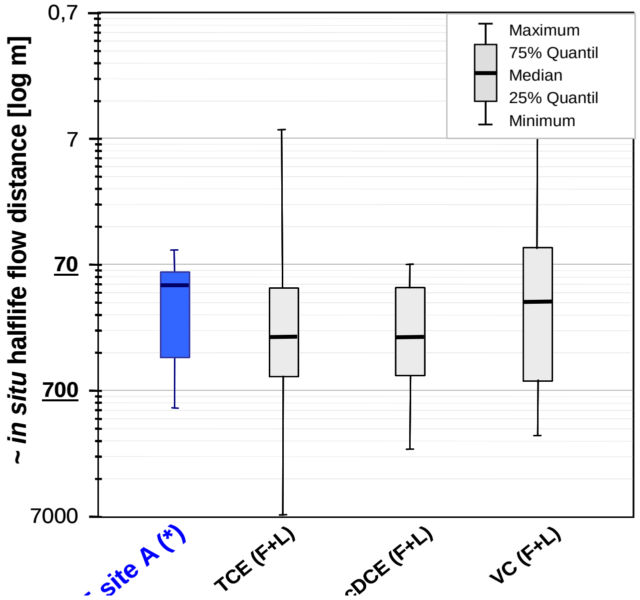

Figure 2: Halflife distance of CE at site A compared to studies on CE degradation at other sites (from US-EPA 2002).

TEMPORAL DYNAMICS

The *temporal dynamics* of isotope and concentration values were clearly different. Bulk isotope values exhibited very constant levels in most of the wells (sd ≤ 2 ‰), while bulk concentration of CE was variable to a large extent. Within the investigated time frame, horizontal groundwater flow was extremely slow. However, the water level altered in the vertical dimension because of hydraulic changes in the course of precipitation. Thus different vertical parts of the contaminant plume might have been collected comprising different amounts of contaminants. Interestingly, the isotope values were less affected by these dynamics as they covered just the state of biodegradation and not of dilution. Generally, an increase of isotope values at the same spot would indicate plume retardation (because of major biodegradation), while a decrease would suggest plume extension (because of minor biodegradation). In the present study, a pattern like this was not discernable for the investigated wells. The time frame probably was too short to reflect these long-term processes clearly. Though the most variable isotope values were found close to the plume fringe (P401, P404, P504), where biodegradation significantly can alter because of changing redox conditions, in particular in the vertical dimension (Bauer et al. 2009).

Only three wells showed a high variability in isotope values within the time frame of 2 years. Thus a single isotopic survey would have provided pronounced evidence to quantifiy total dechlorination at the investigated site. This conclusion can be generalized only for sites with similar hydrogeological features (i.e. non-fractured and slow flow velocity). If more precise quantification of biodegradation is required for specific flow paths, or if the state of retardation/expansion of the plume is in the focus of exploration, repeated isotope surveys are recommended.

CONCLUSIONS

Isotope monitoring clearly demonstrated wide-spread degradation of chlorinated ethenes at the site and discriminated several contaminant sources. However, quantitative considerations as well as repeated isotope monitoring suggested that biodegradation is actually too weak to effect a retardation of the contaminant plume. Active remediation technologies such as ZVI multibarriers are recommended to guarantee a more effective removal of contaminants. The hydrogeological and biological performance of the plume is now understood so far that an advanced concept of ZVI-barrier technology in combination with natural attenuation processes can be developed.

ACKNOWLEDGEMENTS

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Poster Presentations

Toxic hydrocarbons removal form groundwater for Zero Harmful Discharge or reinjection with the Macro Porous Polymer Extraction technology

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In groundwater remediation a wide variety of water treatment technologies are applied. Almost all aiming at creating and/or improving the natural attenuation process so as to minimize costs. There are situations where conventional technologies are insufficient appropriate with regards to separation performance and/or costs efficiency. This can be due to the composition complexity and/or properties of specific products that are outside the feasible area of conventional technologies. The Macro Porous Polymer Extraction technology has been chosen for those situations where conventional technologies are less competitive. Examples will be presented of different cases where a variety of more difficult compounds are removed. Examples of difficult molecules are CS_2, MTBE, heavy/light halogenated hydrocarbons, PAHs, high levels aromatics in various industrial areas such as brown coal sites, refineries, tanker parks, former city gas locations, pharmaceutical industry, fibre industry, former airbases, dry cleaning locations, etc. Finally examples will be presented of surfactant enhanced aquifer remediation (SEAR) for removal of DNAPLs (Dense Non Aqnous Phase Layers) and treated groundwater reinjection to enhance natural attenuation

The broad variety of MPPE applications in groundwater remediation processes proves feasibility of this technology in those areas where remediation becomes more difficult and conventional technologies become less competitive.

Field implementation of an innovative permeable reactive barrier for plume control at an industrially contaminated site

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Verhoeve Groep is an international contracting company with a broad experience in in-situ remediation of complex groundwater pollutions. In 2011, the company was appointed for remediation of a large industrially contaminated site in Lier, Belgium. Former metal degreasing activities on the location have lead to a more than 350 m long contaminated groundwater plume containing primarily cis-DCE and VC at concentrations up to several thousands of µg per liter. The contamination is present down to 7-8 m bgs where a thick clay layer is present, preventing further vertical spreading. The plume is migrating into a downstream water creek.

To prevent further spreading of the plume and to protect the surface water, a 220 m long and 8 m deep permeable reactive barrier was installed along the water creek using the continuous trenching technique. The barrier was filled with 700 m^3 GRANUL-X®, an innovative reactive material which can be used as a cheaper alternative for zerovalent iron. GRANUL-X® is a clay-based, expanded granulate with a high porosity and a very large internal surface area. Tiny, reactive metal particles are incorporated in the granules during production. In this way, a very intimate contact is obtained between the contaminated water and the reactive surface area of the granules. Cracked granules with a size of 0-5 mm are used to increase the accessibility of the reactive surface area even more. Upon contact between the contaminated water and the GRANUL-X® particles, the pollutants are chemically transformed to harmless compounds by reductive dechlorination.

In addition to permeable reactive barrier technology, also other remediation techniques are involved in the total site approach. The source zone - which is mainly located underneath a building - is treated by Perozone® and multiple phase extraction. Perozone® is an advanced in-situ chemical oxidation technology which relies on specially designed microporous spargepoints for the subsurface injection of tiny ozone bubbles surrounded with hydrogen peroxide, thereby creating a high oxidation power. The remediation is further supported by two hydrological barriers. An overview of the total approach, and specifically the permeable reactive barrier implementation, will be presented on the symposium.

Emission-free Groundwater Remediation Technology (SmartStripping®)

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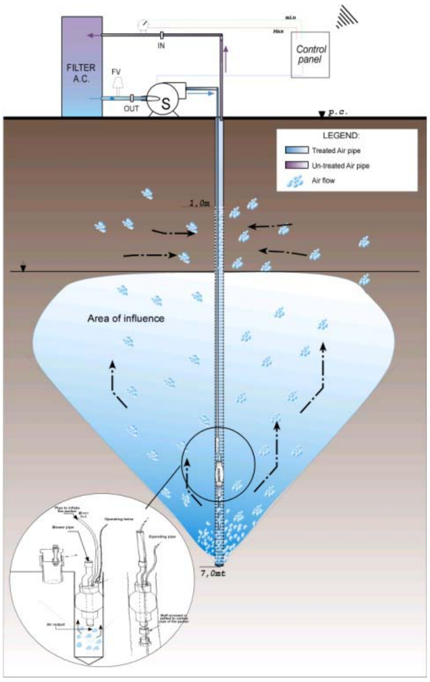
The groundwater remediation technology called SmartStripping® is a innovative process for groundwater on-site remediation that reduces concentrations of Volatile Organic Compounds (VOC) and semi-VOC produced by chlorinated compounds and petroleum fractions. These compounds and fractions are adsorbed into the unsaturated zone and dissolved in groundwater at industrial and civil sites, and especially at sites with underground storage tanks.

The process differs from other groundwater remediation (Pump & Treat, Soil Vapor Extraction) technologies, as it is a “green” remediation process, which has no contaminant expulsion to the atmosphere, surface water or sewage networks. During remediation, water is not extracted and no substances (air nor water) are released into the environment (see figure).



The technology allows the on-site treatment of 30.000 m^3 of groundwater, with a total concentration of contaminants of 10.000 µg/l, by using an activated carbon filter of 600 kg. The remediation results are achieved quickly and the costs associated are lower compared to other remediation technologies.

The technology is under a process of standardisation and simulation through field experience and laboratory scale demonstration to model the proposed solution and to clarify the limitations of the stripping process. The project started in December 2011 through funding received from the European Commission under the program Eco-innovation.

Case studies showed the effectiveness of the process on sites contaminated by petroleum fractions. A case study that recently got underway on a site contaminated by chlorinated compounds will be discussed by outlining the important issues, problems encountered, solutions identified and the remediation results. In addition, the first steps of the standardisation of the technology will be presented.

Using Packed Oxidants for Degradation of Soil Contaminants – UPSOIL WP5 Work

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Packing or coating chemicals is a long-practised method for placing an external, inert layer (shell) on a core, active substance.

The micro-particles[2], just a partial result of the packing work, have been intensively used in the pharmaceutical industry and, recently, more and more for agricultural purposes.

Lab research for soil remediation using packed reagents has also been done, but rather big particles have been produced and tested. Packing aggressive reagents, as strong oxidants or reductants are, even at the micro- level, has been a tough task, not only because they are instable in the reaction/preparation medium, but they are also likely to react with the packing material.

From more than 20-50 packing techniques spray chilling is recognized as the lowest-cost method, but with also a recognized major drawback, – uniformity of the particle size can not be ensured. Within the framework of the recent European UPSOIL project, specifically its Work Package Nº5, three oxidants have been packed by means of the spray congealing technique, and the final focus brought on Potassium Permanganate encapsulation. Two basic, benign packers were selected as hydrophobic materials, based on their chemical stability and availability - Paraffin wax (PW) and Carnauba wax (CW).

Once reactivity proven, more intense research has been conducted for improving the oxidant release, developing more packing material recipes, mostly blends based on the two waxes.

Oxidants packed using this technique were characterized and tested for their release and reactivity for hydrocarbons and chlorinated aliphatics. Although stable – from the chemical point of view – in the presence of packing material, the excess groundwater can washed the oxidants away, so, the oxidant controlled release becomes the basic requirement for packed systems. Under these conditions it is assumed that the oxidants need to stay encapsulated as long as it is not consumed for oxidation of targeted compounds (more days, ideally weeks) and gradually release while they fulfil their role.

Key words: *packing oxidants, Potassium Permanganate, Sodium Persulfate, Paraffin wax, Carnauba wax, oxidant release and reactivity*

INTRODUCTION

A big challenge in using unstable/degradable chemicals is to achieve incorporation of the active ingredients, with their acceptable availability and without altering their function. Once this milestone passed, an even bigger challenge is to have the active ingredient released when, where and as much as needed. Many of the processes for packing materials (more than 20 to 50) were developed in time by different companies, for addressing specific problems. A preliminary selection of packing technique should consider basic requirements, as type of particles (matrix or core-shell), size, size distribution, load, process characteristic, cost, and others (Sparks and Jacobs, 1999).

Some encapsulation methods which may be applicable for packing oxidants are shortly reviewed.

Interfacial poly-condensation, as method for microencapsulating strong oxidants (including Sodium Persulfate) or other materials in an organic, continuous shell has been already patented (Dale London et al., 1999). Anyway, 10% of the encapsulated persulfate was released after 2 hour - the resulting, encapsulating polymer was polyurethane. An advantage of this technique is that, a very high content of the active material can be reached. The active ingredient weight (e.g. fertilizer) can be within 80 – 88%, the polyurethane encapsulant has low water

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[2] Also named further *micro-capsules,* although micro-encapsulation refers to placing a layer of material on the surface of a liquid droplet

absorption exposure (less than 1%) and 50% of the active was released after 4 hours (Peter Markusch, et al., 2002).
Multilayer coating is a technique of the last years. More and more late research works mention *double-coating* as method for

- correcting surface imperfections of micro-particles and
- improve the active material release.

Fluidized bed coating is worth being considered, although recognized as producing quite big capsules (Sparks and Jacobs, 1999). The method was used for encapsulating *Sodium Percarbonate in Poly(vinylidene chloride* (PVDC), and the microcapsules were applied as *solid oxygen source* in bioremediation of *subsurface soil* formations contaminated with *hazardous wastes* (W.J. Davis-Hoover and Vesper, 2007). The microcapsules were in the *0.25 to 2.0 mm* range, with 50% (w/w) sodium percarbonate.
Potassium Permanganate (PP) is particularly difficult to encapsulate, as this destroys/attacks most of the potential encapsulating materials. Sustained efforts for encapsulating PP have been made after 2000s.
More shell materials, consisting of various blends of waxy polymers (Boler wax, Piccolyte resin S115, and Epolene C-16, also Chlorinated wax ~Chlorez 700), were tried to encapsulate PP. Single core grains of 60 to 1,000 µm and multiple particles, of 600 to 2,000 µm, with a mass ratio KMnO4/shell 0.25 to 0.50 were obtained (E. Lee and Schwartz, 2007). Still the average $t_{0.5}$ value was 0.11 day (in the range from 0.020 to 0.339 d), and the total time of release was about 6.6 days.
Waxes, which are esters of long-chains alcohols and fatty acids, are known for their hydrophobicity What makes them particularly attractive are the plate-like crystals that are more efficient in hampering the diffusion of small compounds (Donhowe and Fennema, 1993).
Within many natural matrix materials, *wax* proved a good compatibility with organic actives, allowing good controlled-release properties, due to encapsulation of the active particles in wax coating rather than pore trapping, or chemical interactions. Sometimes an emulsifier is needed (e.g. the case of encapsulating pesticides), and the method used is spray congealing (Darren et al., 1999).
Multinuclear particulate $KMnO_4$ (matrix microcapsules) were prepared incorporating $KMnO_4$ with mean equivalent spherical diameter of 15 (+/- 8.6) µm into paraffin wax matrix, and then pulverized, to obtain microcapsules of about 1 mm (Chapman Ross et al., 2005). Release in water was about 10-45% of the $KMnO_4$ in 4 days.
The use of controlled release KMnO4 (CRP), as an active component in a reactive barrier system, in treating the groundwater, is studied by Lee and Schwartz (E. Lee and Schwartz, 2007). The particles were of matrix-type, and the organic crystalline matrixes were prepared from Polyester Resin. Although cylinders (cm range) of packed PP were implanted in a tasting tank, the PP release (high concentrations) was high initially.

One aspect not enough studied and clarified is that *dissolution of large quantities of paraffin wax in the NAPL phase will decrease the water solubility* in the organic phase, slowing drastically the oxidation rate (Klara Rusevova et al., 2012).
Blends can be also used for encapsulation, but it was found that this increases leakage compared to the pure capsules, probably because the two materials don't mix well with each other in a crystal structure and the capsules become more brittle (M. Mellema et al., 2006).
It is also worth mentioning very recent research (Baoling et al., 2012) focused on PP controlled release for TCE oxidation. Although it is claimed that a “control-release mechanism” of the PP with stearic acid has been developed, the study doesn’t refer to any relations between preparation parameters and release kinetics. Also, no description of the release behaviour for times shorter than 10 days (burst duration) is provided.
Apparently no chemical reaction occurs between KMnO4 solid and stearic acid in the process of CRP preparation. KMnO4 release seems really good (30.9% after 240 h), but the particle size ranged from 2 mm – 5 mm.
A new potassium permanganate reagent with slow-release properties, MnO_2-coated $KMnO_4$ particles (MCP), was prepared by partial reduction of solid $KMnO_4$ (Klara Rusevova et al., 2012). MnO_2 is considered “a promising coating material” for $KMnO_4$, as it can be prepared by low-cost methods and is environmentally harmless. The observation that the oxidation did take place (using MnO_2-$KMnO_4$ microcapsules) in organic phase (heterogeneous medium) could give an advantage over other packing materials. Anyway, one should keep in mind that MnO_2 is the major oxidation product, so it is present in the medium as the oxidation with $KMnO_4$ progresses.

Extensive research was carried in the field of encapsulating *pesticides and fertilizers*, so many technical and conceptual results could be beneficially valued.
For example, for field applications of encapsulated *pesticides*:

- the particles must have a diameter smaller than 100 μm (preferably 50 μm) to enable applications by spraying with conventional equipment[3] and
- particles smaller than 20 μm are not desirable due to greater inhalation risk and wind drift during application (Kelly Smith, 1999).

The term of slow- or controlled-release was first defined by the Association of American Plant Food Control Officials (AAPFCO), in 1997, in relation with *fertilizers* (Martin Trenkel, 1997), but in 2005, Shaviv, (one of the "parents" of fertilizers controlled release), made a difference between the two terms.

Further than this, the concept of "smart fertilizer" was defined: the release profile overlaps the active consumption by plants (Martin Trenkel, 2010).

An imperfect coating may lead to immediate release. In connection with fertilizer release, this situation is called "catastrophic release" (or "failure release").

Adversely, the fertilizer proportion having an almost perfect and thick coating is called "locked-off".

A *slow release fertilizer* must meet each of the following three criteria[4]:

- no more than 15% released in 24 hours,
- no more than 75% released in 28 days,
- at least about 75% released at the stated release time.

Still it is admitted that, due to the fact that the coating material is several times greater in price than the fertilizer material, the cost of encapsulated fertilizers can be 8 – 12 fold the price of the conventional product, and thus, the world consumption of synthetic slow- and controlled-release fertilizers in 2004/05 represented no more than 0.20% of total world fertilizer consumption (Shaviv, 2000).

2. EXPERIMENTAL PART

Materials

Chemicals used in the experiments, potassium
permanganate, sodium persulfate and sodium parcarbonate were purchased from Sigma–Aldrich (Germany) or Merck (Germany) and had had a purity of >99% each. These were grinded using a grinding mill (FRITSCH pulverisette) and sieved (Sieving machine, MATEST) to separate size fractions between 20 μm and 250 μm. Trichoroethylene (TCE) and Perchloroethylene (PCE) were procured from Merck (Germany) and Diesel oil was a commercially available product (OMV Petrom). Paraffin wax (m. p. 70-80^{0}C) was procured from Aldrich (Germany) and Carnauba from Roth (Germany).

Packing the oxidants

Spray congealing method was chosen for packing the oxidants, as this is the safest, cost effective and environmentally friendly (solvent-free) technique. Potasium Permanganate (PP), Sodium Persulfate (PS) and Sodium Percarbonate (PC) were packed in CW and PP and PS in PW. The selection was based on a criteria analysis, balancing between polymer basic characteristics. A Brabender mixer was used for contacting and mixing (about 20 min.) the oxidant particles with the melt wax. The resulting suspension was pulverized with laboratory adapted spraying device, using air as carrier[5]. The packed oxidants were investigated by Scanning Electronic Microscopy (SEM) and the size distribution was determined using a Laser diffraction method (Mastersize 2000 – Malvern).

Testing the packed oxidants

Oxidant release

Microcapsules were dispersed in distilled water and continuously shaken (75 rpm) at room temperature. The oxidant concentration was checked periodically up to 30 days. Permanganate ions (MnO_4^-) were measured spectrophotometrically,(λ = 528 nm), with a SPEKORD 205 Analytic Jena spectrophotometer. Persulfate ions ($S_2O_8^{2-}$) were measured with a similar method, the same equipment (λ = 400 nm). Percarbonate ($CO_3^{2-}.1/2H_2O_2$) was determined as active oxygen, using an internal procedure, by iodometric titration.

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[3] clogging of spray nozzles must be prevented and also microparticles need to be kept in suspension in the spray hopper for even and reproducible coverage

[4] According the Declaration of The European Standardization Committee (CEN) Task Force on Slow-Release Fertilizers (Kloth, 1996)

[5] The preparation of wax-packed oxidant microcapsules by spray congealing method is subject of separate publication

Testing the microparticles reactivity

A testing methodology was developed for checking the reactivity of encapsulated oxidants for TCE/PCE, as DNAPL (dense non-aqueous liquid phase), Diesel oil as LNAPL (light non- -aqueous liquid phase) and mixture of NAPLs. Pure NAPL phase and microcapsules, and also tri-phase systems (water, free phase NAPL and microcapsules) were contacted, ensuring a 100% oxidant excess.

Periodic analyses of NAPL, residual oxidant concentrations and other basic characteristics of aqueous phase were gone.

Total Petroleum Hydrocarbons (TPH) were analysed with FT-IR System (Perkin Elmer) and TPH fractions were determined using a GC-ECD equipment *(*Agilent Technologies 6890N). TCE and PCE were measured using a GC-MS with ionic trap (Agilent 7890 A), and total Mn by Atomic Absorption (AA Nora A300, Analytic Jena). Solid samples were processed by acidic digestion, using temperature control microwave heating. PH and conductivity were electrochemically checked (pH-meter Consort C 532).

RESULTS AND DISCUSSION

Producing packed oxidants

Paraffin wax (PW) and Carnauba wax (CW) were used fist as packing materials and then different blends of them. The microcapsule, with active load between 20 aqnd 25%, and sizes around 100 µm (Figure 1) were successfully obtained.

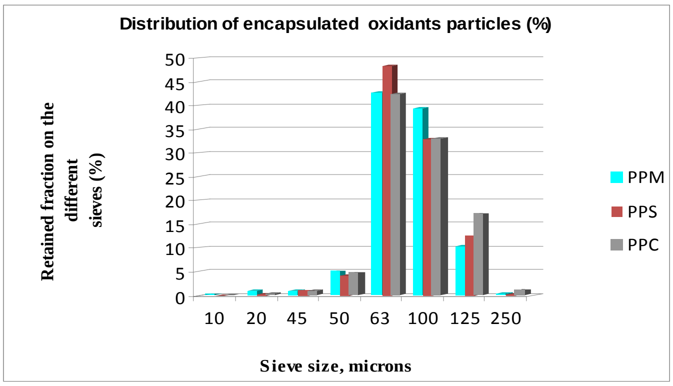

Figure 1 Microcapsule size distribution (PPM – Packed Permanganate, PPS – Packed Persulfate, PPC – Packed Percarbonate)

Using smaller regent particles (e.g. PP fraction with 25 µ), smaller micro-spheres were obtained (Figure 2) but some surface imperfections were noticed.

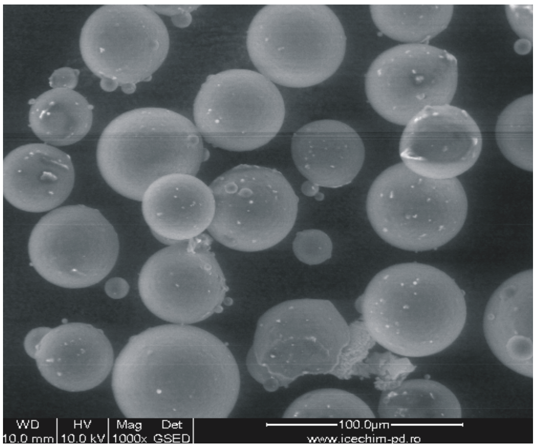

Figure 2 CW-PP micro-spheres obtained from 25 µ PP

Packing the small fraction of oxidants in PW (special grade, m.p. around 80^{0}C) resulted in smaller particle size (between 6 and 8% above 100 µm (Figure 3), with limited surface defects.

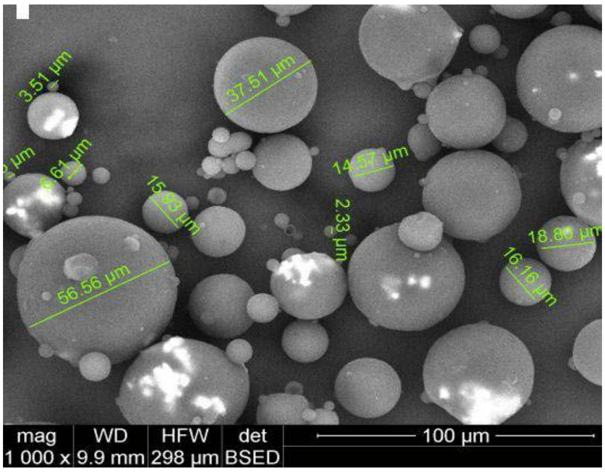

Figure 3 PW-PP micro-spheres obtained from 25 µm PP

Oxidant release tests

CW-packed oxidants (Figure 4) showed interesting differences between the oxidants.

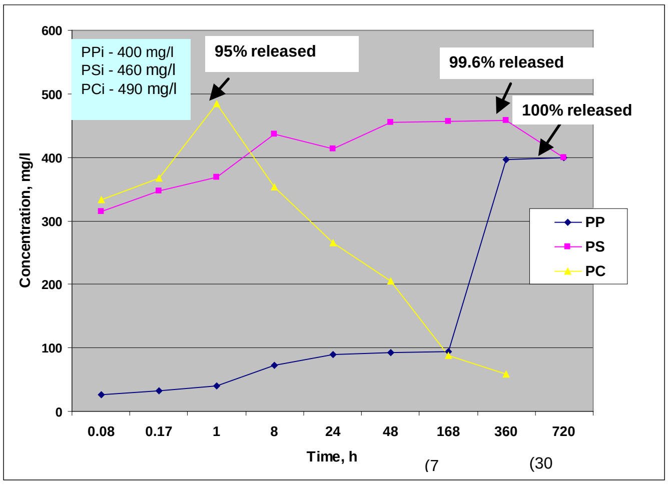

Figure 4 Oxidant release from CW-packed microcapsules, size up to 250 µm

PW-packed oxidants demonstrated a fast release (burst above 80% in about 8 h) when microcapsules were below 100 µm (Figure 5).

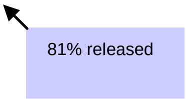

Figure 5 Oxidant release from PW microcapsules <100 µm

After a burst of about 50% in 2 h, PS and PC were more than 90%released in one day, while PP proved slow initial release, with burst after 7 days.

An empirical mathematical equation, a simplified homographic function, was proposed to describe release for both CW- and PW packed oxidants:

$$C(t) = \frac{at}{b+t},$$

where constants *a* and *b* were calculated using the least square estimator for both systems.

Testing the reactivity of packed oxidant

All three oxidants packed in CW and the two oxidants packed in PW were comparatively tested for oxidation NAPLs.

Only some selected results referring to oxidation with PW-packed oxidants are presented.

TCE (DNAPL) seems to be continually oxidized in aqueous phase by both PP and PS and more TCE is dissolved from the free phase (Figure 6).

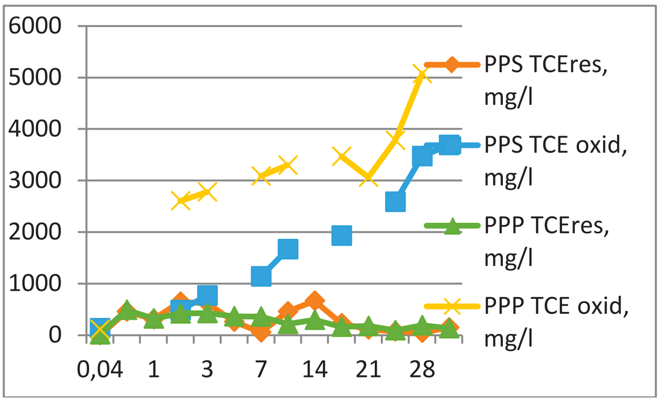

Figure 6 TCE oxidation with PW-packed oxidants; residual concentration is calculated upon Cl$^-$ formed)

Diesel (LNAPL) is obviously better oxidized by packed PS than PP (Figure 7).

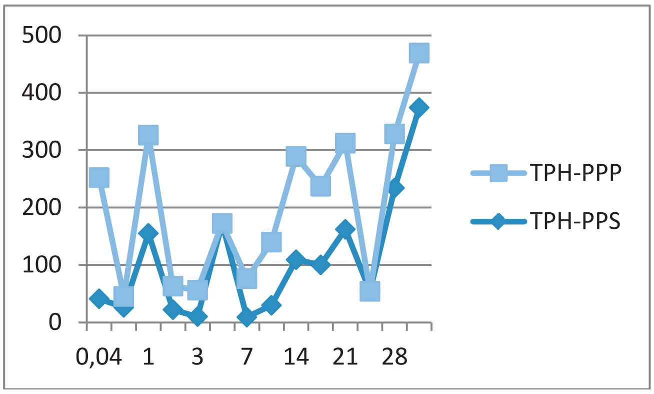

Figure 7 Diesel (as TPH) oxidation with PW-packed oxidants

Fluctuation of total petroleum hydrocarbon (TPH) concentration indicates quite a 3-4 – day cyclic process: after an interval of concentration decrease, more Diesel is dissolved. It was also set that oxidation of dissolved Diesel (aqueous solution) took about 3 days to complete.

CONCLUSIONS

Three oxidants (Potasium Permanganate - PP, Sodium Persulfate - PS and Sodium Percarbonate - PC) were successfully packed in CW, and PP and PS also in PW.

As producing injectable microcapsule of <100 µm was one major objective, it was set that reagent particles <25 µm need to be ensured when spray congealing method is used.

The results showed that the smaller the particles the faster the oxidant release and, consequently, the lower mass content of the active in microcapsules.

All three packed oxidant systems were active for both DNAPL and LNAPL oxidation and differences were more obvious in case of mixed, complex contaminant compositions.

In case of oxidation with PP, MnO_4^- is absent after the 1st hour of testing (self-depletion in aqueous phase), but it was found in the organic precipitate. It still remained active after 28 days.

In case of Diesel oxidation, MnO_4^- stayed dissolved for two days, than transformation to brownish Mn-based compounds takes place.

It was also demonstrated that Diesel oxidation with both Packed PP and PS took place with continuous solubilization of the organic phase (fluctuating concentrations with 3-4 days periodicity), but the residual, dissolved TPH concentration values are constantly lower in case of PW-PS than PW-PP

As a general observation, it should be noted that the final pH values could be an indication in case of TCE oxidation (down to pH = 2 for both oxidants), but not for TPH case

It should be added that over-dosage of PW-PP led to bulky aggregates, which are re-dissolved only if extra-quantities of TCE are brought in contact.

ACKNOWLEDGEMENTS

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Use of Lumped Isotope Enrichment Factors to Delineate Degradation of Chlorinated Ethenes by Zerovalent Iron

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Within the EU-FP7 project AQUAREHAB, compound specific isotope analyses (CSIA) are being examined as a tool to quantify degradation processes at several sites that are treated with zero valent iron (ZVI). An essential target of monitoring these chloroethene (CE) treatments is the proof of complete dechlorination. Isotope monitoring has a high potential to quantify this process, provided that adequate isotope enrichment factors of chloroethenes can be defined.

Generally, isotope enrichment factors describe the proportionality of isotope value increase and concentration decrease of a single compound. For the assessment of complete dehalogenation of total CEs, however, an overall factor has to be defined that integrates the enrichment of several degradation steps. Theoretical maximum assessment concedes the summation of enrichment factors from single compounds, while the minimum assessment regards only isotope enrichment of the final step of degradation. Both scenarios entail a wide range of potential enrichment, which leads to a high uncertainty in quantitative conclusions on degradation. Therefore, we aimed the determination of a lumped isotope enrichment factor (ε_L) representative for the enrichment of weighted average isotope values of chlorinated ethenes ($^{13}C_{\Sigma CE}$) through degradation by ZVI.

Isotope enrichment factors for primary dechlorination of PCE and TCE (ε_{PCE}, ε_{TCE}) as well as for complete dechlorination ($\varepsilon_{L(PCE)}$, $\varepsilon_{L(TCE)}$) were determined in laboratory assays for different types of ZVI. A high correlation of isotope enrichment and concentration decrease was found. Within the broad range of product-specific isotope enrichment factors for zerovalent iron, the ZVI product used in barriers exhibited high fractionation for TCE (ε_{TCE} = -17 ‰) and low fractionation for VC (ε = -9,9 ‰). Only for PCE, the lumped isotope enrichment factor for complete dechlorination ($\varepsilon_{L(PCE)}$ = -14,2 ‰) differed remarkably from the compound-specific enrichment factor (ε_{PCE} = -22,9 ‰), which is induced by the primary step of dechlorination. Thus it was concluded that another step than direct PCE degradation limited total dechlorination, which was supported by the accumulation of TCE in PCE assays.

The lumped isotope enrichment factors from laboratory assays provided the best fit for real dehalogenation compared to theoretically derived factors that had been suggested for quantitative calculations up to now (e.g. maximum/minimum approach). Therefore we recommend to determine lumped isotope fractionation factors for CEs also for other degradation processes (e.g. reductive dechlorination). The application of lumped factors is a promising new concept for a more accurate assessment of complete CE degradation by isotope monitoring.

Feedback driven remediation

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Conventional monitoring and control techniques associated to in-situ remediation technologies (e.g. chemical oxidation/reduction, biostimulation, etc.) involve periodic samplings and analysis from monitoring wells to verify changes of the geochemical environment due to remedial actions, the remediation effectiveness and its long term effects once the active measures have stopped. Accordingly, a good view on the usually complex subsurface conditions is required (hydrogeology, contaminant distribution...) to understand the environmental setting and develop a successful monitoring strategy. Within the FP project UPSOIL, a tool for improved monitoring of in-situ remediation has been developed and tested. This feedback driven monitoring-remediation approach consists of an operational methodology that allows the optimisation of any type of remediation control by using real time measured data in order to adapt and optimize the remediation strategy as new data gradually become available. This new approach supports the cost-effectiveness and potentially reduces the time frame of active restoration measures as well as their impact on the natural media. Within the UPSOIL project, a specific feedback driven remediation strategy has been defined for in-situ chemical oxidation (ISCO) and put into practice into three different field tests in Europe: Belgium, Poland and Spain. This dynamic work approach is based on three interlinked concepts: real time monitoring, hydrogeochemical modelling and feedback instructions. The first step consists on the real time monitoring of key biogeochemical parameters (e.g. pH, redox potential, electrical conductivity, temperature and dissolved oxygen) by means of specific sensors that send the data wirelessly to an online shared data-logging system. The hydrogeochemical model is then automatically fed with the real time measured data, allowing its adjustment and verification. The model is able to predict the ISCO treatment efficiency as wells as its long term effects, and to set the values of those parameters that play a key role in the treatment. Finally, the feedback instructions consist of a list of actions that are needed in order to improve the remediation success taking into account the hydrogeochemical modelling results (e.g. additional injection points, increased volume of injected reactant, etc.).

Amberlite XAD-7HP as a promising candidate for the tailored "smart carrier"/bacteria technology

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The success of a tailored carrier/bacteria technology for the rehabilitation of water-bodies contaminated with pesticides strongly depends on the choice of a suitable carrier. The optimal carrier allows biofilm-formation of pesticide degrading organisms either naturally occurring in the water-bodies or added with the carrier. A "smart carrier" is additionally equipped with adsorption and desorption features which increase the retention time of pesticides and thus the contact time between pesticides and microorganisms and decrease potential toxic effects due to high concentrations without inhibiting microbial degradation by reducing bioavailability. In this study, we examined several carrier materials for their adsorption and desorption characteristics and selected based on this the most suitable "smart carrier" candidate, the adsorber resin XAD-7HP. Within mineralization experiments we further tested whether pesticides are still available for respective microbial degraders. Three different model compounds were investigated: the strongly sorbing pesticide linuron, the moderately sorbing herbicide carbofuran and the highly water soluble pesticide metabolite 2,6-dichlorobenzamide (BAM). Mineralization was tested with the strains *Variovorax* sp. SRS16 (linuron degrader), *Sphingomonas* sp. KN65.2 (carbofuran degrader) and *Aminobacter* sp. MSH1 (BAM degrader). The strains´ capacity to mobilise XAD-7HP-sorbed pesticides was investigated using two different pesticide concentrations (17 µg/l 250 µg/l, using ^{14}C-labelled compounds) in a medium-adsorber ratio resulting in 75%, 95% or 99% pesticide adsorption. Mineralization was detected in all sets, however, mineralisation characteristics for the three different strains differed distinctly. Strain KN65.2 mineralised carbofuran in the presence of XAD-7HP to the same extent as controls without adsorber resin. In contrast, mineralization extents of BAM and linuron by MSH1 and SRS16 were significantly lower the stronger the pesticide was sorbed. However, for the latter two strains differences in the mineralization extents were even detectable without XAD-7HP, solely dependent on the initial concentration added. This indicated that the mineralization rate is not a perfect indicator for bioavailability, but rather influenced by other factors as well. Indeed, methanol extraction of XAD-7HP confirmed that BAM was fully converted. Residual ^{14}C in the liquid phase pointed to the formation of highly water soluble intermediates which were not adsorbed by XAD-7HP. We suggest that *Aminobacter* sp. MSH1 under starvation conditions changes the route of BAM degradation by converting the compound to an accumulated metabolite or extracellular polysaccharides (EPS) instead of mineralization and biomass. Nevertheless, combining all results supports the assumption of XAD-7HP to be a suitable "smart carrier" candidate for the tailored carrier/bacteria technology.

Reduced iron catalysts with polar properties for targeted dehalogenation of chlorinated solvents in groundwater

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We have attempted to make novel catalysts for dechlorination of chloroethenes. These would have hydrophylic surface properties to improve migration in groundwater, but also have high affinity for contaminants that exist as pure product (NAPL). The following hydrophilic materials were selected.

Cyclodextrins: These are large sugar-derived molecules that possess a cavity that can host more hydrophobic molecules like reduced iron particles, which are in that case expected to have a reduced tendency to aggregate and improved transport in the groundwater.

Dithiotreitol (DTT): We have pursued soluble complexes of ferrous iron with DTT. This is a small reducing molecule with sulphide groups that may form a catalytic complex with iron, while it also has two hydroxyl groups that may provide a polar surrounding to the complex.

Thioglycolate (TGA): A similar approach was tested as for DTT. TGA is a reducing molecule with one sulphide group and one carboxyl group that may coordinate to iron atoms yielding polar and soluble catalytic complexes.

The first two tests with cyclodextrin encapsulation (with alfa and beta isomers) facilitated the formation of iron sulfide complexes which did not precipitate. However, TCE-removal capacity of the system was poor. A test with larger amounts of FeS yielded a heterogenous system, which is not favourable for particle migration. This cyclodextrin-FeS complex was more reactive than in the previous tests. Separation of the groundwater and precipitates indicated that the activity was associated with the precipitates. The solution had only limited activity for dechlorination of PCE. Only very small quantities of innocent degradation products were observed.

Different ratio's between dithiothreitol and ferrous iron at different pH have been investigated. One test resulted in soluble complexes with interesting reactivity with a DTT-iron molar ratio of 2/1 and to a minor extent also 1/1, but this was under strong alkaline process conditions which are not ideal for field applications. Optimization was attempted with lower pH and a lower ratio DTT/Fe of ½. The latter showed significant removal of PCE at a pH of 8, but the reaction was incomplete. Also this condition showed formation of precipitate..

Three molar ratios between thioglycolate and Fe were tested, each at 3 pH values, with dithionite as electron donor. Initially clear solutions without precipitates were obtained, but after addition of dithionite precipitates were formed. The complexes did not degrade PCE.

This study was part of the FP7 UPSOIL project (GA 226956).

Session 11
In-situ bioremediation: progress in basic research

Oral presentations

New insights into the resilience of the aerobic/anaerobic *cis*-dichloroethene degrading sediment communities to redox fluctuations

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ABSTRACT*: Cis*-dichloroethene (cDCE) is a product of reductive dehalogenation of polychlorinated ethenes and is highly toxic to humans. Discharge of cDCE to aerobic surface water through stream-bed sediment represents a significant environmental concern. cDCE can be dechlorinated by reductive dechlorination or aerobic biodegradation. Penetration of oxygenated surface water into the stream-sediment across the sediment-water interface can influence cDCE degradation pathways by precluding the growth of obligate anaerobes and/or stimulating the aerobic communities. This study sought to clarify the resistance and resilience of aerobic and anaerobic cDCE degrading populations to varying redox conditions in microcosm experiments prepared from the surficial sediment of the Belgian River Zenne. cDCE dechlorination experiments were conducted under varying anaerobic/aerobic and non-shaking/shaking conditions. Results showed a substantial degradation under both anaerobic and aerobic non-shaking conditions with concomitant enrichment of reductive dehalogenase gene (*vcrA* and *bvcA*) copies as determined by quantitative PCR. Subsequent enrichment of the two functional genes involved in aerobic, growth-coupled oxidation of vinyl chloride (VC) and ethene (*etnC* and *etnE*) under aerobic non-shaking condition showed survival of aerobic degraders after prolonged exposure to anaerobic conditions. Interestingly, cDCE was degraded with much lower rates under aerobic shaking condition and stopped when the accumulation of reduced daughter products ceased. Subsequent reactivation of *Dehalococcoides* spp. and accumulation of reduced daughter products under final anaerobic non-shaking condition revealed high resilience of *Dehalococcoides* spp. to oxygen perturbation in their natural ecosystem.

INTRODUCTION

Chlorinated ethene congeners are among the most frequently detected groundwater contaminants which can find way to surface water representing a significant environmental concern. Microbially mediated degradation is one remedial option which may be used to clean up soil and groundwater contaminated with chlorinated solvents yielding near- and long-term benefits. Hyporheic zone in river-bed sediment can act as a natural biobarrier for biodegradation of chlorinated solvents. Hyporheic zones are storage zones for organic carbon and are characterized by physical and chemical gradients enabling a broad spectrum of microbial processes such as reductive dechlorination. Reductive dechlorination is mainly mediated by *Dehalococcoides* strains which grow exclusively by organohalide respiration. However, incomplete reductive dechlorination of highly chlorinated ethenes in deeper anaerobic layers of river-bed results in production of more toxic daughter products such as *cis*-dichloroethene (cDCE). On the other hand, oxygen in surface water can infiltrate into the river-beds and the resulting more oxic sediment layers at the surface water-sediment interface, can be conducive to aerobic biodegradation of less-chlorinated daughter products.

In spite of remarkable progress in understanding the microbiology involved in detoxification of chlorinated ethenes, far less attention has been paid to the potential of the hyporheic zone as a dual-layer biobarrier for biodegradation of chlorinated ethenes, i.e. reductive dechlorination in deeper layers of river-bed sediment and aerobic biodegradation in surficial oxic layers. However, due to dynamic exchange between ground water and surface water, delineation of such oxic/anoxic zones in a dynamic system such as river-bed sediment will not be possible. As an example, due the downwelling migration of oxygenated surface water into the sediment, the redox conditions can change from anoxic to oxic over short distances exposing anaerobic microbial communities to oxygen which appears to be toxic to chlororespiratory microorganisms. However, after the precipitation events, generally the anoxic ground water recovers its normal upwelling flow. Due to this flow reversal and subsequent local redox fluctuation, portions of the hyporheic zone are repeatedly exposed to varying redox conditions.

This study sought to clarify the response of the site-specific microbial communities involved in biodegradation of cDCE to periodic redox disturbance in their natural ecosystems. Of particular interest was to gain knowledge on the capability of *Dehalococcoides* spp. to react to oxygen exposure in their natural sediment habitat. The obtained knowledge will help us in resolution of underlying degradative pathways and the key players in hyporheic zone which is of high importance for *in situ* sediment bioremediation.

MATERIALS AND METHODS

Microcosm set up and culture condition

Microcosms were prepared in 160 ml serum bottles containing 37 g wet sediment samples collected from the top 20 cm layer of the river-bed sediment from the Zenne River in Machelen-Vilvoorde, Belgium and 90 ml surface water. Microcosms were spiked with 5 mg/L cDCE and incubated at room temperature without shaking (designated as anaerobic non-shaking-1). When 3 additions of cDCE were degraded under anaerobic condition, microcosms were converted to aerobic condition by providing sterile oxygen gas at an initial amount of 7% (vol/vol) of the headspace after the withdrawal of an equal volume of headspace. The originally anaerobic and now-aerobic culture that could degrade three cDCE spikes under newly aerobic condition were converted to originally anaerobic condition (anaerobic non-shaking-2) and degradation was followed to study revival of the anaerobic community. The conditions were always changed when three consecutive additions of VC and cDCE were degraded. Previously we observed that under non-shaking conditions oxygen penetration into the sediment layer could be limited (Atashgahi *et al*., submitted for publication). Therefore, the next step was to study the effect of oxygen exposure under shaking condition. However, first it was necessary to study the effect of shaking under anaerobic condition to make sure that the effects of next step is only from oxygen exposure. Therefore, cDCE degradation was followed in anaerobic microcosms (anaerobic shaking) incubated on a rotary shaker (120 rpm) with bottles laid down horizontally in shaking direction to get the maximum mixing. After this step, in order to alleviate the shaking effect, the microcosms were spiked with cDCE and incubated anaerobically non-shaking (anaerobic non-shaking-3).The subsequent changes were: aerobic shaking (120 rpm, bottles laid down horizontally in shaking direction) and finally anaerobic non-shaking-4.

Quantification of biomarkers

Samples for DNA extraction were withdrawn as ~2 g slurry from all duplicate microcosms after thorough mixing. Samples were taken always at the end of the third spike, unless otherwise stated. DNA was extracted from the samples as described previously (Hendrickx *et al*., 2005). Real-time PCR (qPCR) was used for quantification of reductive dehalogenase genes *bvcA* and *vcrA* as biomarkers of reductive dechlorination (Maphosa et al., 2010) and *etnC* and *etnE* genes as the biomarkers of aerobic biodegradation (Jin & Mattes 2010).

RESULTS

Occurrence of aerobic and anaerobic cDCE degradation activity in sediment microcosms and dynamics of biomarkers

Figure 1 shows cDCE biodegradation and accumulation of VC and ethene as the reduced daughter products of reductive dechlorination of cDCE under different redox conditions. High cDCE biodegradation potential was observed under initial anaerobic condition with stochiometric conversion to ethene (Figure 1, anaerobic non-shaking-1). When converted to aerobic non-shaking condition, disappearance of cDCE in the newly aerobic microcosms was a possible indication of the activity of aerobic populations with concomitant increase in the numbers of *etnC* (11-fold) and *etnE* (6-fold) (Figure 2, aerobic non-shaking). Nevertheless, accumulation of VC and ethene as the reduced daughter products at the end of first cDCE spike in the newly aerobic microcosms was indicative of dehalorepsiration activity. Although the accumulation of reduced daughter products reached plateau at the end of third cDCE spike, 9-fold increase in the numbers of *vcrA* and *bvcA* further verified the activity of reductive dechlorinators under aerobic condition (Figure 2, aerobic non-shaking).

When microcosms were converted back to originally anaerobic condition (Figure 1, anaerobic non-shaking-2), formation of the reduced daughter products was resumed under newly anaerobic condition. Stochiometric conversion of cDCE to ethene during the second and third spikes was incontrovertible evidence of chlororespiration recovery as the main degradation pathway. In accordance, the copy number of *vcrA* and *bvcA* further enriched 5- and 3-folds, respectively (Figure 2, anaerobic non-shaking-2). Under anaerobic shaking condition, cDCE degradation rate was negatively affected specially during third cDCE spike. Accordingly, the number of all biomarkers also declined (Figure 2, anaerobic shaking). However, the 3 subsequent cDCE spikes under anaerobic non-shaking condition (Figure 1, anaerobic non-shaking-3) improved both the degradation cDCE rates and the counts of *vcrA* and *bvcA* as the biomarkers of reductive dechlorination (Figure 2, anaerobic non-shaking-3). Nevertheless, the number of *etnC* and *etnE* decreased 1- and 2-fold so what do you mean?) respectively (Figure 2, anaerobic non-shaking-3). This was expected since there was no oxygen in the microcosms.

Degradation rates were significantly decreased under aerobic shaking condition (Figure 1, aerobic shaking). Negligible accumulation of ethene in cDCE spiked microcosms showed activity of reductive dechlorinators even under vigorous oxygen exposure. Based on the high cDCE degradation rate under aerobic non-shaking condition, it was also expected that high cDCE degradation takes place under aerobic shaking condition. These results show that under aerobic non-shaking condition, the main cDCE/VC degraders were reductive dechlorinators rather than aerobic degraders and raises a thoughtful question whether aerobic degraders of cDCE/VC are really active in their natural ecosystems. The only possible explanation for observed lack of mass balance and increase in the number of *etnC* and *etnE* could be presence of ethenotrophs which are able to assimilate ethene and degrade VC cometabolically (Mattes et al., 2010).

In the last step, when the microcosms were spiked with cDCE under anaerobic non-shaking condition (Figure 1, anaerobic non-shaking-4), removal of cDCE was started after 5 weeks and afterwards coupled to accumulation of reduced daughter products. Interestingly accumulation of VC started 6 weeks after oxygen removal while ethene accumulation took place after an incubation of 15 weeks. This is in line with the results of Amos et al. (2008) who showed that *Dehalococcoides* strains catalyzing the VC-to-ethene dechlorination step are more susceptible to oxygen inhibition. During the second cDCE spike under final anaerobic non-shaking condition, near-complete revival of reductive dechlorinators can be deduced from high cDCE degradation rate and accumulation of VC and ethene as the reduced daughter products (Figure 1, anaerobic non-shaking-4). This indicates that in spite of the reports on high sensitivity of *Dehalococcoides* to oxygen exposure in pure or enrichment cultures (Adrian et al., 2007; Amos et al., 2008), they can have high resistance and resilience to oxygen exposure and redox perturbation in their natural ecosystem.

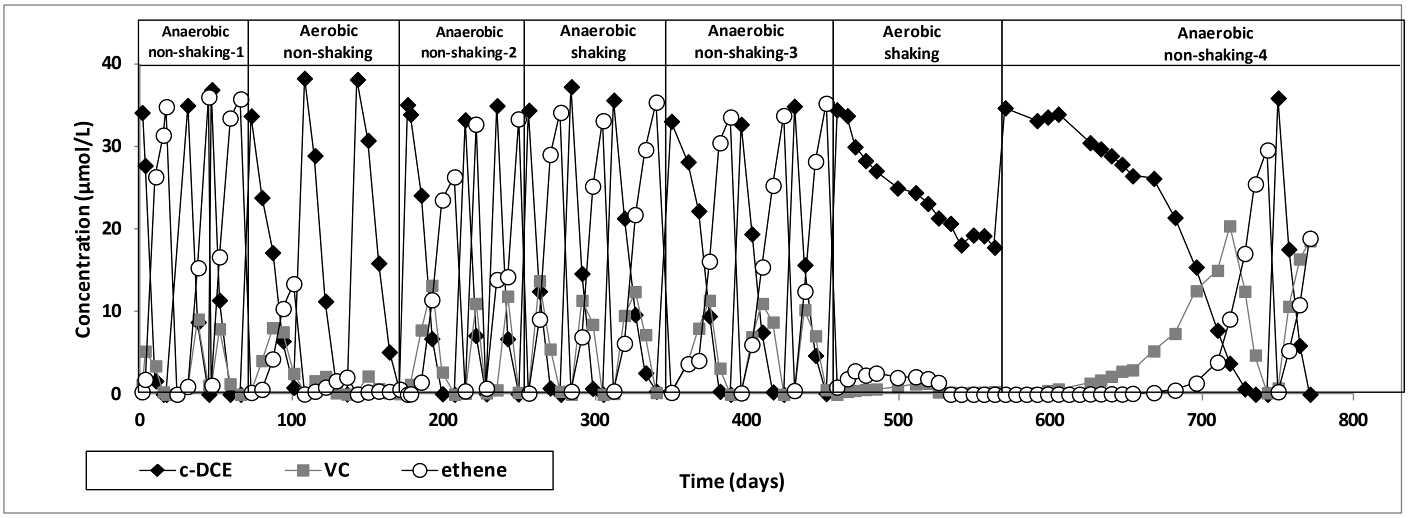

Figure 1: cDCE biodegradation and accumulation of VC and ethene in sediment microcosms

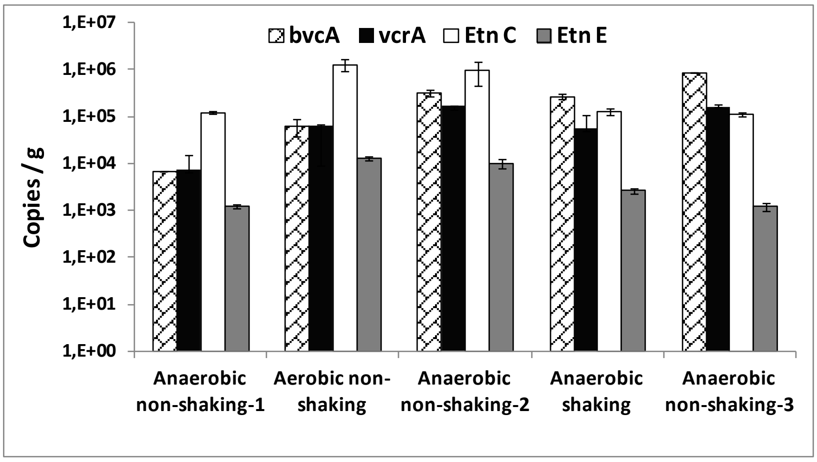

Figure 2: gene copy numbers of vcrA and bvcA as the biomarkers of reductive dechlorination and etnC and etnE as the biomarkers of aerobic biodegradation as determined by qPCR.

CONCLUSIONS

To the best of our knowledge, this is the first study to unravel underlying degradation potential i.e. reductive dechlorination versus aerobic degradation of cDCE under varying redox conditions. The results showed high resistance and resilience of reductive dechlorinators against poisonous effect of dissolved oxygen in their natural habitats. Moreover, no substantial aerobic degradation potential was observed. This can have implications for *in situ* remediation of sites contaminated with chlorinated solvents where the loss in mass balance in the aerobic fringe of the plumes are attributed to aerobic degradation. The results of this study showed that the loss of mass balance under oxic condition can simply be due to presence of ethenotrophs which can assimilate the reductively produced ethene.

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Different surfaces' influence on biofilm communities and contaminants' degradation.

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Introducing micro organisms or enhancing their activities in polluted groundwater depends mostly on their ability to form diverse active biofilm on a solid matrix. In this study, we examined the effects of different solid carriers on the abundance, diversity and activity of the adhered microbial population. We examined, in this study, activated carbon, white and gray chalk, gravel, sand and silica. The carriers' size ranged from 150 to 850 μm while surface area ranged from 0.14 m^2/g for sand to 454 m^2/g for activated carbon.
The carriers were incubated *in situ* in contaminated groundwater that is saline (TDS of between 16 and 24 g/l) and is mostly devoid of oxygen. After incubation, the microbial diversity was estimated by PCR-DGGE analysis and its abundance by viable count. The amount of viable biomass that developed was low and ranged from 10^2 to 10^4 CFU/g without dependence on carrier type. PCR-DGGE analysis of the carriers incubated *in situ* revealed that diverse microbial population development occurred. A cluster analysis was performed in order to evaluate the factors influencing diversity. The cluster analysis suggests that, in a given environment, similar carriers will be colonized by similar microbial populations. However, identical carriers in different environments will be occupied by different populations. Hence, it is clear that both water chemistry and surface characteristics influence the biofilm composition. Water chemistry (salinity, etc.), in this experiment, was the first factor in determining the composition of the microbial population that developed in a given environment, while the carrier's characteristics were second in importance.

Biodegradation of adhered bacteria was tested using ^{14}C labelled benzoic acid, linuron, MCPA and atrazine. Benzoic acid mineralization verified that metabolically active biomass was present on all carrier materials following the *in situ* incubation. No significant mineralization of most of the tested herbicides was measured. Interestingly however, single bottles with sand showed extensive atrazine mineralization. A stable enrichment culture, selecting for populations using atrazine as either a nitrogen source (MSC-cultures) or as both carbon and nitrogen (MS- cultures), was established with sand as the carrier.

In conclusion, the different biofilm carriers studied attracted diverse microbial populations whose compositions depended on the carrier type. The viability of microbial populations appears to be influenced by water chemistry and environmental conditions. Nevertheless, under selective conditions, it is possible to enhance the biodegradation of pollutants by the carrier-adhered bacteria. Thus, these data can be used for better management of polluted water.

Correlations between organohalide respiring genetic biomarkers and chloroethene degradation rates

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The assessment of biodegradation activity in contaminated aquifers is critical to demonstrate the performance of bioremediation and natural attenuation and to parameterize models of contaminant plume dynamics. The aim of the current study was to evaluate whether a correlation exists between dechlorination rates and the amount of specific genes (biomarkers). Lab scale microcosm degradation experiments were set-up with aquifer and groundwater samples from 5 different spots at asite contaminated with chlorinated ethenes. In function of time, the remaining pollutant concentrations and their breakdown products were measured. Degradation rates were deduced assuming first order degradation kinetics. *Corresponding* dechlorination rate coefficients (k') obtained from the microcosms ranged from 0.002 to $0.595\,h^{-1}$.At different moments during the degradation, subsamples were also collected for DNA and RNA extraction. A high-throughput, ligation-based circularization assay was used for simultaneous quantitative detection of multiple organohalide respiring bacteria and their key reductive dehalogenases. We estimated the concentration of phylogenetic 16S rRNA for total *Bacteria* and several organohalide respiring bacteria including *Dehalococcoides, Sulfurospirillum, Desulfitobacterium, Dehalobacter, Geobacter, Desulfuromonas* and *Anaeromyxobacter*. Several reductive dehalogenases (*pceA*s, *tceA, bvcA, vcrA, cprAs, dcaA, and cbrA)* were also analysed. *Analysis was done at both DNA and RNA level. Correlations of the biomarkers and the degradation rates appeared to be batch dependent and influenced by the aquifer material used to setup the microcosm. Multivariate analysis show differing and variable correlations of biomarkers to degradation rates of the chloroethenes. Additionally, we identified differences in the correlation of genes and the corresponding transcripts to degradation rates. Further biostatistical analyses are being applied to the dataset in order to investigate correlations that can be used as parameters for modelling and investigation of contaminated sites.*

Poster Presentations

Multiple lines of evidence to verify the enhanced reductive dechlorination in a chlorinated ethenes-contaminated aquifer

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Chlorinated solvents are among the most ubiquitous anthropogenic groundwater contaminants in the world. Enhanced reductive dechlorination (ERD) via biostimulation has been increasingly used for bioremediation of chlorinated solvents. The performance of ERD for in situ remediation of an aquifer contaminated with *cis*-1,2-dichloroethene (cDCE) and vinyl chloride (VC) was investigated in a long-term field pilot test. Glycerol was injected as an exogenous electron donor to stimulate the indigenous dechlorinating population(s). Contaminant distribution and redox conditions, compound-specific isotope analysis (CSIA), quantitative PCR (qPCR) and microcosm studies were used to gain insight into the contaminant fate and associated microbial changes. Fermentation of glycerol led to decrease of oxygen concentration to below detection levels and establishment of anaerobic conditions within a period of 37 days after injection. After a relatively long-term lag phase, dechlorination of DCE to VC and ethane was observed 195 days after glycerol injection. The occurrence and variability of in situ biodegradation of chloroethenes were revealed by substantial carbon isotope fractionation in the isotope compositions of cDCE (δ13C ranging from −20.2‰ to +1.3‰) and a rather stable shift of VC (δ13C ~ −35‰) due to simultaneous production and consumption of this compound. The numbers of the 16S rRNA gene copies of *Dehalococcoides* spp. and their two reductive dehalogenase genes (*vcrA*, and *bvcA*) were rather stable before the onset of dechlorination. However, their numbers concomitantly increased by 2 to 3 orders of magnitude throughout the test area only when rapid dechlorination was noted at day 195. In contrast, the numbers of iron-reducing and sulphate reducing bacteria and methanogens drastically increased directly after the injection of the glycerol, showing the channelling of reducing equivalents to these side reactions. Microcosm studies confirmed the presence of *in situ* microbial communities capable of the complete dechlorination of cDCE to ethene. The integrated approach using conventional (groundwater monitoring) approaches coupled with CSIA and qPCR provided several lines of evidence for ERD of the chlorinated ethenes. Such a detailed insight can be of high assistance for site management and full-scale design of bioremediation projects.

Isotopic fractionation of nitrogen during the anaerobic metabolism of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)

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The nitramine explosives octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) have been used by the military in warheads and propellants since the mid-1900s. Cyclic nitramines are toxic and have adverse effects on the central nervous systems of mammals. HMX and RDX were found to be contaminating groundwater in Israel, and a method to investigate their potential for natural biodegradation was sought.

Previously, we have demonstrated that it is possible to follow the biodegradation of RDX using Compound Specific Isotopic Analysis (CSIA) of nitrogen within the molecule. We have further demonstrated ^{15}N enrichment in RDX along the flow path of the contaminated plume, indicating *in-situ* microbial biodegradation. Therefore, the aim of the current investigation is to further study the isotopic fractionation of nitrogen within HMX during its anaerobic biodegradation.

We have enriched a microbial culture from contaminated soils that utilizes HMX as the sole nitrogen and electron acceptor while using lactate as energy and carbon sources. The growth of the culture was concurrent with a decrease in HMX concentration. Different reduced intermediates, presumably nitroso HMX, were detected in the growth medium, indicating that the reductive pathway dominates biodegradation by this culture.

Our attempt to use Gas Chromatography, combined with an Isotope Ratio Mass Spectrometer (GC-IRMS), for CSIA was not successful, and therefore, an isotope analysis was done using an Elemental Analyser connected to an IRMS. This demanded the development of an offline purification technique for HMX before isotopic analysis. We tested both High Pressure Liquid Chromatography (HPLC) and Thin Layer Chromatography (TLC) as offline purification techniques and came to the conclusion that TLC is superior.

Our preliminary investigation shows that the δ^{15}N of un-degraded HMX is -1.5±0.761‰. We hypothesize that the nitrogen fractionation of HMX, in planned complementary experiments, would be similar to the fractionation previously observed during RDX anaerobic biodegradation.

The results of this study will provide an additional tool to improve the management of HMX contaminated aquifers.

BACAd - Bioaugmentation with optimized in-situ culture propagation

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A metal processing site in Flanders, Belgium is characterized by a groundwater contamination with chloro-ethenes that has migrated 1 km off-site, underneath a forest and at a depth of 50 mbg. The groundwater has a high seepage velocity and is acidic. Laboratory feasibility tests have indicated that enhanced natural attenuation by addition of an organic substrate induces only partial dechlorination of PCE which stalls at cis-DCE. The main 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 the propagation of injected cultures.

Five microbial cultures, derived from different sites, and two electron donors have been screened with a laboratory microcosm test. The two best performing cultures were grown in a fermentor. They are used for execution of two push-pull tests at the contaminated site. Each push pull test is done with a specific culture and electron donor. Laboratory column tests are 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 will be injected on a larger scale to perform a field test with 4 injection wells. At the same time, another and similar field test will be performed in an adjacent area. The latter will be done by injection of groundwater from another site where complete dechlorination of PCE has occurred. Alternatively, another commercially available culture may be used at the second location. Afterwards, the remediation will be up-scaled to cover the entire contaminated off-site area. This will be done with transfers of the microbial population from the initial remediation area to other contaminated zones. 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. The microbial analyses include monitoring of pathogens.

Laboratory microcosms demonstrated complete dechlorination with bio-augmentation in the presence of the electron donors nutrolase (a residue from potatoe processing) and glycerol (a residue from biodiesel production). The results of the laboratory column tests will be available.

A first push-pull test with a culture grown on nutrolase induced complete dechlorination in the field. The culture was found to be contaminated by pathogenic bacteria. This contamination was shown to be linked to the electron donor nutrolase. The in-situ evolution of the pathogens has been monitored. Some have disappeared in time, but others persisted. Results of microbial analyses by QPCR and DGGE will be presented. A second culture has been grown successfully on glycerol for performing the second push-pull test. It has been injected in august 2011 and all monitoring results will be available by july 2012.

Atrazine biodegration in groundwater by using bioaugmentation with *Pseudomonas* sp. strain ADP

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Triazines are industrial chemicals used for different purposes such as explosives, dyes and pesticides. In particular, atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has been a widely used herbicide in agriculture in the past 30 years. Due to its high mobility and long half life in soil it constitutes one of the most common pollutants in surface water and groundwater worldwide.

Bioremediation of atrazine has recently received a great attention around the world as a main mechanism of atrazine removal from the environment. A large variety of soil microorganisms are known to degrade atrazine but until now, *Pseudomonas* sp. strain ADP is the best-characterized bacterial strain capable to degrade the herbicide atrazine until complete mineralization.

The objective of this work was to investigate the capacity of *Pseudomonas* sp. strain ADP to degrade atrazine in a specific location in Israel (within Secher-Besor basin, northern Negev desert) where the water has a high salinity and contains a high variety of pollutants, including pesticides.

In order to reach this goal batch biodegradation tests with *Pseudomonas* sp. strain ADP were prepared by suspending bacteria in 100 mL synthetic or natural groundwater in sterilized 250 mL Erlenmeyer flasks.

Synthetic groundwater was prepared by mixing different proportions of the culture medium of *Pseudomonas* sp. strain ADP recommended by the supplier (DSMZ) and a high-saline solution surrogate of Secher-Besor groundwater. Natural groundwater from Secher-Besor basin filtered (0.22 µm) and non-filtered was also used for the experiments. Dead controls (with formaldehyde) and abiotic controls (without bacteria) were prepared with the same amounts of synthetic and natural groundwater. All the tests were initially spiked with an atrazine concentration between 2.5 and 7 mg/L and 1 g/L of sodium citrate as carbon source. Experiments were maintained in a dark thermostatic chamber at 20ºC and atrazine and dissolved organic carbon (DOC) were analyzed over time.

Batch biodegradation tests performed with *Pseudomonas* sp. strain ADP and synthetic groundwater with an increasing concentration of salinity demonstrated that this bacteria could efficiently degrade atrazine (removals higher than 98%) and adapt to high saline conditions (10.72 mS/cm and 12.58 mS/cm).

Results from batch tests with natural groundwater obtained from the Secher-Besor basin showed no atrazine removal within 65 days when using non-filtered groundwater and thus, bioaugmentation with *Pseudomonas* sp. strain ADP did not success. However, when testing filtered groundwater, results showed an atrazine biodegradation up to 45%.

It can be concluded that *Pseudomonas* sp. strain ADP, when alone, can efficiently degrade atrazine under saline conditions (up to 19.5 mS/cm), however bioaugmentation with *Pseudomonas* sp. strain ADP might not success under natural conditions probably due to the competition with other indigenous microorganisms to use organic matter.

Biodegradation of carbofuran in saline groundwater

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A possible technology for removing pollutants from contaminated groundwater in a fractured aquitard is a draining system intersecting the fractures, combined with enhancing the biodegradation in the draining channel. The polluted groundwater in the fractures is collected by drainage into a channel filled with gravel that creates a porous environment where the biodegradation of pollutants can be done by either planktonic or sessile microorganisms. In this study, we investigate the ability of introduced bacteria and indigenous microorganisms to degrade a model pesticide, carbofuran, in saline groundwater. The drained water had a salinity that ranged between 18.8 to 20 mS/cm.

The ability of a carbofuran degrading *Sphingomonas* sp*.* KN65.2 that uses carbofuran as its sole source of carbon and energy to degrade the compound under different salinities was tested in a defined medium. The strain was able to degrade the compound at concentrations of 2% NaCl, albeit at a slower rate than in lower salt treatments. To test the ability of this strain to degrade carbofuran in “real” groundwater, an experiment was performed with filtered, filtered amended with R2A, unfiltered, and unfiltered amended with R2A groundwater. *Sphingomonas* KN65.2 was able to degrade efficiently carbofuran in all treatments with faster degradation rates in unfiltered water as compared with a mineral medium. These observations suggest that the strain is a good candidate for the bio-augmentation of contaminated water.

Further experiments were therefore performed to test the effect of the draining channel’s gravel matrix on growth and degradation by the introduced strain. In these experiments, *Sphingomonas* KN65.2 degraded the carbofuran more rapidly in the filtered water treatment then in unfiltered water. However, it was observed that, in the non-inoculated unfiltered treatment, degradation did occur but after a prolonged lag and at a slower rate. This indicated that the indigenous microbial population is also able to degrade carbofuran. Upon transfer of the gravel from this experiment into filtered or unfiltered water, degradation continued, suggesting biofilm development.

An unexplained increase in the peak area of carbofuran during HPLC analysis, in both inoculated and control treatments (filtered water), led us to believe that some chemical reaction took place. This reaction was dependent on temperature and, apparently, was related to the presence of bicarbonate ion. We suggest that this reaction is the hydrolysis of carbofuran under the mild alkaline conditions of the groundwater. Nevertheless, it is clear that the native groundwater microorganisms were able to remove carbofuran and its hydrolysis product, as determined from the HPLC chromatographs.

Summarising, the data point to the possibility for an enhanced biodegradation through bio-augmentation. Yet efficient management of the process requires understanding of the biotic and abiotic removal processes.

How granulometry and surfactants affect desorption and biodegradation (*T.Versicolor*) of PAHs in soil and groundwater

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High hydrophobicity of PAHs is the most limiting factor for the remediation of polluted soils and aquifers. Surfactants are amphiphilic substances that promote the transfer of hydrophobic compounds from the solid to the liquid phase. While the interaction between organic matter and surfactants has been widely studied, there is a lack of knowledge concerning the relationship between surfactant efficiency and the granulometry of soil and/or geologic material.

This work analyses the effect of three non-ionic surfactants (Tween 80, BS-400 and Gold Crew) and the granulometry of soil (1%, 5%, 10%, and 20% of clay and silt) on desorption of PAH mixture (fluorene, phenanthrene, anthracene and pyrene). Moreover, PAH mixture desorption is compared with desorption of pyrene alone, working with same experimental conditions. Results show that total desorption in an aquifer and/or soil with non-organic matter is conditioned by: 1) the characteristic of the PAH mixture, 2) the characteristic of each PAH in the mixture, 3) the soil/aquifer granulometry, and 4) the surfactant employed and its concentration.

To complete the remediation process, biodegradation by the white-rot fungi *Trametes versicolor* was tested with Tween 80 and the PAH mixture. Results indicate that a high concentration of surfactant does not affect the efficiency of fungus bioremediation. Nevertheless, high fine material content in soil/aquifer can reduce the degradation rate. The best biodegradation occurs for anthracene, followed by fluorene, pyrene and phenanthrene. Moreover, desorption and biodegradation used synergically guarantee better overall results in the remediation of soils polluted by PAH mixtures than other methods that separate desorption and remediation.

Preliminary study to use fungus to remediate aquifers

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Biobarriers are a common technology to remediate groundwater in polluted aquifers using manly bacteria. In this study, we propose the use of a ligninolytic fungus, *Trametes versicolor*, due to its capacity to degrade a wide variety of highly recalcitrant and xenobiotic compounds even at low concentration.

An artificial aquifer was constructed at laboratory scale (7.5 L and 1 m long), including the aquifer matrix (sand), to simulate groundwater flow at 1D and the biobarrier (3 L and 0.4 m long), which contained pellets of *T. versicolor* fluidized by air supplied by an aquarium pump. Orange G dye was chosen as pollutant in order to follow visually the hydrodynamic behavior of the system and the discoloration produced by fungus degradation. Flow velocity was calibrated to simulate groundwater flow in the range found in shallow aquifers and it was maintained at 0.014 l/h (0.0056 m/h). Temperature was maintained constant to simulate an aquifer. The optimum temperature and pH for *T. versicolor* biological activity is 25ºC and 4.5, respectively, and it is necessary the presence of a carbon source easily assimilable by the fungus.

First, different batch experiments were carried out in the range of shallow aquifers temperatures (15 ºC, 18 ºC, 20 ºC) and also 25 ºC at two different initial pHs, 6 and 7. The main objective was to study the dye degradation at these conditions to select the appropriate residence time and glucose consumption rate for continuous treatment. Afterwards, a continuous treatment at constant temperature (18 ºC) and pH 7 was carried out in the artificial aquifer. Synthetic non-sterile influent flow composition was 150 mg/L of dye in buffered water (300 mg/L of HCO_3^-) and glucose at the consume rate. The barrier was inoculated with 2.9 g of fungus (dry weight) /L. The hydraulic retention time at the barrier was 70h. Degradation results indicate, for the first time, that the fungus *T. versicolor* is a potential organism to be used as a biobarrier in real aquifers as Orange G degradation percentage reached a maximum value of 97%.

Authorslist

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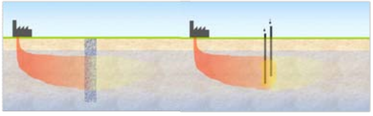

Permeable reactive barriers (PRBs) and reactive zones (RZs) are recognised technologies for the *in situ* improvement of the groundwater quality. Both technologies aim to realise a local stimulation of pollutant removal processes to prevent further migration of pollutions. The newest trends in this field will be presented.

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AQUAREHAB is an EU financed large scale FP7 research project that started 1st May 2009 with 19 project partners (GA No. 226565). Project title: Development of rehabilitation technologies and approaches for multipressured degraded waters and the integration of their impact in river basin management. aquarehab.vito.be

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