Active sediment capping

Generic guideline

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

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Table of Contents

1 INTRODUCTION

Active sediment capping is an innovative in-situ remediation technology for contaminated groundwater. This document intends to provide information about this technology and its application area and boundary conditions for consultants, authorities, contractors and feasibility testing labs. The aim is to offer support when evaluating the feasibility and the impact of the active sediment capping technology to rehabilitate degraded waters, as well as when designing, implementing and monitoring the technology.

This document was composed in the frame of the FP7 project AQUAREHAB (GA 226565), and comprises outcomes and lessons learned during this project.

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

2 BACKGROUND INFORMATION OF THE TECHNOLOGY

2.1 GENERAL EXPLANATION OF THE TECHNOLOGY PRINCIPLE

2.1.1 Natural hyporheic zone – sediment

Hyporheic zone sediment is the area of the streambed which forms an interface between groundwater and surface water (Figure 1). Hyporheic sediments are storage zones for organic carbon and are often characterized by sharp physical and chemical gradients, enabling a broad spectrum of microbial metabolic processes. Such sediments are often hot spots in both diversity and productivity of organisms and can therefore impact the nutrient and pollutant flow into the river system via biotic processes, in addition to abiotic processes such as sorption and dilution. In anaerobic eutrophic river sediments, the high organic matter content in particular can feed a CAH reductive dechlorination activity. Molecular hydrogen, produced from the fermentation of organic substrates is known to serve as electron donor for dechlorinating organisms. Under such conditions, Chlorinated Aliphatic Hydrocarbons (CAH) act as the terminal electron acceptors and undergo stepwise reductive dechlorination where each chlorine atom is replaced with a hydrogen atom mediated by *Dehalococcoides* species.

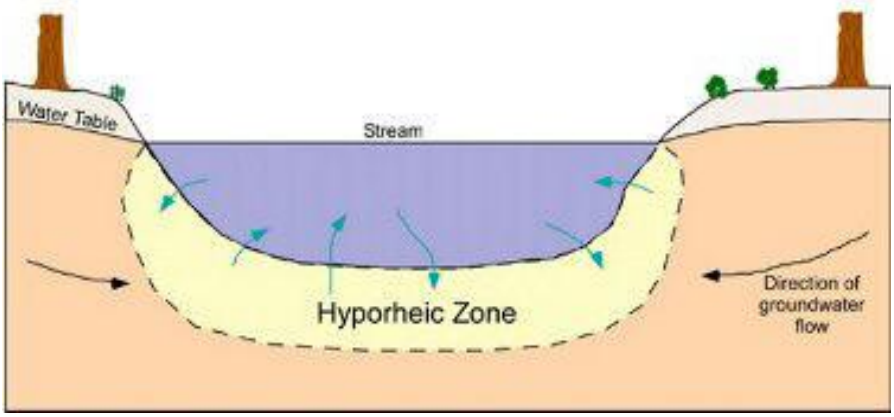


Figure 1. Representation of the hyporheic zone at the groundwater-surface water interface of a river.

If significant natural attenuation processes, including sorption, chemical reaction, and more importantly biodegradation, take place in hyporheic zones, the CAH-contaminated ground water may never reach the surface water, or else discharge with reduced concentrations. Such a scenario would be ideal in minimizing potential risks from CAH-contaminated ground water discharges to the river. However, due to the heterogeneous distribution of biogeochemical gradients, natural bioattenuation may fail to completely dechlorinate tetrachloroethene (PCE) and trichloroethene (TCE) in the subsurface. This may lead to production of even more toxic daughter products like dichloroethene (DCE) and vinyl chloride (VC). Their discharge to the surface water system by the groundwater flow may add to the severeness of the situation. Therefore, remediation of contaminated sediments with chlorinated solvents remains as one of the challenging issues in the field of aquatic sediment management.

2.1.2 Artificial hyporheic zone – capping

In situ capping is a promising technology for reducing exposure and risk to contaminated sediments. It is achieved through containment of the contaminated sediment with clean media. This way, the cap layer forms a barrier between sediment-borne contaminants and potential ecological receptors in overlaying surface waters. Sand is the traditional material employed for passive capping. However, such barriers do not always sufficiently reduce contaminant transport. An innovative *in situ* technique in the field of contaminated sediment remediation is active capping which was recently designed to sequester or transform sediment contaminants. However, the focus of recent developments in the field of reactive caps has been on physicochemical methods of contaminant removal. These act primarily by retarding contaminant migration through sorption, which leads to long-term storage of contaminants in sediments. Due to potential limitations of physicochemical-based active caps such as high material costs and limited sorption and reaction capacities, attempts have been made to develop *in situ* bioreactive caps. In such biologically active cap, the zone of treatment lies within the cap layer (Figure 2). However, the opportunities for incorporating degradative layers into cap materials are not well developed.

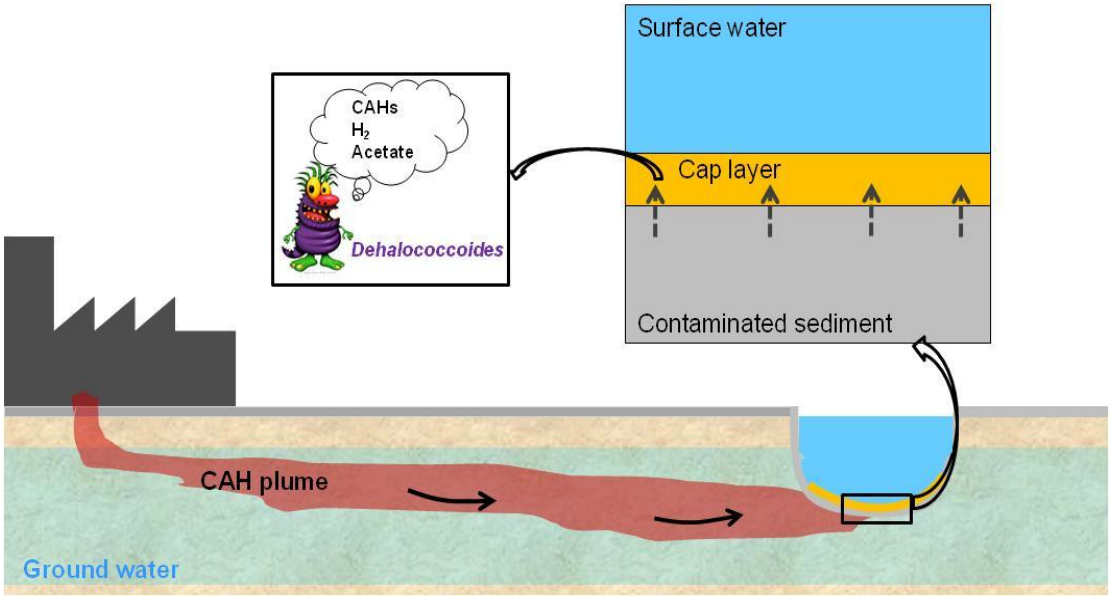


Figure 2. Representation of the bioreactive cap which can be placed on top of the riverbed sediment.

2.1.2.1 Impermeable and permeable caps

For sediment capping two types can be used: impermeable and permeable caps. Impermeable capping systems aim to isolate the contaminated sediments from the overlying water column in a way that no contaminants can pass through the cap. In permeable caps, the porewater can flow through the cap. *AquaBlok*® is an innovative, proprietary clay polymer composite which is used for impermeable capping purposes (http://www.aquablok.com/). It is designed to swell and form a continuous and highly impermeable isolation barrier between contaminated sediments and the overlying water column, and claims superior impermeability, stability, and erosion resistance and general cost-competitiveness relative to more traditional capping materials (EPA, 2007). In the AQUAREHAB project, our aim is however to study the application of permeable caps. We want to find a technique to stimulate the microbial degradation of CAHs in sediments and not physically isolate the sediment from the overlaying water table. Permeable caps should be appropriate for this since they provide better colonization and substrate storage opportunities for the CAH degrading population, resulting in increased degradation capacities towards these CAHs. In what follows, the types and use of permeable caps will be discussed.

Figure 3: Aquablock and its environmental application (from http://www.aquablokinfo.con)

Passive and active permeable caps

Permeable caps can be passive or active. While the main aim of passive caps is to prevent contact between sediment contaminants and the overlying benthic community and surface water, the active caps really sequester and/or degrade the contaminants or stimulate the microbial community to degrade these contaminants. More in particular, active capping approaches can employ physicochemical-based active caps or biologically-active (bioreactive) *in situ* caps. The passive and active caps are described in the following sections.

Passive permeable caps

Passive In situ capping is a remedial option for contaminated sediments in which clean material is placed at the sediment-water interface to prevent contact between sediment contaminants and the overlying benthic community and surface water. Sand is the traditional material employed for capping since it provides excellent protection when contaminants are strongly sorbed to the solid phase and in the absence of rapid contaminant migration processes (Himmelheber et al., 2007). Alternatively, for example in controlling a contaminated groundwater plume that is entering a water body, a sand cap provides a means to control oxygen conditions within the groundwater plume. Thus, the application of a sediment cap can provide a relatively simple means of engineering a reactive permeable barrier as has been developed for subsurface treatment of

groundwater. Specifically, a cap can behave like a two step reactive treatment barrier in that anaerobic conditions are normally maintained in the deeper layers of the cap while aerobic conditions can be maintained near the surface by either diffusion or bioturbation from the surface water body. The cap can potentially increase the residence time necessary to achieve the degradation of halogenated compounds, such as chlorinated solvents, that are common groundwater contaminants (Palermo, 1998). These processes are illustrated in Figure 4. The general availability and lower cost of natural sand is one notable advantage of their employment in capping operations.

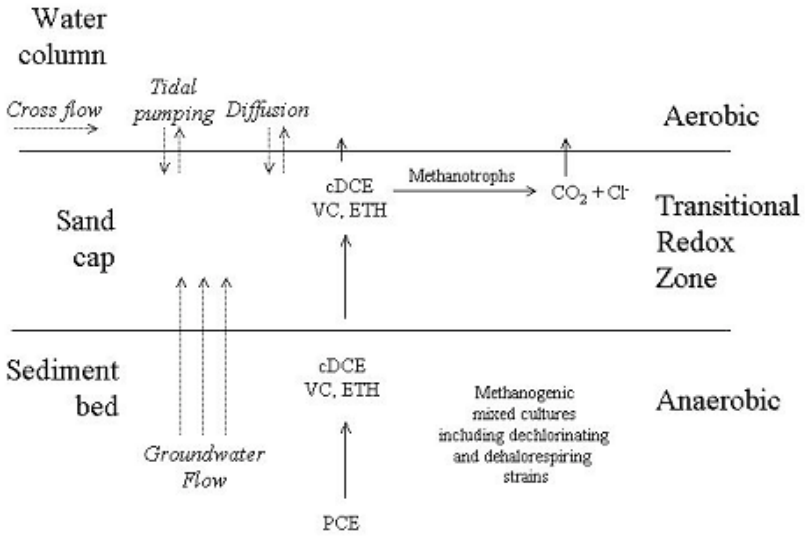


Figure 4 – Flux and transformation processes of chlorinated ethenes in a capped sediment system (Hughes, 2004).

Active permeable caps

Under some situations, such as high rates of groundwater seepage, it is required to use a cap that sequesters and/or degrades the contaminants. These types of caps are often termed active caps to differentiate them from passive sand layers. Active caps incorporate constituents designed to sequester or transform contaminants. As such, active caps can eliminate the threat of contaminant breakthrough and can be utilized at locations dominated by advective flow. The transformation of contaminants within active caps also addresses concerns regarding long-term storage of contaminants in sediments.

Active capping approaches can employ physicochemical-based active caps or biologically-active (bioreactive) *in situ* caps. The latter is preferred, because in a bioreactive *in situ* cap, contaminants are transformed to nontoxic products via microbial reactions. Bioreactive caps and physicochemically-active caps could theoretically be positioned at sediment sites subjected to groundwater discharge for the treatment of both sediment contaminants (e.g., poly chlorinated biphenyls) and groundwater contaminants (e.g., CAHs). The selection of an appropriate active capping material for a site depends on the contaminant of concern, the physical and chemical conditions and processes operative at the site, and feasibility on site.
Constituents and materials proposed for physico-chemical active caps include phosphate minerals (Kaplan and Knox, 2004) and zeolites (Jacobs and Forstner, 1999) for control of metal seepage,

clays and cements (Tarabara and Wiesner, 2005) for permeability control, and organoclays, sorbents (Zimmerman et al. 2004; Murphy et al. 2006), and reactive chemical species like zero valent iron (Lowry and Johnson, 2003) for hydrophobic organic contaminants (HOC) control.
Promising materials for bioreactive capping are solid polymeric organic materials (SPOMs). These include lignocellulosic materials coming from abundant low-cost feedstock such as wood, straw, corn stover, and cellulose containing residues and wastes. SPOMs can be used in bioreactive caps with the dual aim of stimulation of reductive dechlorination (RD) and pollution-load reduction which is of current interest. Typical SPOMs are cellulose, chitin and other complex polysaccharides. These compounds are known to be degraded by both aerobic and anaerobic microorganisms through hydrolysis to mono- or disaccharides (Madigan et al., 1997). Under anaerobic conditions these monosaccharides are fermented predominantly to Volatile Fatty Acids (VFAs) (acetate, propionate, butyrate, and lactate), alcohols (ethanol and methanol), and molecular hydrogen, compounds known to serve as electron donors for reductive dechlorination (Vera, 2001). There are few reports on application of SPOMs for stimulating the reductive dechlorination of chlorinated ethenes. Wu et al. (1998) used corn crop residue, wood chips, and newspaper to support the reductive dechlorination of TCE to ethene in batch experiments. In another study by Brennan et al. (2006), chitin and corncobs were tested as potential electron donor sources for stimulating the reductive dechlorination of tetrachloroethene (PCE) in semi-batch, sand-packed columns. They also studied the type or concentration of fatty acids released during fermentation. Vera et al. (2001) evaluated the potential of corn crop residue, unrefined chitin, and wood shavings for creating conditions that favor reductive processes in groundwater.
Although many pilot- and field-scale studies have utilized enhanced bioremediation to successfully treat chlorinated solvent contamination in subsurface aquifers (Ellis et al. 2000; Song et al. 2002; Lendvay et al. 2003; Rodriguez et al. 2004; Da Silva 2006), none has investigated the application of a single-pass biobarrier placed at the sediment-water interface and the challenges associated with such an application. One such challenge is to design the cap in such a way to accommodate the intrinsic response of native sediments following the *in situ* cap placement, and to ensure that the resulting environment within the cap is conducive to a microbial community performing biotransformations of CAHs.

2.2 MORE DETAILED INFORMATION

2.2.1 Technology name

As mentioned above, passive and active caps exist. However, since only the active caps result in a real destruction of the pollutant, this guideline focusses on active caps and more in particular on the use of biologically active caps for the destruction of CAH.
The term biological reactive cap or bioreactive cap was coined for the new capping technology as the bioreactive layer which is integrated into the cap structure can host CAH degrading microbial communities. *Dehalococcoides* spp. are the only organisms to date that can completely reduce DCE and VC to non-toxic ethane. They need acetate and H_2 as the obligate carbon source and electron donor. By providing the necessary carbon source and electron donor, bioreactive caps can provide an ideal colonization surface and reaction medium.

2.2.2 Targeted substances

An overview of the substances that can be targeted by the sediment capping technology are summarized in Table 1, along with potential emission sources of the different substances.

Table 1 Overview of substances that can be tackled by active sediment capping technology.

Targeted substances		Emission sources
Class	Specific substance	
e.g. CAHs (chlorinated aliphatic hydrocarbons)	Tetrachloroethene (PCE), Trichloroethene (TCE), dichloroethene (DCE), vinylchloride (VC), Dichloroethane (DCA), 1,1,1-Trichloroethane (111TCA)	Drycleaner activities Degreasing activities Electronics ...
Polychlorinated biphenyls PCB	Biphenyl Aroclor	Electrical transformers Coolants and lubricants
Polyaromatic hydrocarbons PAH	Naphthalene, acenaphtene, pyrene, …	Power generation Wood burning Waste incineration Coal tar
Heavy metals	Zn, Cd, Cu, Ni, Pb	Metallurgy Waste water Agriculture
Nutrients	Ammonium, nitrate	Agriculture

2.2.3 Development stage of the technology

The sediment capping technology is very emerging. The opportunities for incorporating degradative layers into cap materials are not well developed. The permeable and reactive nature of bioreactive caps are generally analogous to permeable reactive barriers (PRBs), a common groundwater remediation technology used for *in situ* treatment of contaminants contained within flowing ground water. In an identical manner, solid polymeric organic materials (SPOM) can be adapted to bioreactive caps which can act as the reaction medium by providing substrates and growth supporting surface to the microbial community that performs biotransformations of contaminants. Continuous production of electron donor from a slowly degrading SPOM *in situ* can offer a low cost, and low maintenance biostimulation method.

However, unlike PRBs and physicochemical capping technologies, application of the bioreactive caps for *in situ* bioremediation of the CAH contaminated sediments seems to be in its infancy. Considering the fact that *in situ* capping using inert or chemically reactive materials is rapidly gaining international recognition, it is expected that bioreactive caps soon will reach full implementation stage. The reasons for this can be their relatively lower cost, lower environmental impact and rapid and significant effect on pollutant degradation. The knowledge and experience gained in design and placement of sediment caps in various aquatic systems would accelerate the maturing process of bioreactive capping in the management of CAH contaminated sediments. Overall, due to significant advantages of sediment capping compared to other sediment remediation techniques, it has become a more acceptable method for the regulatory agencies.

Although some examples of *in situ* applications of physicochemical caps exist (Fredette et al. 1992; Brannon and Poindexter-Rollings 1990; Sumeri et al. 1994), to the best of our knowledge, no bioactive cap has already been installed *in situ*. Most studies focus on the selection of appropriate capping materials in the laboratory (with batch and column tests) but do not proceed to the *in situ* level.

2.2.4 Applicability and boundary conditions of the technology (EPA-540-R-05-012)

The active sediment capping technology is recommended under the following conditions:

- Location where contaminated groundwater in discharged in surface water (or where polluted surface water is seeping into the groundwater).
- The pollutants present in the groundwater are degradable under anaerobic conditions since these are the prevailing conditions in the cap. The preferred degradation process is reductive dehalogenation because in this process the carbon source which is present in the cap is being used as an electron donor. Other anaerobic degradation processes such as anerobic oxidation are feasible, but a competition between the applied carbon source and the pollutant for the electron acceptor might occur. The processes do not result in the accumulation of non-degradable harmful metabolites.
- When pollutants are present in the dissolved phase.
- With respect to the hydrogeological characteristics of the site:
    - The groundwater flow direction is known and relatively stable during the year.
    - In principle, the active sediment capping technology is applicable for a wide range of groundwater flow velocities. For higher flow velocity, larger dimensions of the cap are generally needed (mainly achieved by increasing the thickness of the cap to ensure sufficient contact time); the longevity of the system may be lower, resulting in higher costs. In addition, increased flow velocities and turbulence can impact cap stability as they will result in higher shear stresses.
- The hydraulic conductivity of the cap is equal or higher than the permeability of the surrounding sediment.The site is accessible for the installation of the cap, which implies the enrollment and attachment of the cap to the riverbed/river sides. Caps may be most suitable where water depth is adequate, slopes are moderate, contaminants are not mobile, substrates are capable of supporting a cap, and an adequate source of cap material is available.
- Selection of cap placement methods should minimize the resuspension of contaminated sediment and releases of dissolved contaminants from compacted sediment. There are needs to stay accessible for monitoring and potentially for renewal of the cap/cap-filling.
- The geochemical characteristics of the groundwater do not lead to large quantities of precipitates that can block the cap over time.

The use of the active sediment capping technology is not recommended in the following cases:

- For pollutants that have not been shown to be degradable under anaerobic/reductive dehalogenating conditions, or that are transformed in harmful reaction products.
- For sites where free product is expected to migrate into the cap.

- High oxygen concentrations in the groundwater/surface water might lead to fast oxidation of the carbon sources present in the cap (side reactions) and eventually to the inhibition of the pollutant degrading microbial population.
- If the water body is shallow, the cap can suffer from disturbances such as boat anchoring and keel drag. Potential cap erosion caused by propeller wash should be evaluated.

Positive co-effects of the active sediment capping technology:

- An effective rehabilitation technique for the abatement of organic hydrocarbons in stream sediments is most likely to have a positive effect on both above-sediment and sediment biota on the long term. Especially benthic invertebrates can benefit from a reduction of the pressure by chlorinated hydrocarbons.

Negative co-effects linked to the active sediment capping technology:

- Release of dissolved organic carbon (DOC) into the surface water might result in eutrophication of the surface water. A good design of the cap is needed so that the released DOC can be captured by the pollutant degrading population.
- Next to the pollutant degrading population, also other bacteria growing under anaerobic conditions might be stimulated. These bacteria will capture part of the applied carbon sources. A phenomenon often encountered in these caps is the stimulation of methanogenic bacteria resulting in the production of the green house gas methane.
- The capping procedure is expected to have a negative impact on sediment biota on the short term. The technique involves covering the sediment with a solid layer, thus severely disturbing the local habitat of the sediment biota. Especially if anaerobic conditions are established under the layer in the sediment, this may affect the sediment biota considerably at the covered location if it used to be aerobic before.
- To provide erosion protection, it may be necessary to use coarse cap materials that are different from native soft bottom materials, which may alter the biological community. In some cases, it may be desirable to select capping materials that discourage colonization by native deep-burrowing organisms to limit bioturbation and release of underlying contaminants.

2.2.5 Longevity of the technology

An important advantage of the bioreactive caps over traditional cap is its lower need for replenishment. Due to the finite capacity of the traditional caps on sorption of contaminants, replenishment was inevitable to maintain reactivity and prevent the contaminant breakthrough. The contiguous treatment of the upward-migrating contaminant would limit the contaminant breakthrough due to loss of reactivity, a significant shortcoming of physicochemical reactive caps.
Although some field studies have been conducted on long-term effectiveness of physicochemical caps (Fredette et al. 1992; Brannon and Poindexter-Rollings 1990; Sumeri et al. 1994), no knowledge exists about the longevity of the bioactive caps. However, during the AQUAREHAB project, the long term effect (1 year) of different capping materials on the degradation of cDCE was studied at batch level. While methane production decreased over time, cDCE degradation rates were sustained in microcosms amended with the lignocellulosic materials hay, straw, and tree bark (Table 2). This indicates that these SPOMs do not become more recalcitrant over timeand that their slow degradation maintains sufficiently reducing and nutrient-rich conditions to promote reductive dechlorination. In contrast, extensive degradation of shrimp waste appeared to

cause depletion of fermentation intermediates in a shorter time period, leading to diminished cDCE degradation compared with the lignocellulosic materials. Straw amended microcosms degraded the highest mass of cDCE with the highest degradation rates. However, the ratio between the amount of methane and (ethene+ethane) produced was 102 µmol/µmol in these microcosms, while this ratio was only 8 in microcosms amended with tree bark.

Table 2: cDCE dechlorination results with different SPOMs (50 mg/L initial concentration) after 1 year of incubation of the sediment with cDCE

Condition	spike number	Total DCE added (µmol)	Total ETH[a]+ETA[b] produced (µmol)	Total MET[c] produced (µmol)	ETH+ETA/DCE ratio (mol/mol)	MET/ETH+ETA ratio (mol/mol)
NA[d]	4	10.81	10.04	1.33	0.93	0.13
Wood chips	4	10.91	10.03	933.53	0.92	93.06
Hay	18	49.99	48.52	1663.06	0.97	34.27
Straw	23	62.69	61.68	6274.73	0.98	101.73
Tree bark	18	50.37	49.19	393.8	0.98	8.01
Shrimp waste	11	30.35	27.71	2338.63	0.91	84.4

[a] Ethene; [b] Ethane; [c] Methane; [d] Natural attenuation

2.2.6 Cost of the technology

Cost drivers for active sediment capping technology comprise (1) the required dimensions of the cap (depth, length and thickness), (2) the price of the capping material, (3) the local situation on the site (accessibility, surrounding buildings, underground constructions, type of subsurface ...), and (4) the amount of maintenance that is needed to keep the cap active and permeable.

Costs of a number of possible capping materials are indicated **Table 3**.

Table 3: capping materials and their cost in 2014

Capping material	cost	manufacturer
Tree bark	0.119 – 0.189 EUR/kg	www.brico.be
Wood chips	0.025 EUR/kg	http://www.boomschors.net/houtsnippers-kopen
Coconut fibres	0.23 EUR/kg	www.brico.be
Shrimp waste	?	Harbour of Zeebrugge
Unrefined chitin	15-50 dollar/kg	http://www.alibaba.com/showroom/for-chitin-price.html
Corn crop residue	0.086 EUR/kg	http://www.liba.be/liba/uploads/iliba/korrelmais%20verkopen,%20of%20zelf%20CCM%20maken.pdf

The following prices are indicative for active physicochemical caps (Reible et al., 2006). Because the techniques are similar, they can give us an indication of the cost of the bioreactive caps.

- Demonstration approaches: 182 EUR/m²
- Large scale site (~1000 acre)
    - 22 EUR/m² + materials
    - Mobilization/demobilization ~ 0,9 /m²

- Cap placement ~9,1 EUR/m²
- Project Management ~1,8 EUR/m²
- Monitoring ~ 9,1 EUR/m²
- Miscellaneous ~1,8 EUR/m²
  - Site Preparation
  - Construction Management
  - Design and Permits

2.2.7 Performance of the technology

In Table 4, first order degradation rates of cDCE and VC are presented that can be used in the numerical model in section 2.2.8. Degradation rates of aquifer, bottom- and top-sediment were obtained from experiments performed by Hamonts et al. (2012). The rates for the different capping materials were obtained from batch experiments in the AQUAREHAB project and were recalculated to 12°C using the Arrhenius equation, assuming that the rate is halved with a temperature decrease of 10 °C. The values reported in literature were also recalculated to 12°C. If no temperature was reported, a room temperature of 20°C was assumed or an ambient temperature of 12°C for *in situ* data.

Table 4: first order degradation rates of cDCE and VC in sediment, aquifer and capping material at 12°C.

Compartment	c-DCE [day^{-1}]	Range reported in literature, recalculated to 12°C	VC [day^{-1}]	Range from literature, recalculated to 12°C
Aquifer	0.004	0.001-0.002[a,b]	0.004	0.002-0.006[a,b]
Bottom sediment	0.105 ± 0.042		0.088 ± 0.069	
Middle sediment	0.319 ± 0.273		0.359 ± 0.361	
Top sediment	0.656 ± 0.087		0.593 ± 0.343	
Capping (sand)	0.048 ± 0.004		0.075 ± 0.065	
Capping (Wood chip)	0.024 ± 0.009		0.113 ± 0.087	
Capping (Hay)	0.347 ± 0.186		0.224 ± 0.128	
Capping (Straw)	0.644 ± 0.220		0.284 ± 0.196	
Capping (Tree bark)	0.361 ± 0.122		0.234 ± 0.111	
Capping (Shrimp waste)	0.172 ± 0.141		0.201 ± 0.120	
Eucalyptus mulch		0.507[c]		
Compost		0.037-0.461[c,d]		0.346[d]
Chitin		30.493[e]		

[a]Schaerlaekens et al. (1999); [b]Clement et al. (2000); [c]Öztürk et al. (2012); [d]Majcher et al. (2009);[e]Brennan et al. (2006)

2.2.8 Substance flux reduction rate

Biobarriers in the hyporheic zone can reduce the contaminant flux by sorption and/or degradation. The transport of a non-reactive sorbing contaminant through the biobarrier can be estimated from the Darcy equation with retardation where the linear transport velocity is determined by:

$$u = \frac{\frac{K_s \nabla h}{\theta}}{\left(1 + \frac{K_d \rho}{\theta}\right)}$$

With u the contaminant velocity (m/d), K_s the hydraulic conductivity (m/d), ∇h the hydraulic gradient (-), θ the porosity (-), K_d the water-solid partitioning coefficient (m^3/kg) and ρ the bulk density (kg/m^3). The value for K_d can be determined from the oil-water partitioning coefficient (K_{ow}) and the organic carbon fraction (f_{oc}) by $K_d = K_{oc} \times f_{oc}$.

A worst-case scenario can subsequently be developed for a first estimation of the technology's performance depending on the local hydrogeology and the applied technique (fraction organic carbon, porosity and thickness). This should be performed taking into account multi-species reactive transport with sorption in the barrier. However, this requires specific software (e.g. Hydrus, BIOCHLOR etc.) and for a first estimation one can also use a simplified reasoning as follows: the technique is applied to halt the influx of chlorinated ethenes in the surface water and the reaction should therefore proceed to ethene. Since vinyl chloride (VC) has the smallest sorption constant and degradation rate it will show the earliest breakthrough and the worst-case scenario can be developed for this compound. The technique should be dimensioned so that VC degradation proceeds faster than the transport through the biobarrier, i.e:

$$\frac{dVC}{dt} \Big/ u \geq \frac{VC_{in}}{\delta} \rightarrow \delta \geq \frac{u}{k_{vc}}$$

With $dVC/dt = k_{vc} \times VC_{in}$ the reaction rate of VC (µM/d), VC_{in} the concentration (µM) at the bottom of the barrier and δ the thickness of the biobarrier (m). As such, the abatement rate of 100% is a function of ∇h, K_s, θ, ρ, K_{oc}, f_{oc}, k_{vc} and δ. Table 5 indicates the desired characteristics of the biobarrier for different boundary conditions with θ, ρ, K_{oc} and k_{vc} fixed at 0.4, 1.1, 8.2×10^{-3} respectively 0.36. In effect, θ and ρ depend partly on f_{oc} but this is neglected for simplicity. In addition, it is assumed that the sorption capacity of the capping material is not exceeded in the considered timeframe. Scenario 3, 4, 7 and 8 indicate that the technology should be treated with special care in areas where large hydraulic gradients can be expected or where a large heterogeneity creates zones with high flow velocities. This would require a thicker biobarrier for 100% abatement.

Estimation (Table 5) makes use of some important simplifying assumptions related to the type and capacity of sorption, a homogeneous flow and a good approximation of *in situ* reaction rates. It is therefore advisable to develop scenarios taking into account the uncertainty originating from these assumptions for a proper dimensioning of the technique.

Table 5: A rough estimation of the effect of different boundary conditions on the desired thickness of the biobarrier

Scenario	∇h (-)	K_s (m/d)	f_{oc} (-)	δ (cm)
1	1.E-02	1	0.1	**2.1**
2	1.E-02	1	0.3	**0.9**
3	1.E-02	10	0.1	**21.3**
4	1.E-02	10	0.3	**8.9**
5	2.E-03	1	0.1	**0.4**
6	2.E-03	1	0.3	**0.2**
7	2.E-03	10	0.1	**4.3**
8	2.E-03	10	0.3	**1.8**

2.2.9 Positive co-effects

Biota living above and in the sediment are abundant and diverse. Sediment biota include those organisms (microbes to macrofauna) living in, on, or closely associated with aquatic sediments, while above-sediment biota include those organisms inhabiting the water (e.g., fish, plankton, macrophytes) as well as those terrestrial fauna and flora in adjacent habitats in contact with the freshwater.

The most obvious impact on freshwater invertebrates from contaminated sediments is acute toxicity. Chlorinated hydrocarbons have direct toxic effects on both above-sediment and sediment biota. Apart from the death of animals from sediment contaminants, other more subtle chronic impacts may be observed, the effects ranging from community structure changes to life history alterations (e.g., impairment of reproduction and age selective toxicity).

Benthic aquatic invertebrates living in contaminated habitats accumulate chlorinated hydrocarbons. Uptake of these contaminants has been documented in freshwater mussels, oligochaete worms, Chironomidae, crustaceans, and caddisfly larvae. Because these animals comprise a significant proportion of the diet of predatory invertebrates and fishes, benthic invertebrates are an important transfer route between contaminated sediments and higher trophic levels (other invertebrates, fish, and ultimately waterfowl). Bottom-dwelling larvae of aquatic invertebrates tend to accumulate chlorinated hydrocarbons in proportion to the amounts present in the surrounding sediments, although specific attributes of the organisms, the type of sediment, and the chemical properties of the contaminants also influence uptake. Consequently, benthic invertebrates are particularly useful as indicators of degree of sediment contamination.

An effective rehabilitation technique for the abatement of organic hydrocarbons in stream sediments is most likely to have a positive effect on both above-sediment and sediment biota on the long term. Especially benthic invertebrates can benefit from a reduction of the pressure by chlorinated hydrocarbons.

2.2.10 Negative co-effects

Release of dissolved organic matter into the surface water might result in its eutrophication. A good design of the cap is needed so that the released DOC can be captured by the pollutant degrading population.

Besides the pollutant degrading population, also other bacteria growing under anaerobic conditions might be stimulated. These will capture part of the applied carbon sources. A phenomenon often encountered in these caps is the stimulation of methanogenic bacteria, resulting in the production of the greenhouse gas methane.

The capping procedure is expected to have a negative impact on sediment biota on the short term. The technique involves covering the sediment with a solid layer, thus severely disturbing the local habitat of the sediment biota.

Especially if anaerobic conditions occur under the layer in the sediment, this may affect the sediment biota considerably at the covered location. This means that the populations which are already under pressure from the (toxic) pollutants, also need to overcome the habitat disturbance before recovery is possible.

It is impossible to predict the extent of the negative impact on the sediment biota and the time the population will need to recover from both the pollution and the capping, as the extent of the negative impact is influenced by many factors, such as:

- the area covered;
- the time-span during which the cover stays in place;
- the material of which the “cap” is made;
- the location of the cap (near the shore or in the middle of the streambed).

3 GENERIC APPROACH TO DETERMINE THE APPLICABILITY OF ACTIVE SEDIMENT CAPPING FOR A SPECIFIC SITE OR AREA

For a successful application of sediment capping, the following stepped approach is recommended:

Step 1: Site characterization

A site characterisation is required for multiple reasons:

- To identify the location of the pollution in the sediment zone
- To identify the type and concentration of pollution that is present in the sediment zone but also in the inflowing groundwater
- To collect information on the physicochemical characteristics of the sediment zone and the inflowing groundwater (Total organic carbon, electron acceptors, electron donors, pH, grain size distribution, permeability, …)
- To collect hydrological data (groundwater flow direction, groundwater flow velocity, ...)
- To collect information on the ecological characteristics of the sediment and pore water zone and the inflowing groundwater (microbial and overall ecology parameters).

Step 2: Feasibility tests at laboratory scale

To select the most appropriate capping material, batch and column tests should be performed in the laboratory. In these tests, a certain amount of capping material is brought in contact with the sediment and the groundwater or surface water. The concentration of CAH and their degradation products as well as the bacterial numbers are monitored in function of time. From these tests, the effect of the different capping materials on the CAH degradation rate constants as well as the microbial cell numbers can be determined. By performing column experiments, the effect of the groundwater velocity on the CAH degradation, microbial activity and (longterm) performance of the cap can be investigated.

Step 3: Design & dimensioning of the active sediment capping technology

Based on the degradation rate constants and microbial numbers obtained in step 2, as well as the CAH concentration and hydrological parameters (groundwater velocity, hydraulic conductivity, and hydraulic gradient) measured in the field, an active sediment cap can be designed. The most important parameter is the thickness of the cap.

Step 4: Implementation of the active sediment cap in the field

This step comprises the installation of the active sediment cap. Reactive material is encapsulated in a geotextile composite (creating eg a reactive microbial mat) that can be easily unrolled over the sediments. To keep the cap in place, it can be attached to the river shores or covered with sand.

Step 5: Monitoring performance and corrective actions

Monitoring of the sediment active cap is performed at the physicochemical, hydrological, and ecological level. These parameters are being determined in the groundwater, pore water and surface water.

Steps 2 to 5 are elaborated in more detail in the next sections.

4 GENERIC APPROACH TO EVALUATE THE FEASIBILITY OF ACTIVE SEDIMENT CAPPING FOR A SPECIFIC SITE OR AREA (STEP 2)

4.1 INTRODUCTION

Depending on the kind and concentration of pollutant(s) that are present, appropriate capping materials have to be selected. As we are focusing on the stimulation of the degradation of CAHs, the capping material has to have the following characteristics:

- It act as a long term electron donor towards the CAH degrading microbial population. Therefore carbon rich materials should be selected. To increase the longevity of the cap, carbon sources that release carbon in a slow but sufficient and steady rate to sustain the degradation of the CAH, should be selected.
- It can be colonised by the CAH degrading population. This will result in a long term interaction between the capping material and the CAH degrading population. In addition, by applying the cap on the sediment, the thickness of the sediment layer is increased and so is the contact time between the pollutant and the CAH degrading bacteria.
- It has a certain permeability so that the groundwater and surface water can infiltrate into the capping layer and an optimal contact between the CAH degrading bacteria and pollutants exist.
- It should be cheap so that it can be used in big amounts and over a long time period if needed.

As capping material, the materials which are listed in table 5 in section 5.2.6 are proposed: tree bark, wood chips, shrimp waste, unrefined chitin or corn crop residue.

As most of these materials are solid polymeric organic materials, they will be abbreviated as SPOMs in the following sections.

To test the suitability of a material as a sediment cap the following steps are proposed:

- Determine the physicochemical characteristics of the material and more specifically the total organic carbon content (TOC), the dissolved organic carbon content, pH, Nitrogen content, and Short Chain Fatty Acids (SCFA).
- Determine the use of the capping material as electron donor for the CAH degrading population at batch, column and *in situ* level. *In situ* level experiments will be described in section 7.2.
- Determine the colonisation of the capping material by the CAH degrading population at batch, column and *in situ* level. *In situ* level experiments will be described in section 7.2.

All this information will be used to select the most appropriate filling material of the cap and determine the thickness of the cap so that no pollutant flows into the surface water.

4.2 EXPERIMENTAL APPROACH

4.2.1 Determination of physicochemical characteristics of the capping material

Following characteristics should be determined for each capping material:

- Total Organic Carbon (TOC) is determined by the oxidative digestion method (C/N analyzer EA1110).
- Dissolved Organic Carbon (DOC) is determined for 1 g of each SPOM that is cut into pieces of 4-5 mm and incubated at room temperature on a shaker (50 rpm) in 100 mL of groundwater in 500 mL glass vials. After 1 and 8 hours of incubation, samples are taken and analyzed for the DOC concentration. DOC is determined from samples as the difference between total dissolved carbon and dissolved inorganic carbon. Afterwards, based on the DOC release of the SPOM that releases the lowest amount of DOC, the amount of each SPOM to be added to the microcosms, columns or *in situ* can be chosen.
- pH is determined for 1 g of each SPOM that is cut into pieces of 4-5 mm and incubated at room temperature on a shaker (50 rpm) in 100 mL of groundwater in 500 mL glass vials. After 1 hour of incubation, samples are taken and analyzed with a pHelectrode..
- C and N content: Total Nitrogen is detected after all particulate carbon is removed by filtration (pore size 0.45 µm). Carbon and nitrogen content of the SPOMs are determined using a Carlo Erba EA1110 elemental analyser, using acetanilide as a standard as reported in Nieuwenhuize et al. (1994).
- Short Chain Fatty Acids (SCFA) (C2-C5) are analyzed in ether extracts from aqueous solutions using a GC equipped with a FID as previously described (Calli et al. 2008).

4.2.2 Determination of the use of the capping material as electron donor by the CAH degrading population with batch and column tests

4.2.2.1 Batch tests

To determine if the capping material can be used as an electron donor by the CAH degrading population, a first screening can be performed in batch tests. The main objective is to determine if the SPOM can stimulate the biodegradation of the investigated CAH, which bacterial guilds are being stimulated by the SPOM, and over which time period the SPOM can stimulate the CAH degrading population (longevity of the SPOM).

Microcosms are prepared in 160-mL glass serum bottles containing 20 g wet and well-mixed sediment obtained from a certain depth of the riverbed, 70 mL of (polluted) ground water and a particular SPOM. The amounts of SPOM added to the microcosms are different for each SPOM, but are chosen as to obtain an equal amount of initial dissolved organic carbon (DOC) in all set-ups (see point 4.2.1). The SPOMs are placed into non-sorptive and permeable membrane pockets made from polyamide membrane 49 PA 6/5 (Hendrickx et al. 2005) and introduced into the corresponding sediment microcosms in duplicate. These membranes have pores that are big enough to allow migration of bacteria into the pockets. All bottles are sealed with Teflon-lined butyl rubber stoppers followed by addition of a certain amount of the CAH under study. All bottles are incubated at room temperature in an anaerobic glove box under N_2 atmosphere. By monitoring the CAH degradation over a longer time period, the longevity of the capping materials can be studied.

Figure 5: Microcosms containing sediment, groundwater and permeable membrane pockets filled with a certain SPOM.

Time course liquid samples are withdrawn and filtered over a 0.45-µm filter for Dissolved Organic Carbon and SCFA measurements. In addition, headspace analyses of the microcosms are performed for the detection of methane, ethene and ethane and CAHs. Standards for chlorinated compounds, ethene, ethane, and methane are prepared by adding a known amount of each compound to a serum bottle with the same headspace to liquid ratio as the microcosm bottles. Molecular samples are taken as described in point 7.5.2.

4.2.2.2 Column level

After a first screening of SPOMs at batch level, the most appropriate SPOM can be tested in detail in column experiments. The main objectives of the column experiments are to:

- Better simulate the *in situ* conditions than in the batch set-up and more specifically to work under dynamic instead of static conditions, *in situ* groundwater velocity, changing groundwater conditions, ...
- Study the colonisation of the capping materials under dynamic conditions
- Study the longevity of the capping materials under dynamic conditions
- Verify the results that were obtained under batch conditions.

Three column conditions should be tested, preferably in duplicate: i) columns only filled with sediment, ii) columns filled with sediment and a sand cap (passive cap), and iii) columns filled with sediment and a mixed cap consisting of sand and the SPOM under study (active cap).

Columns consist of PVC or glass material and can have different widths and heights (see Figure 6 and AQUAREHAB Deliverable DL3.4 for more details). All columns are filled in the laboratory in an anaerobic chamber containing high purity nitrogen gas with sediment samples collected from top 20 cm surficial sediment of the riverbed. Before filling, the sediment is well mixed to achieve a homogeneous substance. During the filling attention is paid to achieve a homogeneous distribution of the sediment material. The columns are run at the *in situ* groundwater flow rate. Groundwater is filled in collapsible TEDLAR bags (2L, dual valve system, Cole-Parmer, Illinois, USA) and brought into contact with a high purity nitrogen atmosphere within a nalophane bag (PRA Odournet BV, Amsterdam, The Netherlands) to avoid volatilization of the CAH to the headspace. If needed, CAH can be spiked to these TEDLAR bags. Capping material is placed as a layer on top of

the sediment or mixed into the sediment. To avoid floating of the capping material, a sand layer is placed on top of the capping layer.
(Ground)water samples can be taken in function of time from sampling ports present at different positions in the sediment but also in the capping material.
Pore water samples are taken from the selected sampling arms using gastight syringes with fine needles . To avoid too much disturbance of the flow paths in the columns, the samples of 0.5 mL are taken gradually over a period of 1 hour.
By comparing the concentration of the pollutant at the inlet, outlet, or after passage of the groundwater over a certain distance in the column (by sampling the sampling ports at different heights in the column), respectively the natural or stimulated attenuation potential of the sediment and SPOM towards the pollutant can be determined.

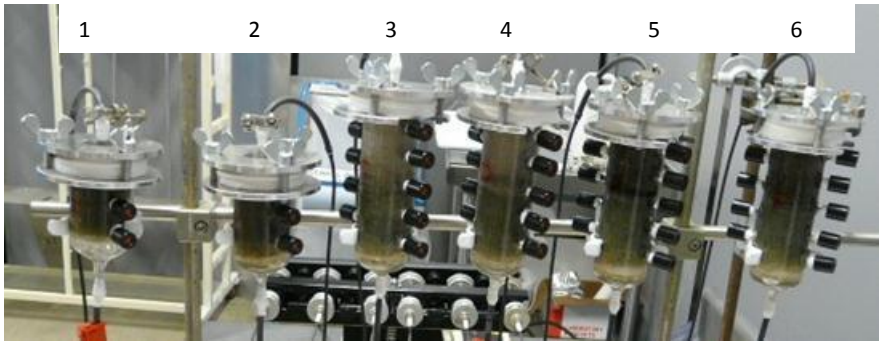


Figure 6: Column set up: 1&2: sediment columns, 3&4: sediment + sand cap, and 5&6: sediment + mixed cap of sand and tree bark.

4.2.3 Determination of the colonisation of the capping material by the CAH degrading population at batch, and column level

From the microcosms and columns described here above in sections 4.2.2.1 and 4.2.2.2, SPOM samples can be taken to study the colonisation of the capping materials by the sediment microbial community and more in particular the CAH degrading population. The microbial numbers present on the SPOM before and after a certain contact time with the sediment and the groundwater/surface water should be compared. In addition, the microbial numbers detected in sediment, groundwater and surface waters samples can be taken into account to investigate the colonisation of the SPOMs by the microbial population.
Before the initiation of the experiment, approximately 0.5 g of each SPOM is used for DNA extraction in duplicate. After certain time points on which dechlorination is going on, the sediment microcosms should be decapped in the anaerobic glove box. The polyamide bags containing the SPOMs are opened and few pieces of SPOM are withdrawn from both replicates. The SPOMs are washed with sterile water to remove sediment particles and used for DNA extraction. Afterwards, the bottles are capped again, mixed thoroughly, opened and approximately 2 gram slurry samples are withdrawn from all duplicate microcosms.
To study the microbial population in the columns, 2 ml (ground)water samples can be taken from the different sampling ports. It should be avoided to sample the sediment or SPOM as such since this will create preferred stream lines in the sediment material.

DNA is extracted from the samples as described previously (Hendrickx et al. 2005) and the microbial numbers are determined as described in point 7.5.2 (see monitoring part).

4.3 DATA INTERPRETATION

The following parameters can be determined from these batch and column tests:

- Degradation constants under static (batch) and dynamic (column) conditions.
- Numbers of CAH degrading bacteria and catabolic genes involved in CAH degradation. These numbers can be determined from the water fraction (in cells/mL water) or from the sediment or active cap fraction (in cells/g sediment or active cap).
- Determination and quantification of side reactions (like methanogenic activity) that scavenge part of the carbon source.
- Longevity of the active cap giving an indication over which time frame a certain amount of cap can stimulate the CAH degradation.

This information can then be used together with the hydraulic characteristics of the site (see 7.4) to calculate the thickness of the mat as presented in 2.2.8.

5 GENERIC APPROACH TO DESIGN ACTIVE SEDIMENT CAPPING (STEP 3)

The design of the barrier depends on the local hydrogeology and the applied capping material (fraction organic carbon, porosity and thickness). Biobarriers in the hyporheic zone can reduce the contaminant flux by sorption and/or degradation. The transport of a non-reactive sorbing contaminant through the biobarrier can be estimated from the Darcy equation with retardation where the linear transport velocity is determined by:

$$u = \frac{K_s \nabla h}{\theta} \Big/ \left(1 + \frac{K_d \rho}{\theta}\right)$$

With u the contaminant velocity (m/d), K_s the hydraulic conductivity (m/d), ∇h the hydraulic gradient (-), θ the porosity (-), K_d the water-solid partitioning coefficient (m^3/kg) and ρ the bulk density (kg/m^3). The value for K_d can be determined from the oil-water partitioning coefficient (K_{ow}) and the organic carbon fraction (f_{oc}) by $K_d = K_{oc} \times f_{oc}$.

A worst-case scenario can subsequently be developed for a first estimation of the technology's performance depending on the local hydrogeology and the applied technique (fraction organic carbon, porosity and thickness). This should be performed taking into account multi-species reactive transport with sorption in the barrier. However, this requires specific software (e.g. Hydrus, BIOCHLOR etc.) and for a first estimation one can also use a simplified reasoning as follows: the technique is applied to halt the influx of chlorinated ethenes in the surface water and the reaction should therefore proceed to ethene. Since vinyl chloride (VC) has the smallest sorption constant and degradation rate it will show the earliest breakthrough and the worst-case scenario can be developed for this compound. The technique should be dimensioned so that VC degradation proceeds faster than the transport through the biobarrier, i.e:

$$\frac{dVC}{dt} \Big/ u \geq \frac{VC_{in}}{\delta} \rightarrow \delta \geq \frac{u}{k_{vc}}$$

With $dVC/dt = k_{vc} \times VC_{in}$ the reaction rate of VC (µM/d), VC_{in} the concentration (µM) at the bottom of the barrier and δ the thickness of the biobarrier (m). As such, the abatement rate of 100% is a function of ∇h, K_s, θ, ρ, K_{oc}, f_{oc}, k_{vc} and δ. Table 5 indicates the desired characteristics of the biobarrier for different boundary conditions with θ, ρ, K_{oc} and k_{vc} fixed at 0.4, 1.1, 8.2×10^{-3} respectively 0.36. In effect, θ and ρ depend partly on f_{oc} but this is neglected for simplicity. In addition, it is assumed that the sorption capacity of the capping material is not exceeded in the considered timeframe. Scenario 3, 4, 7 and 8 indicate that the technology should be treated with special care in areas where large hydraulic gradients can be expected or where a large heterogeneity creates zones with high flow velocities. This would require a thicker biobarrier for 100% abatement.

Estimation (Table 5) makes use of some important simplifying assumptions related to the type and capacity of sorption, a homogeneous flow and a good approximation of *in situ* reaction rates. It is

therefore advisable to develop scenarios taking into account the uncertainty originating from these assumptions for a proper dimensioning of the technique.

Table 6: A rough estimation of the effect of different boundary conditions on the desired thickness of the biobarrier

Scenario	∇h (-)	K_s (m/d)	f_{oc} (-)	δ (cm)
1	1.E-02	1	0.1	**2.1**
2	1.E-02	1	0.3	**0.9**
3	1.E-02	10	0.1	**21.3**
4	1.E-02	10	0.3	**8.9**
5	2.E-03	1	0.1	**0.4**
6	2.E-03	1	0.3	**0.2**
7	2.E-03	10	0.1	**4.3**
8	2.E-03	10	0.3	**1.8**

In Table 4, first order degradation rates of cDCE and VC are presented that can be used in the numerical model presented here above. Degradation rates of aquifer, bottom- and top-sediment were obtained from experiments performed by Hamonts et al. (2012). The rates for the different capping materials were obtained from batch experiments in the AQUAREHAB project and were recalculated to 12°C using the Arrhenius equation, assuming that the rate is halved with a temperature decrease of 10 °C. The values reported in literature were also recalculated to 12°C. If no temperature was reported, a room temperature of 20°C was assumed or an ambient temperature of 12°C for *in situ* data.

Table 7: first order degradation rates of cDCE and VC in sediment, aquifer and capping material at 12°C.

Compartment	c-DCE [day^{-1}]	Range reported in literature, recalculated to 12°C	VC [day^{-1}]	Range from literature, recalculated to 12°C
Aquifer	0.004	0.001-0.002[a,b]	0.004	0.002-0.006[a,b]
Bottom sediment	0.105 ± 0.042		0.088 ± 0.069	
Middle sediment	0.319 ± 0.273		0.359 ± 0.361	
Top sediment	0.656 ± 0.087		0.593 ± 0.343	
Capping (sand)	0.048 ± 0.004		0.075 ± 0.065	
Capping (Wood chip)	0.024 ± 0.009		0.113 ± 0.087	
Capping (Hay)	0.347 ± 0.186		0.224 ± 0.128	
Capping (Straw)	0.644 ± 0.220		0.284 ± 0.196	
Capping (Tree bark)	0.361 ± 0.122		0.234 ± 0.111	
Capping (Shrimp waste)	0.172 ± 0.141		0.201 ± 0.120	
Eucalyptus mulch		0.507[c]		
Compost		0.037-0.461[c,d]		0.346[d]
Chitin		30.493[e]		

[a]Schaerlaekens et al. (1999); [b]Clement et al. (2000); [c]Öztürk et al. (2012); [d]Majcher et al. (2009);[e]Brennan et al. (2006)

6 GENERIC APPROACH TO IMPLEMENT ACTIVE SEDIMENT CAPPING (STEP 4)

Implementation of the reactive cap (eg a microbial mat) consists of two main steps:

1. Construction of the reactive mat
2. Implementation of the reactive mat *in situ*

6.1 CONSTRUCTION OF THE REACTIVE MAT

To construct the reactive mat, a system has been devised that encapsulates reactive materials within a geotextile composite that can be easily deployed as an *in situ* capping material over sediments. Geotextiles are textiles that are manufactured with synthetic fibers into flexible, porous fabrics. Since they are not manufactured with natural fibers, such as cotton, there is no concern with biodegradation. Geotextiles have varying properties based upon the type of polymer, the type of fiber and fabric style. The four main functions of geotextiles are separation, reinforcement, filtration and drainage. More in particular, the reactive material mats are constructed by bringing the reactive material between two geotextile layers. The layers are connected with each other through needlepunching or laminating (Darlington and Olsta, 2005).

6.2 IMPLEMENTATION OF THE REACTIVE MAT *IN SITU*

Reactive material mats may be deployed by unrolling them underwater or on land. When the mats are **unrolled in the water (**Figure 7**)**, a barge mounted crane is used to position the rolls and unroll them underwater. The mats are first submerged to allow them to absorb water and displace entrained air. Then the rolls are positioned approximately 0.5 m above the river bottom and anchored with sand at one end. The crane is able to swing across the area to be capped and unroll the mat as it went.

Figure 7: Schematic overview of reactive core mat application in the field. The reactive core material is applied by rolling it onto the sediment surface from rolls that typically contain 4.5 m wide by 30 m long sheets. Ends of each section are anchored at the shoreline to provide higher stability and tensile strength. After application, the reactive core material is typically covered by at least 15 cm of sand to ensure its stability and to provide a new habitat for benthic organisms (Meric D, 2010).

Land-based deployment techniques may also be used to deploy mats. Rolls are positioned on shore suspended by a spreader bar system with a clamp connected to the leading edge of the roll. The material is then pulled off of the roll using a winch that is either mounted on a barge or on the opposite side of the waterway. Deployment techniques may take advantage of temporary buoyancy before the mat absorbs water and displaces air to allow the material to "float" into position and subsequently sink as they take on water (Darlington and Olsta, 2005).
To keep the mats in place, they can be anchored to the shore or made heavier by placing rocks at certain positions of the mats or overlaying the mats with sand.

7 GENERIC APPROACH TO MONITOR HYPORHEIC BIOBARRIERS (STEP 5)

7.1 INTRODUCTION

Monitoring of the sediment active cap is performed at three levels:

1. Physicochemical level and more specifically by following up the concentration of CAH, ethene, ethane, electron donor (by DOC and TOC) and acceptor, pH, ORP, and compound specific isotope analysis.
2. Hydrological level and more specifically by the contaminant velocity u (m/d), the hydraulic conductivity K_s (m/d), the hydraulic gradient ∇h (-), and the porosity θ (-).
3. Ecological level and more specifically at the level of the overall and microbial ecology.

The frequency of monitoring will depend on the stage of the project but also of the budget. It is advisable to monitor weekly in the beginning of the project (just after placing the mat), but this can be decreased to monthly (during the first six months of the project) or even annually at later stages in the project.

Here beneath the physicochemical, hydrological, and ecological parameters that should be monitored as well as the way in which appropriate samples should be taken, stored and analysed, are indicated.

7.2 APPROACHES FOR MONITORING OF THE PERFORMANCE OF THE REACTIVE MAT

To study the effect of the reactive mat on physico-chemical and ecological parameters of the groundwater, pore water and surface water, samples should be taken from the groundwater, pore water, surface water, sediment and reactive material. Most important parameters to be monitored are the concentration of CAHs, ethene, ethane, and electron donors. Additional valuable information can be gained from compound specific isotope analyses and analyses of the overall and microbial ecology of the different ecosystems. While in section 7 the different analytical techniques are being described, this section describes the different sampling techniques to be used to sample these different types of water, sediment, and reactive mat material at the different positions in the aquifer and riverbed.

7.2.1 Sampling of groundwater

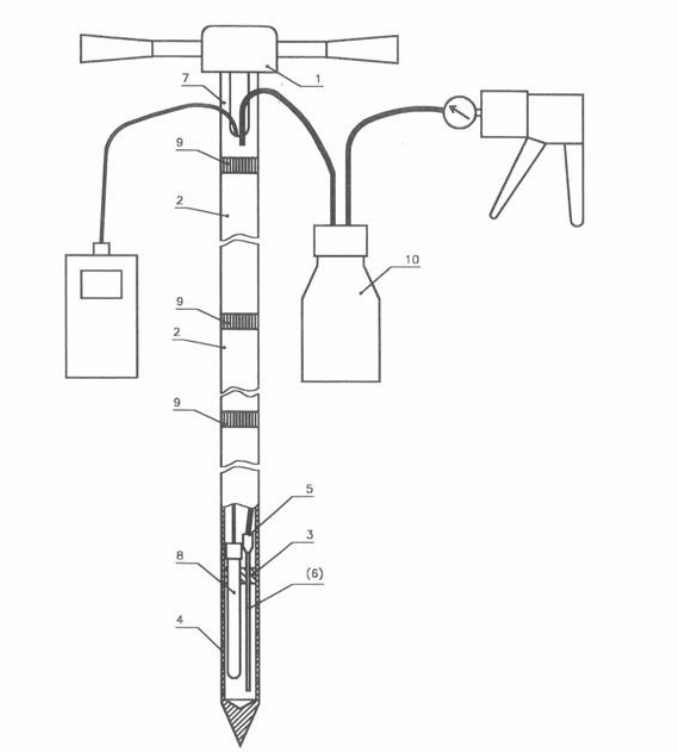
Groundwater can be sampled along the groundwater plume (from the contamination source to the river) and along the edge of the river (to determine the length and area of the river that receives polluted groundwater) in **existing boreholes** or **temporary screenpoints.** The samples can be used to determine the concentrations of CAHs, ethene, ethane, electron acceptors, DOC, pH, and ORP in the groundwater. Screenpoints are temporary boreholes drilled by a direct push system (eg http://www.geoprobe.com/). They can be used to take groundwater at one moment in time since the screenpoint collapses after the sample has been taken. Screenpoints are therefore used as a cost-effective method to get a fast screening of a site since no time is spent to make the castings of the borehole. In this way, the extent of the pollutant plume and the places in the river that receive the highest concentrations of pollutants can be determined. In addition, screenpoints can be used to determine the most optimal positions of the permanent boreholes, the sampling

places in the river (i.e. places with different high and low concentrations of the pollutant) or positions where the reactive mats should be applied.
Groundwater samples are taken in such a way that physico-chemical conditions remain identical (i.e. [electron acceptors], ORP, pH, etc. …) and without loss of the volatile products such as CAH and ethene/ethane. They are taken from boreholes or screenpoints with a peristaltic pump and using PE tubings. Groundwater is collected in glass recipients since CAHs adsorb on plastic. These recipients contain the right conservator (depending on the parameter to be measured (see section 7.2)). Glass recipients are filled by putting the tubing at the bottom of the flask and changing the volume of the flasks three times (by overflow of the groundwater from the bottle, so the bottle is not emptied during the sampling). After sampling, the glass vials are stored at 4 °C and in the dark. In this way a good conservation of the physico-chemical conditions is obtained. The methods to determine the concentrations of different CAHs, ethene, ethane, DOC and electron acceptors are described in section 7.

7.2.2 Sampling of pore water

7.2.2.1 Pore water probe

To determine the CAH influx zone in the riverbed, a “dynamic”, non permanent water probe can be used. With this instrument, pore water can be sampled at different non-permanent locations in the riverbed and the dissolved part of certain parameters quantified. Pore water samples are taken using a 3 cm diameter stainless steel lance equipped with a polyurethane sampling tubing, a tip containing a porous polyethylene filter and probes for temperature and conductivity measurements (UIT, Dresden, Germany; Hamonts et al., 2009). After inserting the probe into the riverbed, water penetrates into the sensor head. When the sediment seals the instruments shaft and stationary conditions of constant temperature and conductivity prevail, pore water is pumped into a sampling bottle via vacuum technology. Therefore, probe and sampling tubing are connected to glass sampling bottles, which in turn are connected to a vacuum pump. By creating a vacuum, pore water is extracted from the riverbed and collected in two 100 mL (nominal volume; 130 mL total volume) glass sampling bottles placed in series with a third 250 mL collector bottle. To minimize volatilization of the CAHs, sampling is continued until the two sampling bottles are completely filled with pore water (260 mL in total) and their volume is changed two times. This pore water probe can be ordered at www.uit-gmbh.de.



1 Head of device, suitable for drill hammer and handle, stainless steel
2 Shaft and extensions, stainless steel (1000 mm and 500 mm), external diameter 30 mm
3 Holder for sensors and canula
4 Sensor head with screen filter, width 0,5 mm, length of filter 10 cm, external diameter 30 mm
5 Tubing for sampling, PUR 2,5 mm
6 Canula for water sampling
7 Instruments head with duct for tubing and sensor cables
8 Sensors for measurement of temperature and conductivity
9 Connectors for shaft segments
10 Sampling bottle or headspace container (depending on required sample volume)
11 Vacuum pump, manual or electric pump, 800 mbar
12 Display instrument for parameters temperature and conductivity, power supply for sensors

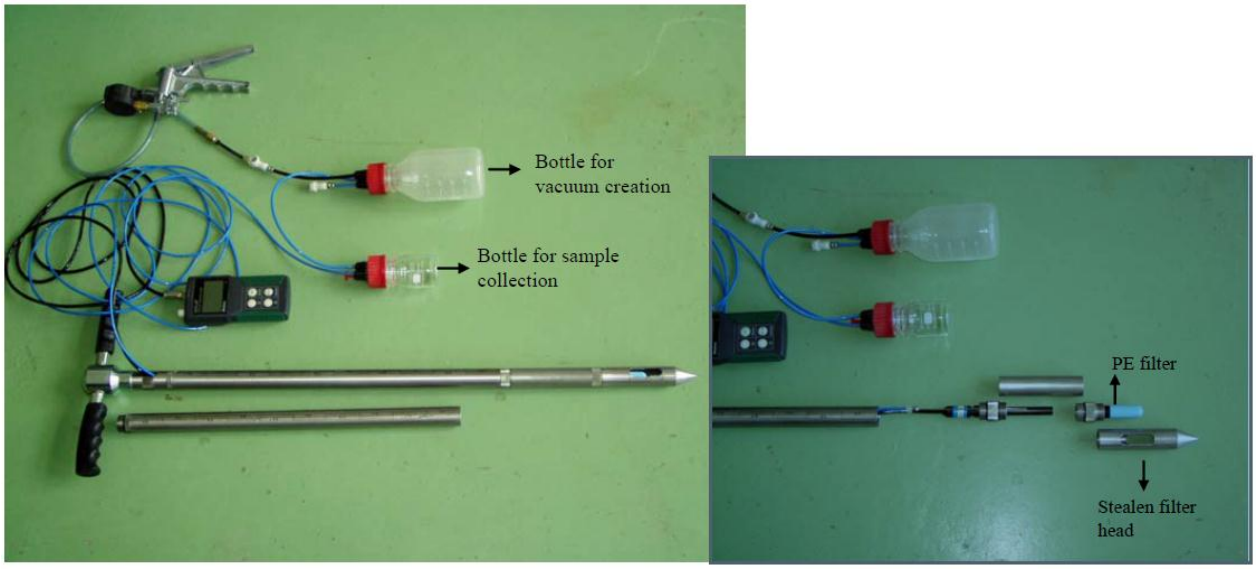


Figure 8: Stainless steel lance to take pore water samples in a non permanent way

7.2.2.2 Mini-porewater samplers

Mini-porewater samplers are installed directly below the base of the reactive mat following sediment excavation. These samplers allow the collection of water samples from the sediments just below the bottom membrane of the reactive mat. Each sampler provides a discrete sampling point and is approximately 25 mm long, and 12.5 mm in diameter. The sampler consists of a 6.25 mm screen placed inside a clean cotton bag that is filled with a clean sandpack. The screen is attached at the end of 6.25 mm diameter Teflon tubing. The tubing runs horizontally for the length of and slightly beyond the reactive mat boundaries to allow access for sample collection. Each device is purged and sampled with a dedicated 60-mL plastic syringe, fitted with a 3-way stopcock and tubing that extends to the top of the screen. This allows samples to be collected slowly without aerating the sample.

Figure 9: Mini-porewater samplers

7.2.2.3 Multi-level diffusion samplers

Multi-level diffusion samplers are constructed to characterize the in-mat porewater at different depths in the cap. The samplers consists of two to three 100 mm long, 25 mm diameter PVC screens with 0.25 mm slots stacked together with internal plugs to isolate each screen. Pore water samples are taken as described for the mini pore water samplers (7.2.2.2).

7.2.3 Sampling of surface water

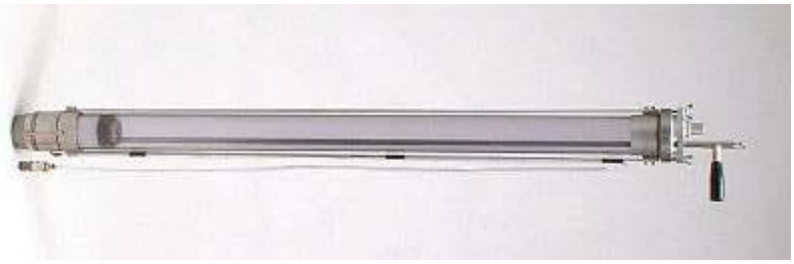
Sampling of the surface water occurs along that part of the river that becomes polluted with the CAHs. Since the pollutants will be mainly diluted in the surface water, detection of CAH compounds in the surface water will be rather limited. However, when the concentration of CAHs in the groundwater sampled at the edge of the river, are very high, it may be that CAHs that are entering the surface water can be measured. Samples of surface water are taken in glass bottles containing the right conservator (depending on the parameter to be measured (see section 7). These bottles are totally inserted in the surface water so that no air enters the bottle during sampling. Surface water is stored at 4°C and in the dark before the concentrations of different CAHs, ethene, ethane, electron acceptors, and DOC are determined. pH, and ORP are measured directly in the field.

7.2.4 Sampling of sediment material

To take undisturbed samples from the sediment (sum of pore water and sediment particles), a piston sampler or Sediment corer Beeker type can be used (http://www.eijkelkamp.com/). The piston sampler consists of an iron tube that can be pushed into the sediments until a certain depth. As the sediment enters the tube, a piston is pushed out of the iron tube. With this piston the sediment is pushed out of the iron tube into a gutter after which sediment samples can be taken at different depths in the sediment. While the piston sampler is used to sample more coarse sediment, the Sediment corer Beeker type can be used to take undisturbed samples from more muddy sediment. This device is closed by a balloon, preventing the muddy sediment to fall out of the sampler. On the other hand, Van veen grabs can be used to take disturbed sediments. Bigger amount can be sampled with the grab sampler than with the piston sampler of Beeker sampler.
Ways to conserve and analyse these sediment samples are described here below (section 7).

(a)

(b)



(c)

Figure 10: sediment samplers such as piston sampler (a), Sediment Corer Beeker type (b), and Van Veen grabs (c)

7.2.5 Sampling of reactive mat material

Sampling of the reactive mat can only be performed at the end of the monitoring campaign as the mats will have to be opened. Samples should be taken in an anaerobic way and conserved in the same way as the sediment samples sampled in section 7.2.4.

7.3 MONITORING OF PHYSICOCHEMICAL PARAMETERS

7.3.1 CAH concentrations

CAH concentrations are determined by GC-MS or GC-FID detection according to information provided by the supplier of the gas chromatograph. Groundwater, surface water, and pore water samples are conserved with a final concentration of 1.7 % phosphoric acid, at 4 °C and in the dark before analysis. Sediment and active cap samples are conserved with a final concentration of 50 % methanol, at 4°C and in the dark. To obtain a total extraction of CAHs from the sediments into the methanol, samples are sonicated for 30 minutes and a sample of the methanol phase is taken and diluted before GC analysis.

7.3.2 Ethene, ethane and methane concentrations

Etene, ethane, and methane concentrations are determined by GC-FID detection according to information provided by the supplier of the gas chromatograph. Groundwater, surface water, and pore water samples are conserved with a final concentration of 1.7 % phosphoric acid, at 4 °C and in the dark before analysis. Sediment and active cap samples are conserved with a final concentration of 0.00255 % phosphoric acid, at 4°C and in the dark.

7.3.3 Electron donor concentrations

7.3.3.1 Dissolved organic carbon (DOC)

DOC in groundwater, surface water, and pore water samples are determined by a TOC- analyzer after storage of the samples at – 20 °C and filtration before analysis.

7.3.3.2 Total organic carbon (TOC)

TOC in sediment samples is determined by oxidative digestion method (C/N analyzer EA1110). Samples are dried at 105°C and stored at room temperature before analysis.

7.3.4 Electron acceptor concentrations

The concentration of electron acceptors in groundwater, surface water, and pore water is determined by Ion Chromatography. Samples are stored at – 20 °C before analysis.

7.3.5 pH and ORP

pH and ORP are measured in the groundwater, surface water, and pore water *in situ* with dedicatedelectrodes.

7.3.6 Carbon isotope analysis

Carbon isotope analysis are determined by GC-C-IRMS detection according to information provided by the supplier of the gas chromatograph. Groundwater, surface water, and pore water samples are conserved with some NaOH pellets (1 pellet/250 mL), at 4 °C and in the dark before analyses.

7.4 MONITORING OF HYDROLOGICAL PARAMETERS

7.4.1 Flow velocity

Contaminant velocity u (m/d) in the groundwater and pore water can be described by the following relationship:

$$u = R \cdot v$$

where v is the velocity of groundwater flow (m/d) and R is the retardation factor.
The velocity of the groundwater flow (v) is the product of hydraulic conductivity, K, (see below) and hydraulic gradient i (see below), with adjustment for the porosity, n (see below) of an aquifer:

$$v = K \cdot i / n$$

Besides calculating the velocity of groundwater flow based on hydraulic conductivity, hydraulic gradient and porosity, it can also be determined by groundwater tracer experiments using a conservative tracer, for which it can be assumed that mimic the groundwater flow, i.e.: $v_{groundwater} \approx v_{conservative\ tracer}$. In practice, the conservative trace is injected in a groundwater well or borehole and its time course of concentration is recorded at an observation well/borehole located within the direct groundwater downstream of the injection point of the conservative trace. The average travel time of the groundwater (t) is approximately the time when the maximal concentration of the conservative tracer ($t_{max\ conservative\ tracer}$) is observed. , i.e.: $t \approx t_{max\ conservative\ tracer}$. Based on this assumption, the velocity of groundwater flow can be determined as follows:

$$v = s / t_{max\ conservative\ tracer}$$

where s is the distance of the injection point and the observation well/borehole.

Retardation is a measure of the reduction in contaminant velocity relative to the velocity of groundwater flow caused by adsorption of the contaminant to the aquifer matrix and is expressed as retardation factor ($\mathcal{R}$). It is usually estimated from soil and chemical data using the following expression:

$\mathcal{R} = 1 + K_d \cdot \rho_b / n$ where $K_d = K_{oc} \cdot f_{oc}$.

The variables of this equation mean K_d = distribution coefficient, K_{oc} = organic carbon partition coefficient, f_{oc} = fraction organic carbon on uncontaminated aquifer matrix, ρb = bulk density and n = porosity.
In practice, the retardation factor ($\mathcal{R}$) and the contaminant velocity (u) can be determined by groundwater tracer experiments using besides a conservative tracer the pollutant of interest as sorptive tracer. Both tracers are injected in a groundwater well or borehole and their time courses of concentration are recorded at an observation well/borehole located within the direct groundwater downstream of the injection point. However, it needs to be taken into account that the pollutant of interest exhibits negligible concentration in the aquifer transect of the groundwater tracer experiment. This criterion is mostly not fulfilled, since the retardation factor ($\mathcal{R}$) and the contaminant velocity (u) is important to know for areas where the pollutant of interest is present. In this case, isotopically labeled pollutants of interest can be used as sorptive tracer. Deuterium labeled analogues of pollutants are mainly used for groundwater tracer experiments. The average contaminant velocity (u) can be estimated based on maximal concentration of the sorptive tracer ($t_{max\ sorptive\ tracer}$) as follows:

$u = s / t_{max\ sorptive\ tracer}$

The Retardation factor can be estimated as follows:

$R = t_{max\ sorptive\ tracer} / t_{max\ conservative\ tracer}$

7.4.2 Hydraulic gradient (i)

Hydraulic gradient is the change in hydraulic head over the change in distance between the two monitoring wells. It can be estimated as follows:

$i = (h_2-h_1)/s$

where h_2 and h_1 are the hydraulic heads of two wells and s is the distance between these two wells, respectively.

7.4.3 Porosity (n)

The porosity of a porous medium (such as rock or sediment) describes the fraction of void space in the material, where the void may contain, for example, air or water. It is defined by the ratio:

$n = V_V / V_T$,

where V_V is the volume of void-space (such as fluids) and V_T is the total or bulk volume of material, including the solid and void components. Both the mathematical symbols **θ** and **n** are used to denote porosity. Porosity can be measured by Water evaporation method (pore volume = (weight of saturated sample − weight of dried sample)/density of water).
Porosity of aquifer matrices: Typical bulk density of sandy soil is between 1.5 and 1.7 g/cm³. This calculates to a porosity between 0.43 and 0.36. Typical bulk density of clay soil is between 1.1 and 1.3 g/cm³. This calculates to a porosity between 0.58 and 0.51.

7.4.4 Hydraulic conductivity (K)

Hydraulic conductivity describes the ease with which a fluid (usually water) can move through pore spaces or fractures. It depends on the intrinsic permeability of the material and on the degree of saturation, and on the density and viscosity of the fluid. Saturated hydraulic conductivity, K_{sat}, describes water movement through saturated media.

In situ determination of hydraulic conductivity:
When the water table is shallow, the augerhole method, a slug test, can be used for determining the hydraulic conductivity below the water table. The method uses the following steps:

1. an augerhole is perforated into the soil to below the water table
2. water is bailed out from the augerhole
3. the rate of rise of the water level in the hole is recorded
4. the K-value is calculated from the data as:

$$K = F (H_0-H_t) / t$$

where: K = horizontal saturated hydraulic conductivity (m/day), H = depth of the water level in the hole relative to the water table in the soil (cm), H_t = H at time t, H_o = H at time t = 0, t = time (in seconds) since the first measurement of H as H_0, and F is a factor depending on the geometry of the hole:

$$F = 4000r / h'(20+D/r)(2-h'/D)$$

where: r = radius of the cylindrical hole (cm), h' is the average depth of the water level in the hole relative to the water table in the soil (cm), found as $h'=(H_o+H_t)/2$, and D is the depth of the bottom of the hole relative to the water table in the soil (cm).

7.5 MONITORING OF ECOLOGICAL PARAMETERS

7.5.1 Monitoring of overall ecology parameters

Ecological parameters to be monitored are benthic invertebrate fauna and to a lesser extent macrophytes and phytobenthos. The sampling frequency for benthic invertebrate fauna should be at least two times per year, once in spring and once in autumn. The first survey should be performed before the cap is implemented, to record the situation at the start of the rehabilitation activities. The surveys should continue for as long as the cap is in place, and until well after its removal, so that long-term monitoring results can provide insight into the potential recovery of the benthic invertebrate fauna in particular. It may take several years until the sediment biota can

recover from the rehabilitation activities. Some species colonise the area again quickly after the activities have been finalised, but especially the species which are sensitive to disturbance need (much) longer to recover. If anaerobic conditions persist underneath the cap, it may take longer for the sediment biota to recover.

In order to be able to monitor the positive and/or negative effects of the hyporheic barrier, at least two sampling points are essential:

1. a representative upstream sampling point with conditions similar to those of the location of the cap
2. a suitable sampling point at the location of the cap.

If it is not possible to sample directly through/under the cap, a sampling point as close as possible to the cap should be found. A comparison between results from the upstream point and the point at the cap should provide information on the (short-term) positive or negative effects of the cap.

Additionally, the top of the cap should be investigated for species colonisation. The material of the cap determines whether colonisation by benthic invertebrate fauna or macrophytes and phytobenthos is actually possible.

The AQEM method (Assessment System for the Ecological Quality of Streams and Rivers throughout Europe using Benthic Macroinvertebrates; EU-project EVK1-CT1999-00027) can be used for the selection of an appropriate sampling location, sample processing and the assessment of results (AQEM Consortium, 2002). Detailed information on the sampling procedures for benthic invertebrate fauna can be found in European Guidance Standard EN 16150 and EN 27828.

7.5.2 Monitoring of microbial ecology parameters

DNA or RNA based real-time PCR is used to determine the copy number of 16S rRNA genes (phylogenetic marker) of CAH-degrading bacteria (as an indicator of cell numbers), or to determine copy numbers of reductive dehalogenase (RDase) genes coding for CAH-degrading enzymes (as an indicator of CAH-degrading capacity). The important micro-organisms or RDase genes to target are dependent on the chlorinated pollutants present at the site. In addition, since the methanogenic population consumes the produced short chain fatty acids (SCFA), it is also very important to follow this population by measuring the produced methane gas or the number of *Methanosarcinaceae* and *Methanosaetaceae* (Table 8).

The following real-time PCR primers are available to target CAH-degrading bacteria, their reductive dehalogenase genes and methanogens:

Table 8: Overview of DNA oligonucleotide primers used to quantify 16SrRNA gene of CAH-degrading bacteria or methanogens and reductive dehalogenase genes

Primers/probes	Sequence (5'-3')	Targeted gene	Amplicon length (bp)	Reference
Eub341F	CCTACGGGAGGCAGCAG	16S rRNA gene of *Bacteria*	194	
Eub534R	ATTACCGCGGCTGCTGGC			
Dhc1200F	CTGGAGCTAATCCCCAAAGCT	16S rRNA gene of *Dehalococcoides* spp.	72	He et al., 2003
Dhc1271R	CAACTTCATGCAGGCGGG			
Dhc1240Probe[b]	FAM-TCCTCAGTTCGGATTGCAGGCTGAA-TAMRA			
TceA1270F	ATCCAGATTATGACCCTGGTGAA	*tceA* gene of *D. mccartyi* strain 195 and FL2	67	Aiello, 2003; Johnson et al., 2005
TceA1336R	GCGGCATATATTAGGGCATCTT			
TceA1294Probe[b]	FAM-TGGGCTATGGCGACCGCAGG-TAMRA			
Vcr1022F	CGGGCGGATGCACTATTTT	*vcrAB* gene of *D. mccartyi* sp. strain VS and GT	72	Ritalahti et al. 2006
Vcr1093R	GAATAGTCCGTGCCCTTCCTC			
Vcr1042Probe[b]	FAM-CGCAGTAACTCAACCATTTCCTGGTAGTGG-TAMRA			
Bvc925F	AAAAGCACTTGGCTATCAAGGAC	*bvcA* gene of *D. mccartyi* strain BAV1	93	Ritalahti et al. 2006
Bvc1017R	CCAAAAGCACCACCAGGTC			
ARC787F	ATTAGATACCCSBGTAGTCC	16S rRNA gene of Archaea	272	Yu et al. 2005
ARC1059R	GCCATGCACCWCCTCT			
Probe	AGGAATTGGCGGGGGAGCAC	16S rRNA gene of *Methanosarcinaceae*	408	Yu et al., 2005
Msc380F	GAAACCGYGATAAGGGGA			
Msc828R	TAGCGARCATCGTTTACG	16S rRNA gene of *Methanosaetaceae*		
Probe	TTAGCAAGGGCCGGGCAA		164	Yu et al., 2005
Mst702F	TAATCCTYGARGGACCACCA			
Mst862R	CCTACGGCACCRACMAC			
Probe	ACGGCAAGGGACGAAAGCTAGG			

[b] All TaqMan probes have 6-carboxyfluorescein (FAM) as a reporter fluorophore on the 5' end, and N,N,N',N'-tetramethyl-6-carboxyrhodamine (TAMRA) as quencher on the 3' end

Sediment, reactive mat or aquifer samples should be taken in the field (7.2) without disturbing the physico-chemical characteristics. These samples should be frozen in the field directly after sampling, to ensure that no degradation of DNA/RNA occurs. For the groundwater, pore water and surface water, 1 L of water is filtered over 0.45 µm filters (Millipore, Molsheim, France) using a membrane filtration unit (Pall Life Sciences, New York, USA). All samples can be stored at – 80 °C for 6 months before analyses. For RNA analysis storage in RNAlater buffer (Ambion, USA, www.ambion.com) is recommended.

DNA/RNA extraction methods
Only small amounts of sample are necessary for DNA extraction, since e.g. 0.5 to 2.0 g sediment should be enough to extract DNA for molecular analyses. However, it is recommended to take larger and replicate samples to improve the reproducibility of the real-time PCR results (often 5.0 g of sediment and aquifer should be sufficient). High quality total RNA can be extracted from small samples too (0.5 g), however for measurable quantities of mRNA larger amounts are probably required (Salek-Lahka S., Journal of Microbiological Methods, 2005). Good results can be obtained using commercial DNA/RNA extraction kits for soils, such as the FastDNA® SPIN Kit for Soil or FastRNA® Pro Soil-Direct Kit (MP Biomedicals, USA, www.mpbio.com), PowerSoil™ DNA or Total RNA Isolation Kits (MoBio Laboratories Inc., USA, www.mobio.com), but also standard phenol-chloroform extractions might be used (Sambrook, Fritsch and Maniatis, 1989; Hendrickx et al., 2005). Best is to perform the (real-time-)PCR analyses immediately on the DNA and RNA extracts but, if necessary, these extracts can be stored for up to 3 months for RNA and 6 months for DNA at – 80 °C.

Real-time PCR quantification reagents and detection systems
Several real-time PCR reagents for SYBR Green assays or Taqman assays are commercially available, such as the iQ SYBR Green Supermix kit (BioRad, Netherlands, www.bio-rad.com), iQ Supermix kit for Taqman assays (BioRad, Netherlands, www.bio-rad.com), or QuantiTect SYBR Green PCR Kit (Qiagen, Germany, www1.qiagen.com). Commercial real-time PCR detection systems that can be used are e.g. the iQ iCyclers (BioRad, Netherlands, www.bio-rad.com), Lightcyclers (Roche Applied Science, Switzerland, www.roche-applied-science.com), Applied Biosystems machines (USA, www.appliedbiosystems.com), or Rotor-Gene machines (Corbett Life Science, USA, www.corbettlifescience.com).

7.6 DATA INTERPRETATION

Based on the physico-chemical (7.2), and hydrological parameters (7.4) measured *in situ* in the groundwater, pore water, and surface water, the functioning of the mat can be verified *in situ*. The main objective is that no CAH reach the top of the mat or the covering sand layer. Based on the formula found in section 2.2.8 , the thickness of the mat should be recalculated and increased if CAH reach the surface water.

The measured physicochemical data can be used to calculate the CAH degradation constants in the aquifer (through the groundwater CAH concentrations), sediment (pore water CAH concentrations in the sediment), and active cap (pore water CAH concentrations in the cap).

The hydraulic parameters should be taken into account together with the degradation constants to determine the thickness of the active cap based on the formula presented in 2.2.8.

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