SV-308

Bitterfeld: Bioremediation of regional contaminated aquifers

Integrated final report

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Samenvatting
Het NOBIS/SKB-consortium heeft een sequentieel anaëroob/aëroob behandelingssysteem onderzocht voor de afbraak van chloorethenen en chloorbenzeen. In de anaërobe fase wordt een elektrondonor en een stikstofbron toegevoegd om de reductieve dechlorering te stimuleren. In de aërobe fase worden nitraat en zuurstof gedoseerd als elektronen-acceptoren. Het onderzoek is grotendeels uitgevoerd op de SAFIRA test site in Bitterfeld, Duitsland, onder supervisie van TNO.
Het systeem is toepasbaar op plaatsen waar de concentraties gematigd zijn; het gaat om een pluimtechniek die voorkomt dat verontreinigd grondwater zich verspreidt naar het oppervlaktewater.
In de veldsituatie bestaat het systeem uit een elektronendonor - infiltratiezone voor de anaërobe afbraak en een landschapgeïntegreerde aërobe zone dicht bij het oppervlaktewater, mogelijk in combinatie met een wetland, een cascadesysteem en/of het gebruik van natuurlijke afbraakprocessen in het grensvlak van grond- en oppervlaktewater.
Naast Bitterfeld, kan het onderzochte tweefasen systeem ook toegepast worden in andere gebieden of locaties, zowel klein- als grootschalig, met een combinatie van gechloreerde alifatische en aromatische verbindingen of andere (cocktails van) verontreinigingen waarvoor een tweefasen-aanpak noodzakelijk is.

Trefwoorden
Gecontroleerde termen
bioremediatie, chloorbenzeen, chlooretheen,
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Abstract
The NOBIS/SKB consortium has investigated a sequential anaerobic–aerobic treatment system to degrade chloroethenes and chlorobenzene in groundwater in Bitterfeld, Germany. In the anaerobic stage, an electron donor and nitrogen source are added to stimulate the reductive dechlorination, while in the aerobic stage, nitrate and oxygen are dosed as electron acceptors. The research has largely been carried out at the SAFIRA test site in Bitterfeld under supervision of TNO.
The system design for field application consists of a two-phase approach: an electron donor infiltration zone for the anaerobic degradation and a landscape integrated aerobic zone near the surface water, possibly in combination with a wetland, cascades and/or the use of natural attenuation processes in the interface between groundwater and surface water.
Apart from the Bitterfeld area, the investigated 2-phase system can also be applied at other areas or sites, either large or small scale, with a combination of chlorinated aliphatic and aromatic compounds or other (cocktails of) contaminants that need a 2-phase approach.

Keywords
Controlled terms
bioremediation, chlorinated aliphatic compound,
chlorinated aromatic compounds, chlorobenzene,
chloroethenes, contaminated groundwater,
in situ, on-site

Uncontrolled terms

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[1] The composition of the Knowledge Exchange Group was subject to several changes during the project; * indicates involvement during part of the project.

SUMMARY

Bitterfeld: Bioremediation of regional contaminated aquifer

This integrated final report describes the activities within the project “Bitterfeld: Bioremediation of regional contaminated aquifers” (1999-2003).
Due to mining and other industrial activities in this region, located near Leipzig, Germany, an area of ca. 25 km^2 has been contaminated with a several hazardous organic pollutants. In 1999, a project has been started to assess the possibility of an enhanced natural attenuation approach to remediate the groundwater at this site. This NOBIS/SKB project has been carried out by a consortium consisting of TNO, Tebodin, BAM/HBG and Shell, and is part of the German “Sanierungsforschung in regional kontaminierten Aquiferen” (SAFIRA) project. In the SAFIRA project, the feasibility of physicochemical and biological technologies is tested in on site columns and *in situ* reactors. The ultimate goal of the SAFIRA project is to find suitable methods to deal with the pollution at a large scale.

The NOBIS/SKB consortium has investigated a sequential anaerobic–aerobic treatment system to degrade the chloroethenes and chlorobenzene, respectively. In the anaerobic stage, an electron donor and nitrogen source are added to stimulate the reductive dechlorination, while in the aerobic stage, nitrate and oxygen are dosed as electron acceptors. The research has been carried out in the laboratory of TNO in Apeldoorn, The Netherlands, and at the SAFIRA test site in Bitterfeld under supervision of TNO in on-site column- and *in situ* reactor (4*4 m^3) systems.

For the first, anaerobic phase, it was found that chlorinated ethenes can be completely dechlorinated under anaerobic conditions. It turned out to be possible to overcome the problem of the high sulphate concentrations in the groundwater by dosing lower electron donor concentrations. This led to extensive trichloroethene dechlorination, while only limited sulphate reduction took place. This indicates the possibility to achieve dechlorination activity in the presence of high sulphate concentrations.

For the second, aerobic phase, in which hydrogen peroxide and nitrate were dosed, complete degradation of chlorobenzene was observed in the columns.
In the *in situ* reactors, MCB removal was limited to 25-30%. This was most likely caused by the fact that these reactors had been running under anaerobic conditions during two previous years, which means that the reducing sulphide precipitates have to be re-oxidised before aerobic conditions can prevail.

In the laboratory column experiments it was shown that an anaerobic dechlorinating system that is directly linked to an aerobic system resulted in badly sustainable or no MCB degrading prerformance in the latter system. Therefore, in the field, a buffer zone should be created to prevent negative effects from the effluent of the anaerobic phase to the aerobic phase.

To date, sufficient results have been gained from the column and reactor systems for up scaling to field condititons. Besides, after about four years of research in the *in situ* reactors and the possible occurrence of deficiencies in the aquifer material, it is considered no longer useful to continue the research in the present systems.

Possibilities for large-scale application have been studied within the framework of a separate mission to the Bitterfeld region. The results have been reported separately [39].
Based on the findings on the SAFIRA test site and the study of available data, the mission team came to a concept on field scale. The concept is applicable at the site where concentrations are moderate. This means it is suitable for application in the plume and not in the source area. It is

meant to prevent that contaminated groundwater is draining into the surface water system. The system consists of a two-phase approach: an electron donor infiltration zone for the anaerobic degradation and a landscape integrated aerobic zone near the surface water, possibly in combination with a wetland, cascades and /or the use of natural attenuation processes in the interface between groundwater and surface water.

SAFIRA has shown that multi-stage technologies are basically capable of dealing with the mix of contaminants present at the mega-site.
Abiotic multi-stage technologies have successfully passed the laboratory, bench-scale and reactor-scale testing phases. The technologies are applicable in reactive walls, funnel-and-gate approaches or as on-site technology. Prolonged reactor tests and pilot tests will be needed to assess the flexibility of each of the technologies, to be able to include flexibility into the design and to build and operate large-scale applications effectively and efficiently.

During the SAFIRA research period a general paradigme shift occurred within most of the SAFIRA research groups: in most cases, not a single technology, but a smart combination of technologies will lead to the most efficient approach to the contaminated groundwater.

Due to the flooding catastrophe in the Bitterfeld region in August 2002, but also the specific conditions in the Bitterfeld area, it has not yet been possible to carry out field measurements as a preparation for a pilot test on field scale.

Solutions for the Bitterfeld region are currently being investigated within the framework of the EU-WELCOME (Water, Environment, Landscape management at COntaminated MEgasites) project. This project focuses on a megasite approach and includes natural attenuation in the groundwater and in the groundwater / surface water interface.
Continuing research in the Bitterfeld region has also been planned within the framework of the EU-AQUATERRA project, which is expected to be started early 2004. The work will focus on interaction fluxes of the groundwater with the surface water. The emphasis will lay on the survey of transport processes with the seepage water from soil surface via the vadose zone to the groundwater and further in to the surface water body.

Apart from the Bitterfeld area, the investigated 2-phase system can also be applied at other areas or sites, either large or small scale, with a combination of chlorinated aliphatic and aromatic compounds or other (cocktails of) contaminants that can be eliminated in a 2-phase approach. A recent example is the successful field pilot of a site contaminated with hexachlorocyclohexane (HCH) in Hengelo, the Netherlands.

It is worthwhile to put effort in a search for a substantial number of applications for the system that was subject of research within this project.

SAMENVATTING

Bitterfeld: Bioremediation of regional contaminated aquifer

Dit integrale eindrapport beschrijft de activiteiten binnen het project “Bitterfeld: Bioremediation of regional contaminated aquifers”(1999-2003).
Ten gevolge van mijnbouw- en andere industriële activiteiten in de regio Bitterfeld, nabij Leipzig in Duitsland, is een gebied van circa 25 km^2 ernstig verontreinigd met een cocktail van organische verontreinigingen. In 1999 is een project gestart om de mogelijkheden van gestimuleerde biologische afbraak van grondwaterverontreinigingen in dit gebied te onderzoeken. Dit NOBIS/SKB-project is uitgevoerd door een consortium bestaande uit TNO, Tebodin, BAM/HBG en Shell en maakt onderdeel uit van het Duitse SAFIRA-project (“Sanierungsforschung in regional kontaminierten Aquiferen”). In het SAFIRA-project wordt de haalbaarheid van verschillende fysisch-chemische en biologische technieken onderzocht in on-site kolommen en *in situ* reactoren. Het uiteindelijke doel van SAFIRA is om toepasbare methoden te ontwikkelen om de grootschalige verontreinigingen te beheersen.

Het NOBIS/SKB-consortium heeft een sequentieel anaëroob/aëroob behandelingssysteem onderzocht voor de afbraak van respectievelijk chloorethenen en chloorbenzeen. In de anaërobe fase worden een elektrondonor en een stikstofbron toegevoegd om de reductieve dechlorering te stimuleren. In de aërobe fase worden nitraat en zuurstof gedoseerd als elektronen-acceptoren. Het onderzoek is uitgevoerd in het laboratorium van TNO in Apeldoorn, Nederland en op de SAFIRA test site in Bitterfeld, onder supervisie van TNO in on-site kolom- en *in situ* –reactor (4*4 m^3) systemen.

Voor de eerste, anaërobe fase, is gebleken dat gechloreerde ethenen volledig kunnen worden gedechloreerd onder deze condities. Het probleem van hoge sulfaatconcentraties in het grondwater kan worden voorkomen door lage elektronendonor-concentraties te doseren. Dit leidt tot dechlorering van trichlooretheen, terwijl slechts beperkte sulfaatreductie plaatsvindt. Dit betekent dat het mogelijk is om de dechlorering ook bij hoge sulfaatconcentraties te laten plaatsvinden.

Voor de tweede, aërobe fase, waarin peroxide en nitraat werden gedoseerd, werd volledige afbraak van chloorbenzeen (MCB) aangetoond in de kolommen. In de *in situ* kolommen was de MCB-verwijdering beperkt tot 25-30%. Waarschijnlijk is dit veroorzaakt door het feit dat deze reactoren eerder gedurende twee jaar onder anaërobe condities gedraaid hebben, waardoor de gevormde sulfideneerslag eerst gere-oxideerd moet worden voordat aërobe condities kunnen worden bewerkstelligd.

In de kolomsystemen bleek dat een directe koppeling van het anaërobe aan het aërobe systeem leidt tot slecht functioneren van het laatste. Daarom dient in de veldsituatie een bufferzone te worden gecreëerd om negatieve effecten van de anaërobe fase op de aërobe fase te voorkomen.

Tot dusver zijn voldoende resultaten bereikt in de kolom- en reactor-systemen om opschaling naar de veldsituatie te realiseren. Na circa vijf jaren onderzoek in de *in situ* reactoren en het mogelijke optreden van deficiënties in het bodemmateriaal, wordt het bovendien niet langer als zinvol beschouwd om het onderzoek in de huidige systemen te continueren.

Mogelijkheden voor opschaling van het systeem zijn onderzocht in het kader van een separate missie naar de Bitterfeld regio [39].
Gebaseerd op de resultaten van de SAFIRA test site en beschikbare data, kwam het team tot een concept voor de veldsituatie. Dit concept is toepasbaar op plaatsen waar de concentraties

gematigd zijn; het gaat om een pluimtechniek die de verspreiding van verontreinigd grondwater naar het oppervlaktewater voorkomt.
Het systeem is een tweefasen-benadering die bestaat uit een elektronendonor - infiltratiezone voor de anaërobe afbraak en een landschapgeïntegreerde aërobe zone dicht bij het oppervlaktewater. De aërobe zone kan mogelijk gerealiseerd worden in combinatie met een wetland, een cascadesysteem en/of het gebruik van natuurlijke afbraakprocessen in het grensvlak van grond- en oppervlaktewater.

SAFIRA heeft bewezen dat meerfasen-technologieën in principe in staat zijn om de cocktail aan verontreinigingen die op de megasite Bitterfeld aanwezig zijn te behandelen. Ook enkele fysisch-chemische technieken hebben succesvol het onderzoek op laboratorium- en reactorschaal doorlopen. De technieken zijn toepasbaar in reactieve zones, als funnel-and-gate systeem of als on-site techniek. Aanvullend toegepast onderzoek is noodzakelijk om de flexibiliteit van de afzonderlijke technieken te bepalen en om ze full-scale effectief en efficiënt toe te passen.

Tijdens de onderzoeksperiode van SAFIRA heeft er een algemene paradigmaverschuiving plaatsgevonden binnen de meeste onderzoeksgroepen: in de meeste gevallen zal niet een enkele technologie, maar één specifieke combinatie van technologieën tot de meest efficiënte aanpak van het verontreinigde grondwater leiden.

Ten gevolge van de overstromingsramp in de Bitterfeld regio in augustus 2002, maar ook vanwege specifieke omstandigheden in Bitterfeld, is het nog niet mogelijk geweest om veldmetingen uit te voeren als voorbereiding van een pilot test op veldschaal.

Oplossingen voor de Bitterfeld regio worden momenteel onderzocht in het kader van het EU-WELCOME project (Water, Environment, Landscape management of COntaminated MEgasites). Dit project richt zich op een megasite benadering, waarbij ook natuurlijke afbraak in het grondwater en in het grondwater / oppervlaktewater worden meegenomen.
Aansluitend onderzoek in de Bitterfeld regio is ook voorzien in het kader van het EU-AQUATERRA project, dat waarschijnlijk begin 2004 zal starten. Dit zal zich richten op de interactieve fluxen tussen grond- en oppervlaktewater. De nadruk zal liggen op het onderzoek van transportprocessen van infiltratiewater van het bodemoppervlak via de onverzadigde zone naar het grondwater en verder naar het oppervlaktewater.

Behalve in Bitterfeld, kan het onderzochte tweefasen systeem ook toegepast worden in andere gebieden of locaties, zowel klein- als grootschalig, met een combinatie van gechloreerde alifatische en aromatische verbindingen of andere (cocktails van) verontreinigingen waarvoor een tweefasen-aanpak noodzakelijk is. Een recent voorbeeld is de succesvolle pilot van een locatie verontreinigd met hexachlorocyclohexaan (HCH) in Hengelo, Nederland.

Ten behoeve van verdere opschaling is het zinnig om een aantal concrete toepassingen op veldschaal te zoeken voor het systeem dat in het kader van dit onderzoek is ontwikkeld.

LIST OF ABBREVIATION USED THROUGHOUT THE REPORT

CB	chlorobenzene
cis-DCE	*cis*-1,2-dichloroethene
DCE	dichloroethene
DDT	dichlorodiphenyltrichloroethane
DOC	dissolved organic carbon
ED	electron donor
HCH	hexachlorocyclohexane
KEG	knowledge exchange group
eeq	electron equivalents
MeOH	methanol
PCE	tetrachloroethene
TCE	trichloroethene
TOC	total organic carbon
trans-DCE	*trans*-1,2-dichloroethene
VC	vinyl chloride
VFA	volatile fatty acids

CHAPTER 1

INTRODUCTION

In Europe, many sites are contaminated at a large scale because of the presence of first generation chemical industries, which started the production of bulk organic chemicals, like chlorinated aliphatic and aromatic compounds and pesticides (DDT, HCH, etc). Many of these industrial activities resulted in large scale contaminations in several regions. Since then, most of the chemical production facilities were improved and replaced by environmentally safer plants and products. Nevertheless, the presence of these industries in many cases has resulted in contaminated soil and groundwater. Such contaminated areas can be found in many countries. In many of these regions measures have to be taken to protect public health and ecosystems to provide a basis for further ecological, social and economic development.

In general, in large scale contaminated areas, a complete and fast clean-up cannot be achieved through the application of conventional pump-and-treat methods because of the large amounts of contaminated soil and groundwater involved. Natural or enhanced remediation is also less suitable as a sole measure for risk mitigation due to the high contaminant concentrations and unacceptable expansion of groundwater plumes. Instead, safe and cost effective long term containment is required, like large scale reactive barriers coupled with funnel-and-gate techniques that could be combined with natural or enhanced attenuation. The development of such barriers or *in situ* techniques for large scale polluted areas is therefore an important issue on the environmental and economical political agenda in many European countries.

In the NOBIS/SKB project “Bioremediation of regional contaminated aquifers” the feasibility of barrier and *in situ* techniques has been studied in cooperation with a German initiative, the SAFIRA (SAnierungs Forschung in Regional kontaminierten Aquiferen) project. The SAFIRA project is managed by UFZ (Umwelt Forschungs Zentrum Leipzig-Halle), and various other German research institutes and universities participate in the project. The project aims to test several reactive barriers/*in situ* reactors at pilot plant scale at a model site at Bitterfeld/Wolfen, a town north of Leipzig in the eastern part of Germany (figure 1). This region is an example of a large polluted area for which the implementation of containment and remediation measures is expected to be needed within the next few years.

Within the SAFIRA project several physicochemical approaches and biological techniques have been tested and compared with respect to the containment and remediation of the contaminated groundwater plume. The techniques tested are:

- adsorption to activated carbon combined with biodegradation;
- degradation by zero-valent iron (Fe^0) reduction combined with (magnesium) peroxide oxidation. Dechlorination of chlorinated ethenes with Fe^0 and subsequent oxidation of chlorinated aromatics with oxygen, which is released by the peroxide. Different combinations of reduction and/or oxidation have been tested;
- zeolite incorporated palladium. Catalytic dehydrochlorination by zeolite based palladium of the aliphatic and aromatic compounds with molecular hydrogen. Hydrogen should be generated via electrolysis *in situ* or should be externally dosed;
- electrochemical processes. Dechlorination of chlorinated aromatics via dehydrochlorination with at a palladium catalyst activated hydrogen;
- ultrasound assisted catalytic oxidation;
- intrinsic bioremediation.

Most of the technologies in the SAFIRA project are focussing on chlorinated aromatic compounds alone. NOBIS/SKB has participated in the project by testing and evaluating an enhanced natural attenuation approach $(NA)^+$ for the removal of both chlorinated aliphatic and chlorinated aromatic compounds from the groundwater.

The NOBIS/SKB project "Bioremediation of regional contaminated aquifers" has been carried out by a consortium consisting of TNO-MEP, Tebodin, Shell, HBG/HWZ and TNO-NITG. The research project was based on a contract between UFZ/SAFIRA and TNO-MEP.
The main research aims of the NOBIS/SKB project are:

- to select a suitable biological technique (i.e. a bioactivated zone and a funnel-and-bioreactor approach) under real-scale conditions and to compare this method to the other physico-chemical approaches tested in the SAFIRA-project;
- to develop a biological test unit for a smaller scale mobile on-site field facility.

This final report comprises the results of all activities within the four subsequent phases of the NOBIS/SKB project (December 1998 - February 2003).

Fig. 1. Location of the experimental site.

1.1 Description of the Bitterfeld-Wolfen contamination situation

In the Bitterfeld/Wolfen region, lignite mining was a main industry for more than a century. These mining activities led to a lowering of the groundwater level, at some places with 10 to 15 m, and a severe change in the hydrogeological situation. In former Eastern Germany, the chemical industry was built in these (former) mining areas with artificially low groundwater levels resulting in large subsurface contaminations with compounds like DDT, HCH, chlorinated benzenes, chlorinated aliphatic compounds, etc. In most cases, the industrial waste deposits are in direct contact with the groundwater. At present, an area of about 25 km^2 is polluted to a depth of several tenths of meters and this forms a large scale contaminated area threatening the flood plain of the river Mulde and the Elbe [48].

The need for containment and remediation of this area has been foreseen because of the changes in the hydrogeological situation in the region. The mining activities have ceased and large scale groundwater extraction wells have been shut down. The result of such a shut down will be the rise of the groundwater to its original natural level, which will result in large scale contamination and consequently a strongly enhanced mobilisation of the pollution out of the contaminant source area towards the surrounding lakes and rivers. The area under the site is contaminated with compounds like HCH, but further downstream chlorinated ethenes and chlorinated aromatic compounds are the main pollutants. Some of the areas in the Bitterfeld region are designated to be recreational areas. These ecological, social and economical aspects explain the need for implementation of a large scale containment and/or remediation [48].

A geological section of the area is given in figure 2. The contaminated area consists of a lignite layer with sand and gravel on top and another sandy layer below and underneath Middle Olygocene clay. This clay layer functions as the base of the groundwater pollution and the lignite layer (when present) is the aquitard between the two sandy aquifers [48].

The problem of the Bitterfeld/Wolfen area is that a large source of a mixture of contaminants must be controlled under varying hydrogeological conditions. Key research issue is the natural and enhanced degradation of the mixture of contaminants, containing contaminants that can only be degraded under anaerobic conditions (chlorinated aliphatic contaminants like trichloroethene (TCE), and dichloroethene (DCE)) or under aerobic conditions (chlorinated aromatic compounds like di- and chlorobenzene (DCB and CB) and benzene).

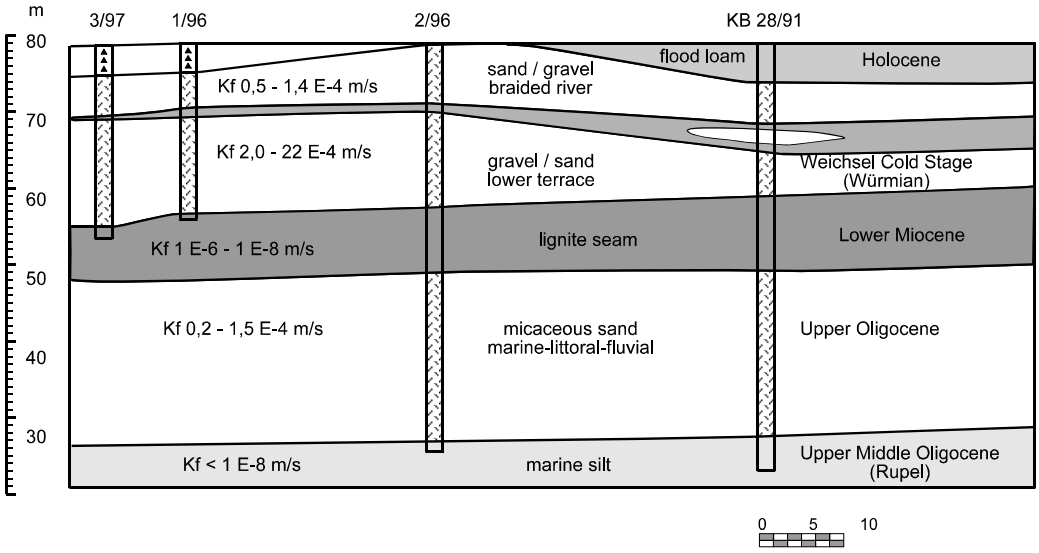


Fig. 2. Geological section of the Bitterfeld Wolfen area [48].

The contamination levels vary among the upper and lower aquifers. The lower aquifer was mainly chlorinated benzenes [49]. This stratification trend can be observed both in soil and groundwater samples (table 1). The groundwater was also geochemically analysed (Appendix A). Besides the compounds mentioned in the tables 1 and Appendix A, also trace amounts of bromobenzenes, PCE, and other compounds like HCH, higher chlorinated benzenes and dioxins were found in the groundwater. The highest concentrations measured for AOX and chlorobenzene are 9 and 45 mg l^{-1}, respectively. The chloride and sulphate concentrations are relatively high; whereas the nitrate and nitrite concentrations are low. The pH of the groundwater appears to be fairly constant among different sampling wells and sampling dates. The redox potential is relatively high, and is variable among the different samples. As a mean value for the redox potential of the groundwater used a value of -160 mV was given.

Table 1. Contaminants (µg l-1) found in the groundwater at Bitterfeld/Wolfen [48].

Contaminant	Upper aquifer	Lower aquifer	Dutch intervention level
TCE	50-200	10,000	500
Trans-1,2-DCE	10-40	4,600	
cis-1,2-DCE	30-200	7,400	20[a]
DCB	700-1,000	n.d.[b]	50
CB	8,000-51,000	100	180
sulphate (mg l^{-1})	550-1000	740	
chloride (mg l^{-1})	100-400	1250	

[a] Intervention level for sum of *trans*-1,2-DCE and *cis*-1,2-DCE
[b] n.d. = not determined

The cations which could cause clogging problems, due to the formation of carbonate and/or sulphide salts are iron, calcium and, to a lesser extent, magnesium. The iron content in the groundwater in most cases was low. As far as iron is concerned, not too many problems are expected under aerated conditions. Calcium and magnesium concentrations are fairly high. This could cause a problem under sulphate reducing conditions because of the sulphate concentration (550-1000 mg l^{-1}), which could lead to calcium and magnesium precipitation as sulphide salts. With the exception of sodium and potassium, all other compounds measured are only present in minor amounts.

1.2 Aim and significance of the Bitterfeld project

The aim of the SAFIRA project framework and the NOBIS/SKB project was to test and compare different reactive barrier and *in situ* treatment approaches for managing and remediating large areas polluted with mixtures of organic contaminants. The specific aim of the NOBIS/SKB contribution was to test a suitable biological alternative (i.e. bioactivated zone and funnel-and-bioreactor approach).

1.3 Description of the SAFIRA test-site

Most of the research has been carried out at the SAFIRA test site, which is located in Bitterfeld, at the edge of a contaminated groundwater plume.

The first phase of the project included runs of with small scale on-site columns. All research groups in the SAFIRA project were given the opportunity to carry out small scale experiments in an on-site mobile test unit (figure 3). This mobile unit is located at the test site and is continuously supplied with local groundwater (figure 4). For practical reasons, the experiments concerning the anaerobic transformation of chloroethenes as well as the additional experiments were carried out at the laboratory of TNO-MEP in Apeldoorn. For those experiments groundwater from the location was transported to Apeldoorn. Results from the on-site experiments (including the laboratory column tests) are discussed in chapter 2.

Fig. 3. Mobile on-site test unit at the Bitterfeld/Wolfen site.

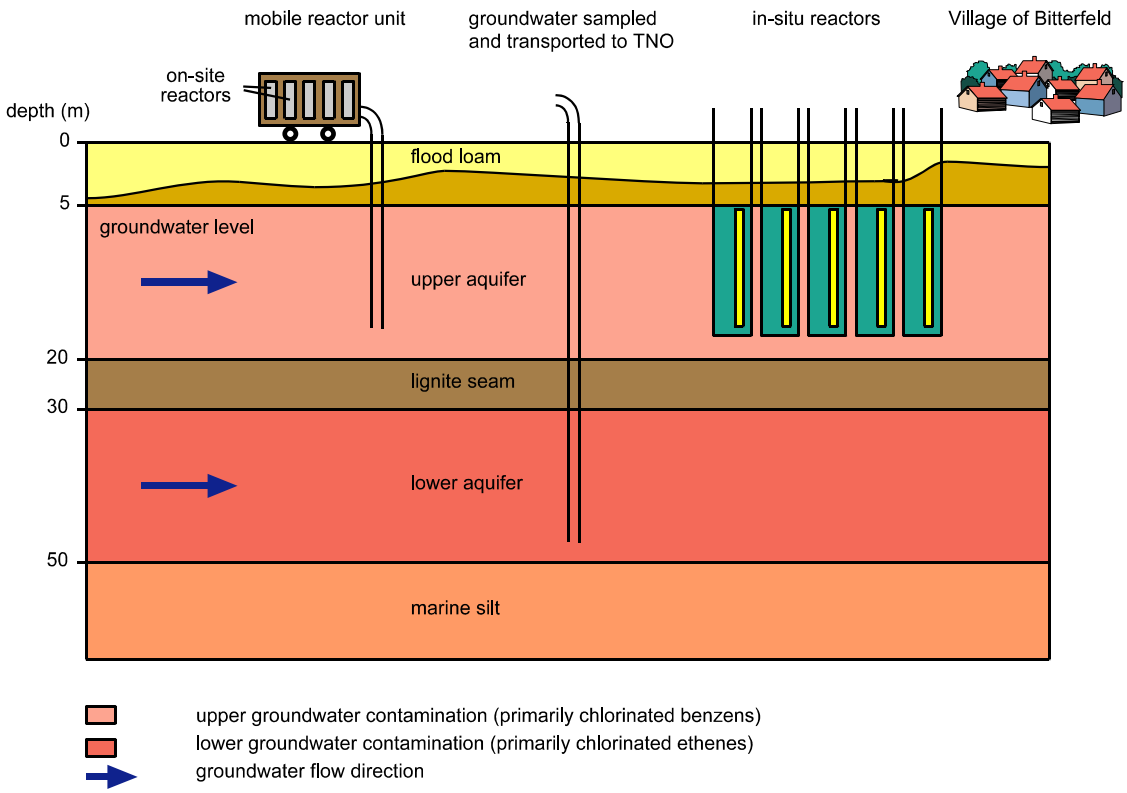
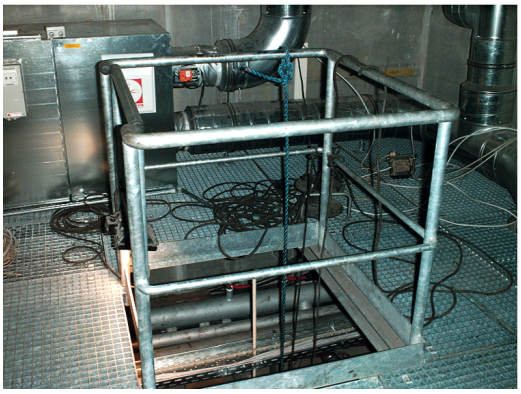


Fig. 4. General set-up of the on-site mobile test unit.

In the following phases of the project, also experiments with larger scale *in situ* reactors at the Bitterfeld location have been started. Five 22 meter deep shafts (figure 5) were made available for the research groups within the SAFIRA project. The four reactors used in the NOBIS/SKB project were placed in such a shaft (figure 6) and are, similar to the on-site reactors, fed with groundwater from the location (figure 4). This groundwater originates from the upper aquifer and contains mainly chlorobenzene. For the *in situ* test runs carried out within the NOBIS/SKB project, the groundwater was amended with TCE. A brick shelter was build on top of each shaft for protection of the equipment and to guarantee the safety of the people working at the location (figure 7). The test site is also equipped with laboratory facilities. The test-site as a whole was managed by UFZ.

Fig. 5. The shaft containing the in situ reactors.



A: Top of the shaft

B: Upper reactor

C: One of the reactors in the shaft

D: Bottom of the shaft

Fig. 6. The NOBIS/SKB shaft from bottom to top.

Fig. 7. Shelters covering the shafts at the Bitterfeld/Wolfen site.

1.4 Evaluation of suitable processes for the biodegradation of the contaminants and critical parameters

1.4.1 *Introduction*

The site at Bitterfeld/Wolfen is contaminated with a mixture of chlorinated ethenes, chlorinated benzenes, small amounts of 1,1,2,2-tetrachloroethane (1122TeCA) and trace amounts of higher chlorinated compounds like HCHs and DDT. This mixture of contaminants has to be converted to harmless compounds via a stimulated intrinsic bioremediation variant (NA^+ approach).

Given the high sulphate concentration (up to 1000 mg l^{-1}, table 1), biotransformation, should occur under sulphate reducing conditions. However, complete reduction of the sulphate present should be avoided because of possible problems related to the formation of high concentrations of sulphide (i.e. formation of sulphide salts and a high oxygen/nitrate demand in the microaerobic reaction step). The main contaminants found in the groundwater are trichloroethene (TCE), dichloroethene (DCE) and chlorobenzene (CB). The possibilities for anaerobic and aerobic conversion of the different compounds are evaluated below.

1.4.2 *Biodegradation of chlorinated ethenes*

TCE and lower chlorinated ethenes are biodegradable under both aerobic and anaerobic conditions. PCE is only substantially (bio)degraded under anaerobic conditions. Several pure cultures of bacteria have been isolated which are able to use PCE as an energy source [10, 21, 26, 36]. However, the transformation in those cases is often limited to the removal of one or two chlorine atoms. Normally, *cis*-1,2-DCE (*cis*-DCE) is the main product formed. *Dehalococcoides ethenogenes* is the only bacterium able to transform PCE to vinyl chloride (VC) and ethene [26]. In this case, the last step in the transformation (VC to ethene) is believed to be cometabolic.
Complete reductive dechlorination of PCE and TCE (figure 8) is almost exclusively observed with mixed cultures e.g., [17, 33, 41]. In most cases, it is not clear whether sulphate reducers, fermen-

tative or other bacteria are responsible for the complete reductive dechlorination of PCE and TCE [1, 9, 11]. Under methanogenic conditions, PCE has been suggested to be transformed to CO_2 via the formation of VC [46]. The reductive dechlorination of TCE was observed both in soil and groundwater e.g. [23, 33]. Sulphate reducing enrichment cultures were found to transform PCE to TCE and *cis*-DCE [2].

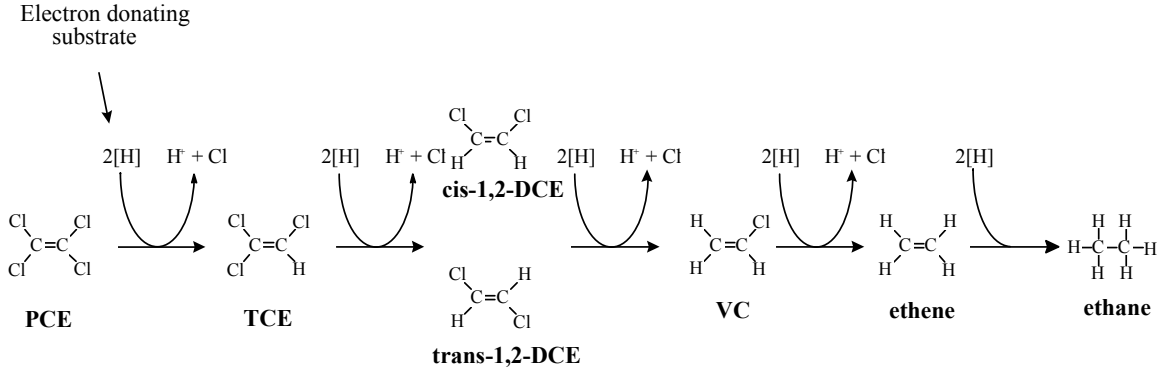


Fig. 8. Complete reductive dechlorination of PCE and TCE under anaerobic conditions.

In all cases, an external growth substrate has to be added as carbon source and electron donor. Probably, the nature of the electron donor influences the dechlorination both in relation to the products formed and the dechlorination rates observed [20]. Also, the capacity of an electron donor to slowly release hydrogen in low concentrations for prolonged periods of time seems to be of importance, especially in mixed cultures. When the hydrogen concentration is kept at a low level, the dechlorinating bacteria are able to outcompete the other (mainly) sulphate reducing and methanogenic bacteria. This is due to the fact that dechlorinators normally have a high affinity (lower K_m value) for hydrogen compared to other groups of bacteria. Therefore, at low hydrogen concentrations, a relatively larger part of the hydrogen will be used for the dechlorination reaction, thus preventing the flow of electron equivalents for other than the dechlorination reaction, e.g. sulphate reduction [16, 38, 53]. Lactate, but also volatile fatty acids like propionate and butyrate have been shown suitable substrates to support dechlorination of chlorinated ethenes. This, however, seems to be strongly dependent on the microorganisms present.

The transformation of lower chlorinated ethenes (DCE and VC) under anaerobic conditions was also found without the addition of an external carbon source. In that case, DCE and VC were oxidised and CO_2 was formed. Apparently, this process can occur under methanogenic conditions, as well as iron and manganese reducing conditions in microcosm studies [5, 6 and 7].

Under aerobic conditions, TCE and lower chlorinated ethenes are degraded via cometabolic reactions [1, 22, 31, 44]. VC is the only compound that can serve as a carbon source for aerobic microorganisms. Cometabolic conversion of chlorinated ethenes usually occurs with microorganisms which grow on methane, ethene, propane, ammonia, or propene and show mono- or dioxygenase activity [1]. The bacteria involved usually have a broad substrate range and gratuitously transform TCE to toxic oxidised intermediates (epoxides), which in turn results in a deterioration of the degradation, via inactivation of the enzymes responsible for their formation. Recently also, the formation of an epoxide from *cis*-DCE, and other DCE isomers (figure 9), and VC has been reported [1].

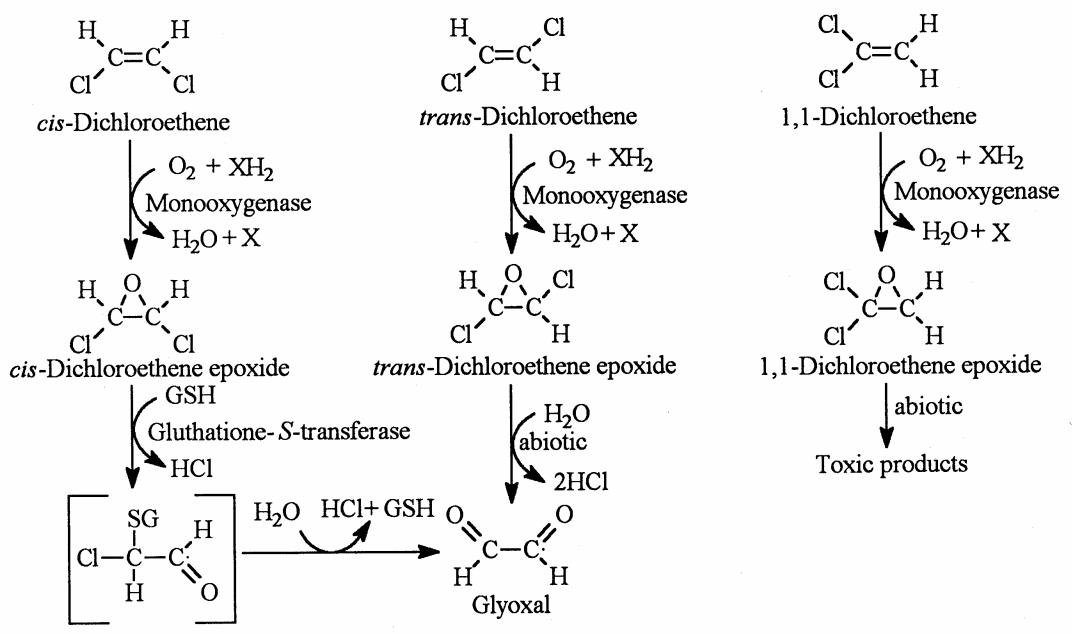


Fig. 9. Epoxide formation from the DCE isomers under aerobic conditions
(Figure taken (with kind permission of Kluwer Academic Publishers) from [1]).

1.4.3 *Biodegradation of chlorinated benzenes*

The information on the anaerobic transformation of dichlorinated benzenes is limited. Complete dechlorination of higher chlorinated benzenes has only been observed in a few cases [25,30]. However, the formation of benzene in those cases was not irrevocably shown, because either benzene was not measured or observed benzene concentrations were very low. Most reports show accumulation of tri-, di- and monochlorinated benzenes with mixed cultures under anaerobic conditions, e.g. [3, 8, 15, 28, 34]. Methanogenic conditions seem to be more favorable than sulphate reducing conditions and conditions with higher redox potentials [8]. Nevertheless, this may also be strongly dependent on the source of the microorganisms.

Anaerobic dechlorination of lower (tri- and di-) chlorinated benzenes to (mono)chlorobenzene has been reported under anaerobic conditions by microorganisms, which had been first adapted to higher chlorinated benzenes [4]. Mineralisation of benzene was observed under methanogenic, sulphate reducing and iron reducing conditions. So far, little is known about the pathways used by microorganisms to degrade benzene. Information about benzene transformation under denitrifying conditions is divers. Some authors find the degradation of benzene under denitrifying conditions in BTEX contaminated aquifers, others do not, or find no enhancement of benzene transformation after the addition of nitrate to a microcosm [1]. The addition of small amounts of oxygen enhanced the transformation of aromatic compounds under denitrifying conditions in some microcosms studies. Apparently, under these conditions, the aromatic ring is activated via hydroxylation and after ring cleavage, the products are mineralised under anaerobic conditions. Nevertheless, the presence of oxygen could also lead to more favorable environmental conditions [51].

Under aerobic conditions, higher chlorinated benzenes (hexa- down to tetrachlorobenzene) are hardly or not microbiologically degradable. Tri-, di- and monochlorinated benzenes on the other hand can be used as sole source of carbon and energy [35,37,42]. In that case, chlorinated benzenes are degraded via an initial oxygenation of the aromatic ring. These reactions are catalysed by a dioxygenase (figure 10). After the hydroxylation of the compounds, the catechol can be cleaved via ortho- (in between the hydroxyl groups) or meta-(next to one of hydroxyl group) cleavage. Ortho cleavage of the aromatic ring leads to the formation of a chloromuconic acid,

which can be further metabolised. Meta-cleavage of chlorinated benzenes, on the other hand, may result in the formation of toxic intermediates, which inhibit the meta-cleaving enzymes, thus resulting in accumulation of toxic products and subsequential cell death. A variety of microorganisms can use benzene as sole carbon and energy source and subsequently degrade it via the ortho- or meta-cleavage pathways mentioned above for chlorinated benzenes [1].

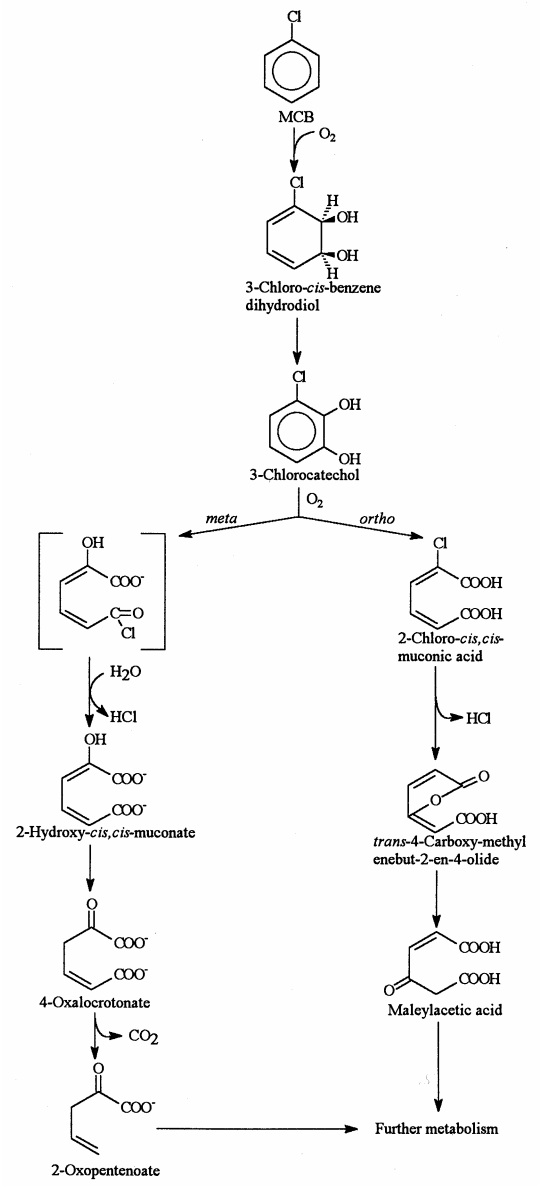


Fig. 10. Aerobic transformation of chlorobenzene.

(Figure taken (with kind permission of Kluwer Academic Publishers) from [1])

1.4.4 *Combined removal in the NA$^+$ approach*

The groundwater in Bitterfeld/Wolfen is polluted with a mixture of aliphatic and aromatic chlorinated compounds, which implies the application of a two-phase system to remediate the groundwater. The Bitterfeld/Wolfen site is contaminated with chlorinated ethenes, which should preferably be degraded under anaerobic conditions, since aerobic cometabolic conversions often lead to the formation of toxic intermediates. The lower chlorinated benzenes are converted under aerobic conditions. Therefore, a sequential anaerobic-aerobic process should be implemented.

The anaerobic reactor
In the anaerobic step TCE should be completely dechlorinated to ethene and/or ethane (figure 8). Given the contaminants found both in the soil cores and the groundwater, it is likely that addition of an electron donor will enhance the dechlorination process. The TOC content of the groundwater is low (3-30 mg TOC l^{-1}) and the redox potential is relatively high. The main TCE dechlorination product found is *cis*-DCE. No VC or ethene has been detected. Therefore, the addition of an electron donor was thought to be necessary to lower the redox potential and serve as a supply of electrons for dechlorination.

The electron donor is added in the form of a mixture of lactate, acetate, propionate, and butyrate. This mixture of fatty acids was likely to guarantee a successful dechlorination, based on the literature data discussed in section 1.4.2. In case of complete dechlorination of the chloroethenes, the addition of electron donor would be minimised for operational (clogging etc.) and financial (costs) reasons. The role of sulphate in the dechlorination process was given special emphasis in the project, because of the large amounts of electron donor involved to reduce all sulphate present. The amount of electron donor needed for sulphate reduction is around 500 to 1000 times higher than the amount of electron donor needed for the complete reduction of the chlorinated ethenes.

In the anaerobic reactor, a microbial population may also develop, which is able to dechlorinate the dichlorinated benzenes leading to the formation of chlorobenzene.

The (micro)aerobic reactor
In the second aerobic reactor, the chlorinated benzenes will be degraded. A three step strategy was developed, which included the increase of the electron acceptor concentration in time.

Firstly, the aim was to degrade the chlorobenzene present in the groundwater under denitrifying conditions (pathway I, figure 11). Results from other researchers within the SAFIRA project showed that chlorobenzene conversion under these conditions may be possible [24]. Also, the addition of nitrate to the groundwater is simpler than the supply of oxygen.

Secondly, trace amounts of oxygen will be added to the influent (as hydrogen peroxyde) when transformation of chlorobenzene under denitrifying conditions is not possible (figure 11, pathway II). From the literature and TNO research we know that the addition of small amounts of oxygen to waste streams contaminated with (chloro)aromatics may lead to an enhanced degradation of the aromatic compounds [43 and 51]. In such cases the amount of oxygen added was not enough to completely oxidise the aromatic compounds. However, the oxygen may have oxidised other compounds in the sediment (iron or other electron acceptors), thus leading to favourable conditions for anaerobic degradation.

Thirdly, “(initial) oxidation of chloroaromatics” will be tested. Mono- or dioxygenation of the (chloro)aromatic compounds will be the main activating process, which requires the addition of molecular oxygen. This may be in the form of oxygen saturated water or via the addition of H_2O_2 to the influent. After the initial oxidation, the formed catechols may be mineralised to CO_2 via anaerobic routes. If anaerobic conditions are not favourable, complete mineralisation under aerobic conditions will be tested. Aerobic mineralization should be easily achieved [1].

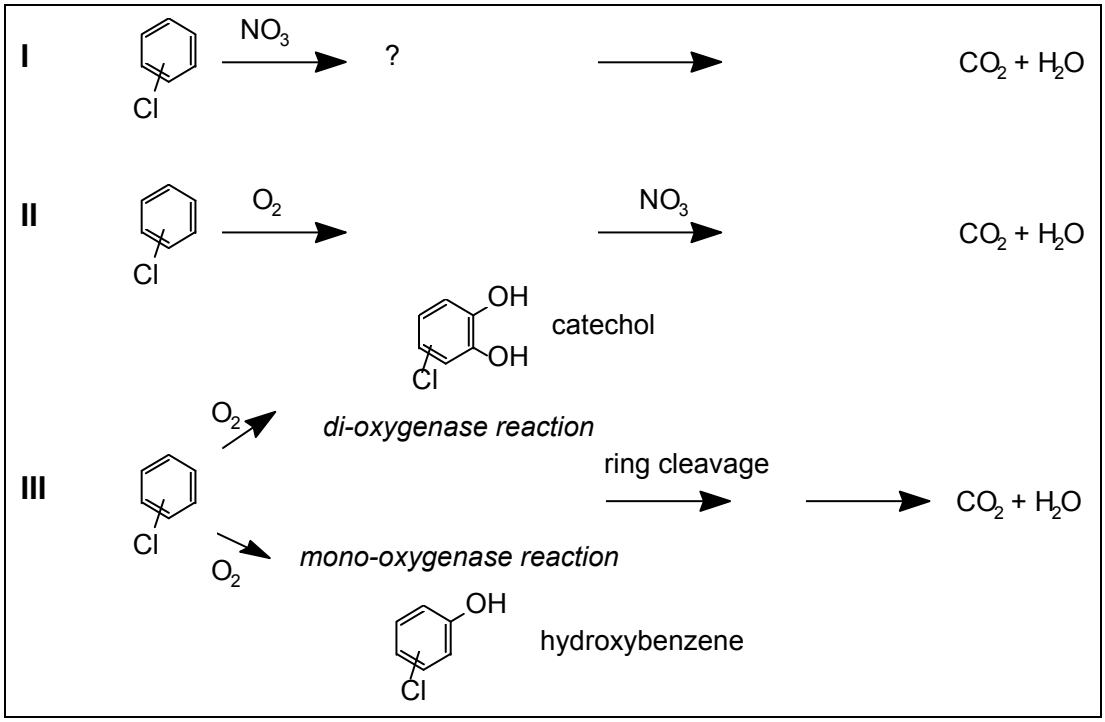


Fig. 11. Operation strategies of the microaerobic reactor.

The carrier material in the reactors

There are a few criteria which have determined the nature of the carrier material used in the on-site and *in situ* reactors at the Bitterfeld/Wolfen location:

- Resemblance to the *in situ* situation; the proper translation of the data from the on-site and *in situ* reactors to the situation in the field should be ensured. Therefore, both the (micro)biological and the (geo)chemical characteristics should be well defined;
- Availability; the carrier material should be available in relatively large quantities (the *in situ* reactors have a volume of 4.4 m^3);
- Quality of the carrier material; the quality should be constant in order to be able to compare results from the on-site and *in situ* reactors and transpose these results to the field situation.

The following carrier materials were considered:

- undisturbed aquifer material from the contaminated site;
- mixed aquifer material from the contaminated site, but chemically and biologically undisturbed;
- course sand fraction of the aquifer material (without clay and organic material);
- lava slugs.

The use of undisturbed aquifer material was highly preferred, because of its obvious resemblance with the real situation *in situ*. However it was foreseen that, if both the on-site and *in situ* reactors had to be filled with this material, this could lead to problems, due to the large volume required and possible difficulties with maintaining the correct (geo)chemical and (micro)biological qualities.

Mixed aquifer material, which is chemically and biologically undisturbed was second in line of preference. Larger soil cores could be mixed and stored in the proper conditions for further use. The effects of exposure to oxygen should be minimised during and after sediment storage. For both options mentioned above it was ideal to use the aquifer material which was removed from the building site for the in site reactors directly in the on-site or *in situ* reactor and preserve the appropriate redox conditions.

In both cases, clogging of the system could become a problem and should be monitored closely. One advantage of using the aquifer material, either undisturbed or mixed, could be a fast start up of the processes in the on-site and *in situ* reactors, provided the appropriate microorganisms are already present *in situ*. With this material, it could also be possible to monitor the development of the microbial composition in the soil, which would help to predict the outcome in the field situation.

The third option was to use the coarse sand fraction of the aquifer material (without clay and organic material) as a carrier. This material resembles the (geo)chemical environment in the field. However, the microbial activity would have to come largely from the microbes in the groundwater. Clogging would probably be less of a problem.

A fourth option was the use of lava slugs. These slugs have no resemblance to the soil, but clogging of the system would only be a minor problem. The microbial activity would have to originate from the groundwater, which could lead to a slow start up of the process and difficulties with the translation of the results from the on-site to the *in situ* reactor and furthermore to the field situation.

Ultimately, the choice was made to use the sediment, which was dug out during construction of the shafts.

1.5 **Set-up of the report**

This report is a compilation of all previously published reports on the NOBIS/SKB project “Bitterfeld: Bioremediation of regional contaminated aquifers” [12-14, 29], including the results of the last part of the project in 2002.

The activities carried out within this project comprise batch experiments, laboratory and on-site column experiments, *in situ* reactor experiments and desk studies. Table 2 shows a short summary of the activities and in which part of the report they are described in detail.

Table 2 Set-up of this report.

Description of activity	Reference
- Introduction to the Bitterfeld/Wolfen situation, geological properties of the area and threats to the environmental quality of the area - Description of the SAFIRA test facility in Bitterfeld - Aims of the SAFIRA and NOBIS/SKB project - Scientific background on the biodegradation of the most common contaminants - Set-up of the report	Chapter 1
- Set-up and results of anaerobic and (micro)aerobic laboratory batch experiments - Set-up and results of the anaerobic, (micro)aerobic and sequentiall anaerobic-micro-aerobic laboratory column experiments - Set-up and resultsof the column experiments run at the SAFIRA test facility in Bitterfeld - Summary and conclusions of the laboratory and on-site experiments	Section 2.2.1 and 2.3.1 Section 2.2.2 and 2.3.2 Section 2.2.3 and 2.3.3 Section 2.4
- Set-up and results of the *in situ* reactor experiments at the Bitterfeld test site - Summary and conclusions of the *in situ* reactor experiments	Sections 3.2 and 3.3 Section 3.4
- Inventory of available electron donor sources in Germany for the full scale application in the Bitterfeld/Wolfen region	Chapter 4
- General discusion of the results from all NOBIS/SKB experimental research on the Bitterfeld case	Chapter 5
- Short description and comparison of the different technologies, developed within the SAFIRA project	Chapter 6
- A discussion on the possibilities for plume management according to the two-phase approach in the Bitterfeld/Wolfen region	Chapter 7
- Knowledge exchange activities within the NOBIS/SKB project	Chapter 8
- General conclusions and recommendations, application perspectives for a wider range of (mega)sites, future activities in this field	Chapter 9

CHAPTER 2

LABORATORY AND ON-SITE EXPERIMENTS

2.1 Introduction

The transformation of chlorinated ethenes and chlorinated benzenes has been studied under different conditions. Batch experiments have been carried out under anaerobic and aerobic conditions for a rapid screening of suitable electron donors, acceptors and other additions. Laboratory column experiments have been carried out to test and fine-tune the results from the batch experiments. Anaerobic and micro-aerobic column experiments have been carried out at the laboratory of TNO-MEP, while a column experiment similar to the microaerobic experiment run at TNO has been run in the on-site test unit in Bitterfeld.

All batch and column experiments were performed with the same sediment. For practical reasons, the columns that have been used for the anaerobic laboratory experiments were smaller than the column used in the on-site unit at Bitterfeld. However, they had scaled-down dimensions according to the on-site column. Although different systems were used, it was expected that the general outcome of all experiments can be compared to each other.

The aim of the experiments was to obtain information on the biodegradation processes which are expected to take place at the Bitterfeld site under anaerobic and microaerobic conditions.

2.2 Experimental aims and set-up

2.2.1 *Laboratory batch experiments*

Anaerobic batch experiments

These batch experiments have been carried out to determine the role of the electron donor in the competition between sulphate reduction and dechlorination. The aim of the experiment was to assess the influence on the reduction rates of both TCE and sulphate by applying different electron donors at variable concentrations. On the one hand high electron donor concentrations may be necessary for dechlorination. The sulphate concentration in the groundwater is high and complete reduction of the sulphate could be necessary for stimulation of dechlorination in the system. However, applying large amounts of electron donor may also lead to an undesired increased reduction of sulphate. On the other hand low electron donor concentrations could be beneficial for the dechlorinating bacteria, because they are known to be more effective in using low hydrogen concentrations compared to sulphate reducing bacteria (figure 12). Hydrogen is the electron donor which is most commonly used by dechlorinating bacteria.

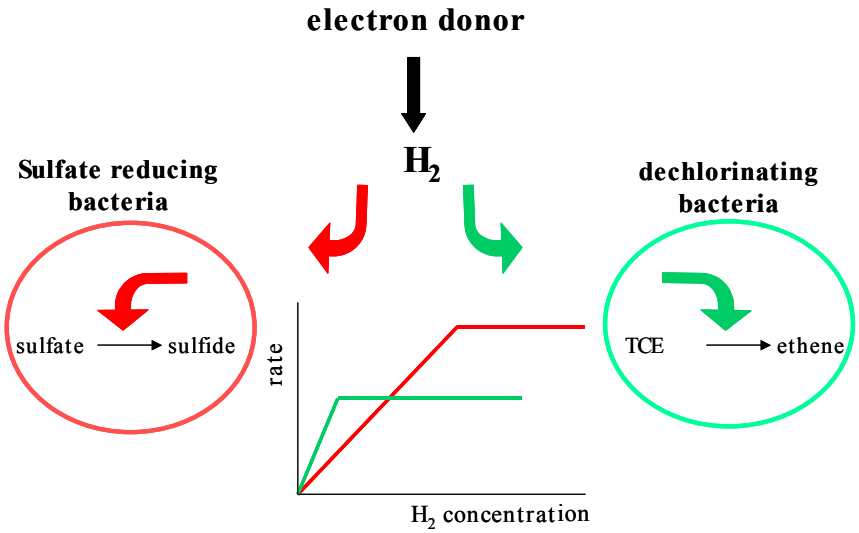


Fig. 12. Flow of electrons to sulphate reduction and dechlorination and the effect of hydrogen concentration on the reduction rate of sulphate and TCE.

The experiments were carried out with anaerobic effluent of the MeOH/G31 column as the inoculum. At the time of sampling, this reactor was dechlorinating TCE to a mixture of DCE, VC and ethene and sulphate reduction in the column was complete. Therefore the effluent was considered to be a suitable source for both dechlorinating and sulphate reducing activity. Acetate, lactate and a mixture of MeOH/G31 (ratio 80%/20%) were used in separate experiments as the electron donors. Acetate is known to generate hydrogen at very low concentrations, whereas the addition of lactate results in pulses of high H_2 concentrations. MeOH/G31 was used because it is the electron donor used in the parent column. The electron donors were applied 0.1, 1 and 10 times the concentration needed for complete dechlorination and sulphate reduction. A detailed set-up of the experiments is given in appendix B.

(Micro-)aerobic batch experiments

The degradation of chlorobenzene has been observed by several groups working within the SAFIRA framework. From the results obtained by those groups and the results generated within the NOBIS/SKB framework it can be concluded that the microaerobic chlorobenzene transformation is very difficult to establish or maintain for prolonged periods of time without the addition of large amounts of oxygen. Therefore, batch experiments were carried out to investigate the possibilities of applying other alternative compounds to stimulate the chlorobenzene degradation under denitrifying or microaerobic conditions. Firstly, compounds like toluene, benzoate and phenol are known to be degraded under denitrifying conditions[1]. The enzyme systems involved in the first steps of the micro- or anaerobic conversion of these compounds could have large substrate spectra, thus enabling the conversion of chlorobenzene as a cosubstrate (figure 13).

Secondly, the role of an iron/nitrate(/oxygen) cycle in the transformation of chlorobenzene was investigated because the chlorobenzene transforming column slowly turned reddish in colour indicating the a possible role of iron (see section on laboratory column experiments).

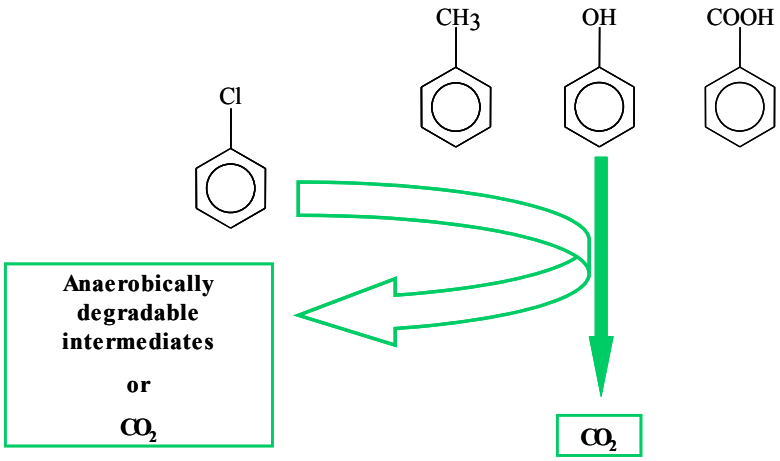


Fig. 13. Schematic representation of theoretically possible cometabolic transformation of chlorobenzene.

The experiments were carried out with a mixture of microaerobic sediment and microaerobic effluent as the inoculum. Groundwater was added as the chlorobenzene source. At the time of sampling the microaerobic column was converting both chlorobenzene and nitrate. Nitrate and iron (if applicable) were added at two times the concentration needed for complete degradation of chlorobenzene. The primary substrates were added at 2 times the concentration of chlorobenzene. All the auxiliary compounds were replenished after depletion (or suspected depletion in the case of benzoate and phenol that could not be analysed). Oxygen (if applicable) was added weekly to a final concentration of 3 mg l^{-1} in the total volume. A detailed set-up of the experiments is given in appendix C.

2.2.2 *Laboratory column experiments*

Anaerobic columns

The anaerobic column experiments were run to provide information on:

- whether or not complete reductive dechlorination of TCE and DCE in the Bitterfeld groundwater occurs under anaerobic conditions;
- the amount of electron donor needed for complete dechlorination of the chlorinated ethenes.

The latter is especially of interest because of the high amounts of sulphate (700-1000 mg l^{-1}) present in the groundwater. At the start of the project, it was unknown, whether dechlorination of the chlorinated ethenes can occur simultaneously with sulphate reduction or only after all sulphate has been removed. If all sulphate must be removed, the amount of electron donor needed for the reduction of sulphate will be around several hundreds of times the amount needed for the complete reduction of the chlorinated ethenes in the groundwater. This would negatively affect the technical and economical feasibility of the anaerobic treatment process in this situation.

The groundwater containing TCE for the anaerobic columns was taken from the Safbit 2 sampling well from 28 meters depth. The groundwater was sampled with a procedure to prevent contact with oxygen and transported to TNO in glass flasks (volume 2 l) which were air tight and completely filled. The composition of the groundwater was analysed after it was received in the lab. The analysis was carried out in 15 bottles, which were randomly picked from the stock supply of 150 bottles. The TCE concentrations were somewhat lower than the results reported earlier (table 3) [47]. The sediment was delivered in glass flasks and covered with groundwater.

Table 3. Concentrations of pollutants (mg l-1) in the groundwater used in the anaerobic column (DL = Detection Limit).

Component	Groundwater experiments Anaerobic column	Safbit 2/96 28 m-bgl [47]
Chlorobenzene (CB)	0.0002 ± 0.00001	0.16
Benzene	0.014 ± 0.003	0.19
Tetrachloroethene (PCE)	< DL	n.q.[1]
Trichloroethene (TCE)	1.3 ± 0.4	8.64
cis-1,2-Dichloroethene (*cis*-DCE)	2.8 ± 0.6	6.70
trans-1,2-Dichloroethene (*trans*-DCE)	1.0 ± 0.2	3.62
Vinyl chloride (VC)	0.28 ± 0.03	n.q.
Ethane	0.08 ± 0.04	
Trichloroethane	0.033 ± 0.015	n.q.
Chloroethane	< DL	
Ethane	< DL	
Toluene		0.01
Methane	2.2 ± 0.2	
Chloride	665 ± 55	1207
Nitrite		< DL
Nitrate	0.44 ± 0.28[3]	4.1
Sulphate	706 ± 97	738
Bromide	2.1 ± 0.3[2]	4.9
Na	473 ± 79	241
Al		0.28
B		0.20
Ba		0.07
Ca	476 ± 42	582
Fe		2.40
K	87 ± 28	45
Mg	82 ± 10	73
Mn		1.9
Ni		<DL
P		<DL
Zn		0.14
pH	6.7 ± 0.0	7.0
Redox	225 ± 4	

[1] Below Detection limit
[2] Not Quantified
[3] Mean value of two sample bottles

The degradation of TCE in the groundwater was tested in duplicate multiport columns, made of airtight PVC. The columns have a volume of 880 ml (figure 14). Assuming a sediment porosity of 40% this leads to a working volume of 350 ml. The columns have 7 sampling ports placed along the height of the columns.

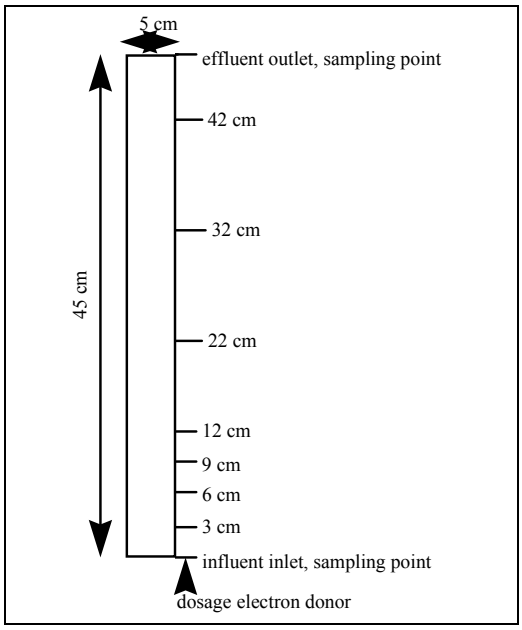


Fig. 14. Set-up of anaerobic column.

Two columns were packed with sediment from the Bitterfeld location and TCE containing groundwater was infiltrated. A volatile fatty acid mixture (VFA) of lactate, acetate, propionate and butyrate (ratio 1:1:1:1 based on electron equivalents) was applied as the electron donor. Previous investigations and literature show that this mixture should be able to sustain dechlorination. The mixture of electron donor was added to the columns in amounts larger than necessary for complete reduction of the oxidised compounds present in the groundwater (sulphate, chlorinated ethenes).

The groundwater containment vessel was closed airtight and connected to a gas bag filled with N_2 to prevent the influx of oxygen (figure 15).

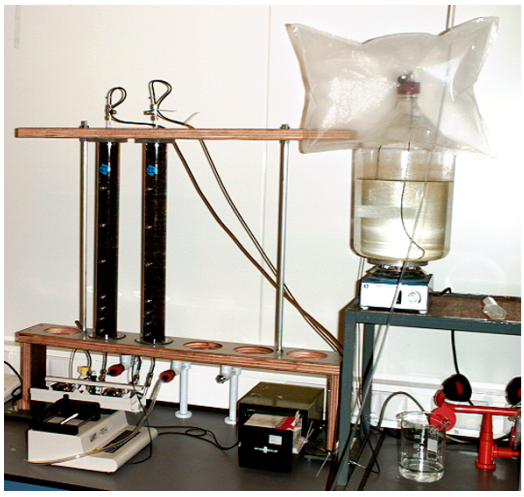


Fig. 15. Set-up of the anaerobic columns.

The influent groundwater was pumped into the columns. All connecting lines and tubes in the system were made of viton or stainless steel to prevent the adsorption of the chlorinated compounds. The column was operated with an initial hydraulic retention time of 2 days (groundwater flow around 178-200 ml d^{-1}). The columns were run in the dark in a temperature controlled room at 20°C.
The latter means that the dechlorination obtained in the laboratory would probably be faster than in the *in situ* reactors, since temperatures in the shafts are lower (14°C). The factor by which the rates are increased is, depending on the microorganisms involved, a factor around 2 to 3 times higher at 20°C compared to rates at 14°C.

The column was fed with groundwater during 4 retention times to establish a steady state situation. Thereafter, the electron donor was added to the influent groundwater. The VFA mixture was dosed to a concentration of 187, 206, 137, and 110 mg l^{-1} for lactate, acetate, propionate and butyrate, respectively (all applied as neutralised sodium salts). This amount of electron donor is 1.25 time the amount needed for complete reduction of all the chlorinated compounds and sulphate (this amount of ED is referred to as 1 * ED).
During the first six months, the effect of the electron donor amount and the addition of a nitrogen source (NH_4^+) on the reductive dechlorination of the TCE was studied.

After ca. 7 months of operation, column 1, which was initially run with VFA as the electron donor, was transferred to methanol (4*ED) as the electron donor. A nitrogen source was not added at that stage. Methanol was chosen because it was expected to have an inhibiting effect on the sulphate reduction.

Three months later, a change was made from using groundwater from the lower Bitterfeld aquifer that contains TCE to groundwater from the upper aquifer that lacks TCE. Therefore, TCE was added to the groundwater from a water saturated solution to a final concentration in the groundwater of 10 mg l^{-1}.

After one year of continuous operation, both columns were connected in front of two micro-aerobic columns, which are described hereafter, to simulate the previously described NA^+ concept. The set-up and conditions after this connection are described later in this section.

After ca. six months of coupled operation, the anaerobic columns were uncoupled again from the micro-aerobic columns. Column 1 was maintained on a complex organic electron donor mixture (G31) and methanol (20%/80%) at a level of 2*ED. Column 2 was switched to a very low dose of volatile fatty acids (0.1*ED) and 75 mg l^{-1} NH_4^+.

During the whole operation period, the influent and effluent of the columns were analysed on a regular basis for organic pollutants, sulphate and nitrate.

Micro-aerobic columns
Two columns with the same dimensions and general set-up as the anaerobic columns described above, were run under micro-aerobic conditions to study the degradation of chlorobenzene. Groundwater containing chlorobenzene was sampled from well “Safbit 30-98” in Bitterfeld. The composition of the groundwater is similar to the groundwater used in the anaerobic column tests and contained as main pollutant 4.6 mg l^{-1} of chlorobenzene. The groundwater was sampled anaerobically, transported to TNO in airtight and completely filled glass flasks and stored at 4°C until use.
Sediment from the upper aquifer at Bitterfeld, which is primarily contaminated with chlorobenzene, was used as packing material for the columns.

The sediment was continuously saturated with groundwater to assert the degassing of the soil and uniform packaging of the column.
After about four weeks, 2.4 mM KNO_3 (twice the amount needed for complete chlorobenzene removal) was added to the groundwater to the microaerobic reactor. One month later, also a low concentration of oxygen was added to the influent (3 mg l^{-1} as 6 mg l^{-1} H_2O_2).
The columns were fed in upflow modus with groundwater with a hydraulic retention time of 2 days and were operated in the dark at a temperature of 20°C.

The influent and the effluent of the columns were analysed regularly to measure the pH, the concentration of the chlorinated contaminants and nitrate. The columns have been running for a period of 181 days, after which they were coupled to the effluent of the anaerobic columns (see next section).

Combined sequential anaerobic-aerobic columns
The micro-aerobic columns that were used in the experiments described in the previous section were used to treat the effluent of the earlier mentioned anaerobic columns. In this way a sequential anaerobic - microaerobic system was created.

The two sequential systems were set-up as follows:
System 1: VFA column - Microaerobic column 1
System 2: MeOH/G31 - Microaerobic column 2
where G31 is a complex organic electron donor mixture.

Before entering the micro-aerobic columns the anaerobic effluents were collected in a vessel. This precaution was taken to avoid pumping problems due to (unexpected) different pumping rates for the anaerobic and the microaerobic columns. The hydraulic retention time in the intermediate vessel was less than 2 days.
To investigate the role of iron in the microbial chlorobenzene transformation, column 2 was amended with iron (II) at day 118 after the start of the sequential operation. Iron may play a role due to the following reaction:

$$\text{Nitrate} + 2Fe(II) + 2H^+ \rightarrow \text{Nitrite} + 2Fe(III) + H_2O$$

Chlorobenzene would subsequently be degraded with Fe(III) as the electron acceptor. Nitrite would be further converted via denitrification.

The influent and the effluent of the columns were analysed regularly to measure the concentration of the chlorinated contaminants, iron and nitrate. The columns have been running for a period of 218 days, after which they were uncoupled.

2.2.3 *On-site (micro-)aerobic column experiments*
The microaerobic column experiment was designed to provide information on:
- whether transformation of chlorobenzene is possible under the conditions tested;
- the minimum amount of nitrate and/or oxygen needed for the removal of chlorobenzene.

The degradation of CB and other chlorinated aromatic compounds in the groundwater was tested in a stainless steel column with a volume of 7.85 liter (figures 16 and 17). Assuming a porosity of 40%, this leaves a working volume of 3.1 liter.
The column has 5 sampling points which are placed along the height of the column. The column was filled with the soil, while continuously saturating with groundwater to assert the degassing of the soil and uniform packaging of the column. The column was upwardly flown through with groundwater from the location, and was operated by the crew of the UFZ Pilot plant in Bitterfeld.

The composition of the groundwater used for the experiments is given in table 4. Initially, the column has been operated with nitrate as the sole electron acceptor at a concentration of 2.4 mM (KNO_3). This is twice the concentration needed for complete oxidation of 20 mg l^{-1} chlorobenzene in the groundwater. After ca. 2 months, a small amount of oxygen (3 mg l^{-1} as 6 mg l^{-1} H_2O_2) has been added to the influent together with the nitrate, in order to enhance the degradation of chlorobenzene according to the schedule presented in figure 11.
The column is operated with an initial hydraulic retention time of 2 days (groundwater flow around 65-70 ml h^{-1}).

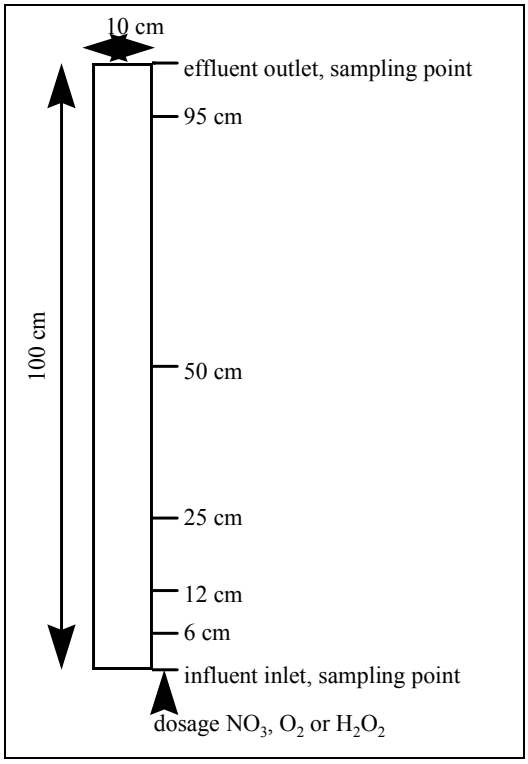


Fig. 16 Set-up of micro-aerobic column.

Fig. 17 The micro-aerobic column in the mobile on-site test unit.

The column was run in the mobile on-site test unit. In this unit, the temperature was controlled at 20°C. The influent and effluent of the column were analysed on a weekly basis, while on request samples from all sample ports along the column were taken.

Table 4. Concentrations of pollutants (mg l-1)in the groundwater used in the aerobic column in the mobile on-site test unit (Storage tank sampling date: 15-03-99; Mean of duplicate measurements) (DL = Detection Limit).

Component	Groundwater Micro-aerobic Column
1,4-dichlorobenzene	0.23 ± 0.01
1,2-dichlorobenzene	0.045 ± 0.005
Chlorobenzene (CB)	16.8 ± 0.32
Benzene	0.09 ± 0.00
Hexane	0.08 ± 0.00
Bromobenzene	< DL
2-Chloortolueen	0.03± 0.00
Tetrachloroethene (PCE)	< DL
Trichloroethene (TCE)	< DL
cis-1,2-Dichloroethene (*cis*-DCE)	< DL
trans-1,2-Dichloroethene (*trans*-DCE)	< DL
Vinyl chloride (VC)	0.01 ± 0.00
1,1,2,2-Tetrachloroethane	0.03 ± 0.00
Chloride	497
Nitrite	< DL
Nitrate	< DL
Ammonium	5.23
Sulphate	745
Phosphate	9.1
Iron	< DL
Manganese	0.122
Copper	< DL

2.2.4 *Laboratory column transfer to Bitterfeld*

To have a better comparison between the laboratory and the on-site columns, in August 2001, micro-aerobic laboratory column 1 was transferred from Apeldoorn to Bitterfeld. Here, it was connected to the local groundwater that served as the influent, identical to the on-site column, which was already present. Oxygen and nitrate concentrations as well as the other operating conditions were set as in the laboratory (2.4 mM NO_3, 9 mg l^{-1} oxygen). The CB concentration in the column was followed during the rest of the project. After 100 days, the residence time of the groundwater in the column was increased form 2 to 4 days while maintaining the same nitrate and oxygen concentrations.

Samples form the influent and the effluent were taken weekly and analysed for a.o. chlorobenzene and nitrate.

2.3 Results of the laboratory and on-site experiments

2.3.1 *Laboratory batch experiments*

Anaerobic batch experiments

Different electron donors were tested at different electron equivalent concentrations were tested for the stimulation of the dechlorination of TCE (for a detailed setup, see Appendix B)

Results after 15 weeks of incubation show dechlorination in almost all the incubations (table 5). Dechlorination was first observed in the 10*ED MeOH/G31 batches. The dechlorination process started after complete reduction of the sulphate present (figure 18). This was the case with all the incubations with high electron donor concentrations, although acetate was hardly used in the 10*ED incubations. Hydrogen levels reached several hundreds of nM in the lactate and MeOH/G31 incubation, while H_2 concentrations were as low as a few nM in the 10*ED acetate incubations.

Table 5. Results of duplicate batch experiments after 15 weeks
(- = <10% degraded; ± = 10-50% degraded; + > 50% degraded;
Prod. = Main products: c = cis-DCE and VC = VC)

	0.1*ED			1*ED			10*ED		
E-donor	SO_4	TCE	Prod.	SO_4	TCE	Prod.	SO_4	TCE	Prod.
Lactate	+/±	+/+	c/c	+/+	-/-		+/+	+/+	VC/VC
Acetate	+/±	+/+	c/c	+/+	+/+	c/c	-/±	+/+	c/c
MeOH / G31	±/±	+/+	c/c	+/+	+/+	c/VC	+/+	+/+	VC/VC

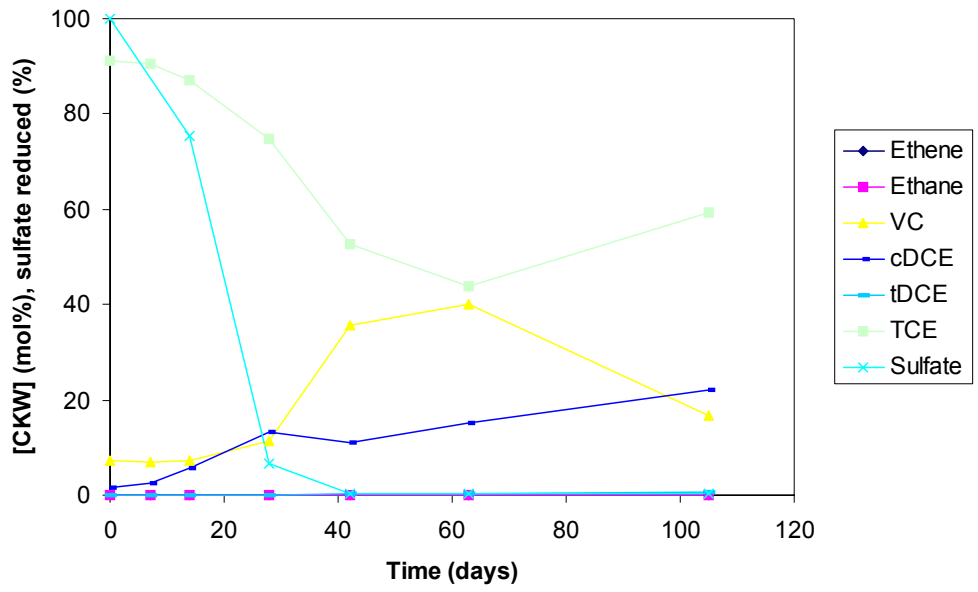


Fig. 18 Reduction of sulphate and TCE in high electron donor (10*ED, MeOH/G31) concentration batches.

However, dechlorination of TCE was also observed in those batches that had been supplied with the lowest concentration of electron donor. In those cases sulfate reduction was far from complete at the start of dechlorination indicating that the dechlorinating bacteria are indeed able to outcompete the sulphate reducers at low hydrogen concentrations (figure 19). These results

show that a low electron donor concentration could be beneficial for dechlorinators. The electron donors are used in these batch experiments leading to steady state hydrogen concentrations of < 2nM.

Dechlorination is less effective at the low electron donor concentration. At 10*ED VC is observed after 15 weeks, while the 0.1ED batches dechlorinate mostly to *cis*-DCE. The 1*ED incubations show intermediate results. If the addition of low electron donor would prove to be effective to reduce sulphate reduction and promote dechlorination, one would have to settle for less dechlorination of TCE to cDCE. The latter compound has been proven to be removed in the microaerobic step. Unfortunately, the amount of sulphate reduced is much higher as would be expected from the amounts of electron donor used. Most likely, alternative electron donors were still present in the effluent of the anaerobic column. Therefore, the effectivity of the "low electron donor approach" will have to be confirmed in a column experiment.

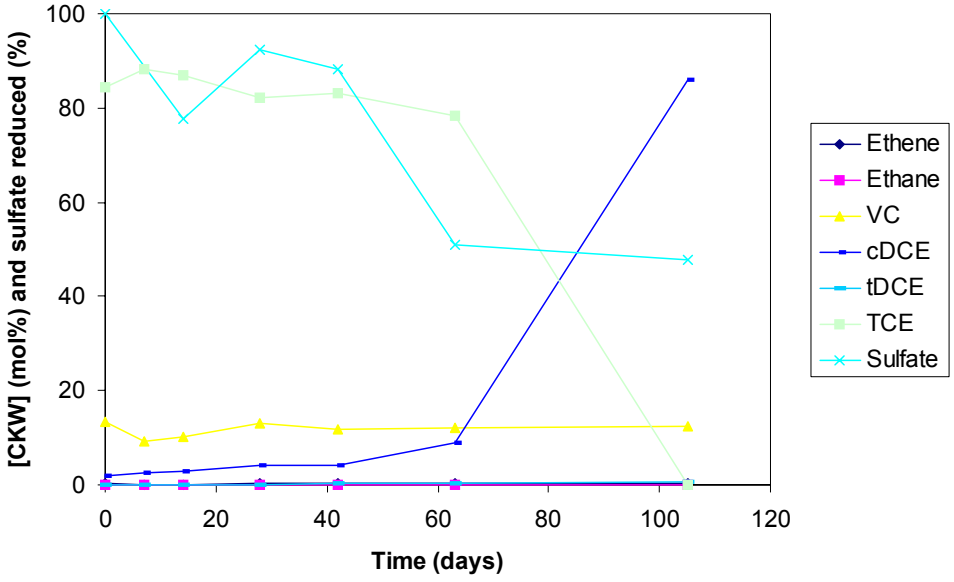


Fig. 19. Reduction of sulphate and TCE at low electron donor (0.1 ED as acetate) concentration.

(Micro-)aerobic batch experiments

Batch experiments were carried out with a mixture of microaerobic sediment and microaerobic effluent as the inoculum, in orer to investigate the possibilities of applying alternative compounds to stimulate the chlorobenzene degradation under denitrifying or microaerobic conditions. The compounds tested were toluene, benzoate and phenol. Also the role of an iron/nitrate(/oxygen) cycle in the transformation of chlorobenzene. A detailed set-up of the experiments is given in Appendix C.

The results after 8 weeks show that the presence of oxygen is absolutely necessary to obtain removal of chlorobenzene (figure 20). The batches without oxygen addition did not show any chlorobenzene transformation. The nature of the primary substrate was not of any influence. The batches, in which the primary substrate was omitted showed also chlorobenzene transformation when oxygen was present. Iron does not seem to affect the chlorobenzene transformation in the system studied here.

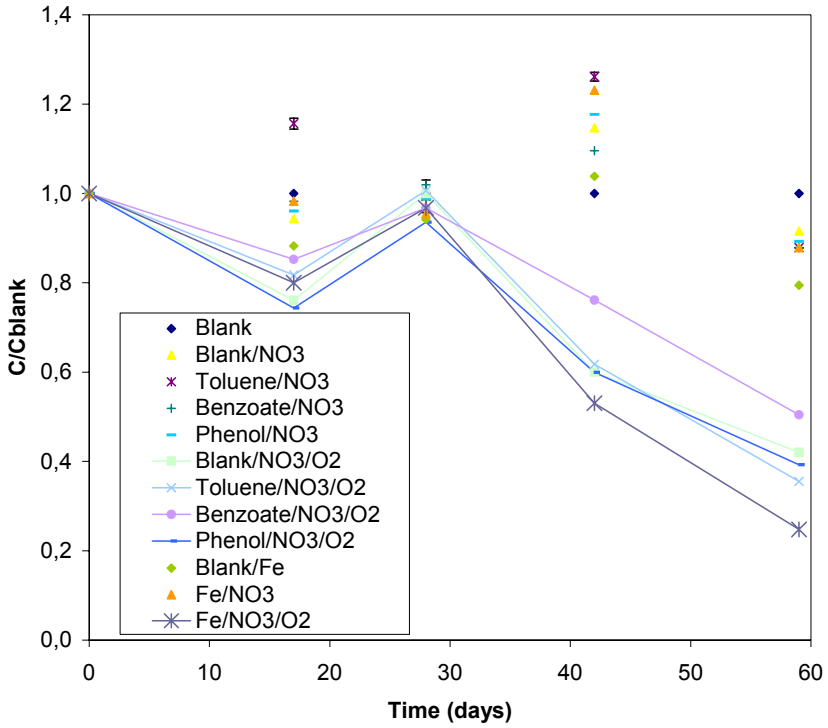


Fig. 20. Chlorobenzene concentration relative to the concentration in blanks without any addition (Cblank) given in time.

A 28 day lag phase was needed to overcome the reducing conditions, which were apparently prevailing in the sediment and effluent of the microaerobic column. This is supported by the fact that the blanks that received no addition, clearly showed sulphide precipitations, whereas the other incubations were more clear and colourless.

2.3.2 *Laboratory column experiments*

Anaerobic columns

The anaerobic transformation of chlorinated ethenes present in the Bitterfeld groundwater was tested in two separate column systems. The experiment was divided into several periods (table 6) to test different methods to enhance the reductive dechlorination of the chloroethenes in the groundwater.

Table 6. Operating conditions of the two anaerobic columns.

Period	Days	Column 1	Column 2
I	0-33	1 * ED (VFA)	1 * ED (VFA)
II	34-78	2 * ED (VFA)	2 * ED (VFA)
III	79-120	3 * ED (VFA)	2 * ED (VFA) + 50 mg l^{-1} NH_4^+
IV	121-149	4.5 * ED(VFA)	3 * ED (VFA) + 75 mg l^{-1} NH_4^+
	244	4 * ED (MeOH)	2 * ED (VFA) + 75 mg l^{-1} NH_4^+
V (coupled)	351	2 * ED (G31/MeOH)	1 * ED (VFA) + 75 mg/l NH_4^+
VI (uncoupled)	567	2 * ED (G31/MeOH)	0.1* ED (VFA) + 75 mg/l NH_4^+

Period I

The addition of electron donor at a dosage, which would have been enough for the complete reduction of both sulphate and chlorinated ethenes present (1*ED) in the groundwater, did not lead to the transformation of the chlorinated ethenes (table 7). Small amounts of PCE and TCE are converted to presumably *cis*-DCE, but little transformation of higher chlorinated ethenes to lower chlorinated ethenes occurred under these conditions. More than 90% of the VFA and lactate were converted to unknown products. During this period sulphate reduction started, but removal of sulphate was not complete.

The lack of dechlorination could have been caused by:

1. an insufficient amount of electron donor present in the groundwater;
2. an insufficient supply of nutrients (N/P);
3. the absence of microorganisms which are able to degrade chlorinated ethenes.

Table 7. Chlorinated ethenes present in the groundwater and in the effluent of the anaerobic columns with the addition of (in theory) sufficient electron donor to completely reduce all sulphate and chlorinated ethenes present in the groundwater. Concentrations are given as the percentage of the total amount of chlorinated compounds present in the groundwater and effluent after 30 days (DL = Detection Limit).

Compound	PCE	TCE	*cis*-DCE	*trans*DCE	VC	Ethene
Groundwater	3.8	15.6	60.9	17.6	5.9	< DL
Effluent 1	1.8	14.1	63.4	15.7	5.0	< DL
Effluent 2	1.7	13.9	62.4	16.6	5.7	< DL

These options were tested in following periods of the laboratory experiments. The pH of the effluent of the anaerobic reactor throughout the different periods was 7.9-8.0. At this pH, less than 4%[2] of the total amount of sulphide-S is present in the toxic form H_2S. The remaining part of the sulphide-S is present as HS^-. Toxicity of H_2S towards the anaerobic bacteria is therefore not a problem.

Period II

The amount of electron donor was increased to two times the amount needed for complete removal (2*ED) in both columns, which did not lead to a significant increase in the reduction of sulphate (figure 21). The dechlorination of TCE to *cis*-DCE was complete in both columns (figure 22). Also PCE was slightly converted to lower chlorinated ethenes (figure 23). The reason for the incomplete dechlorination is not clear. PCE is expected to be dechlorinated at least as easily as TCE.

During this period *cis*-DCE, *trans*-DCE and VC were not converted to (lower chlorinated) ethene(s) (figures 24 to 26).

Period III

The increase of the electron donor concentration in column 1 to 3*ED did not lead to further extensive dechlorination of the *cis*-DCE to VC and ethene (figure 25). PCE was almost completely converted in both columns. Only a small amount of VC was formed from *cis*-DCE under these conditions, because *trans*-DCE was hardly degraded (figure 27).

The addition of 50 mg NH_4^+ l^{-1} in column 2 caused little effect. The results for the reductive dechlorination were similar to the dechlorination in column 1.

In both columns sulphate reduction was nearly complete. There was a fairly good balance of the chlorinated ethenes in both columns, i.e. the chlorinated ethenes in the influent were almost completely recovered as (chlorinated) ethenes in the effluent of both columns.

[2] Based on pK_a of 6.52 and 12.92 of H_2S and HS^-, respectively, at 25°C.

Period IV

A further increase of the electron donor concentration to 4.5 * ED in column 1 did not significantly enhance the dechlorinating performance of the column.

A further increase in the nitrogen concentration in the groundwater of column 2 did result in an enhanced dechlorination of the chloroethenes (figure 28). The groundwater is very poor in nutrients. This could be the reason for the insufficient dechlorination taking place in both columns. The addition of extra nitrogen did not immediately lead to an improved dechlorination of *cis*-DCE (in Period III: 2*ED + 50 mg l^{-1} NH_4). A further increase of the amount of electron donor and nitrogen, however, resulted in the formation of substantial amounts of VC and complete dechlorination to ethene in this period. Because the increase of the electron donor concentration (from 2*ED to 3*ED) alone did not lead to the desired transformation of *cis*-DCE (figure 27), the presence of extra nitrogen in the groundwater is believed to be the major cause for this enhanced dechlorination. The formation of ethene is believed to become more extensive during prolonged operation times of the column, because the size of the microbial population in the column that is able to transform *cis*-DCE to ethene will grow.

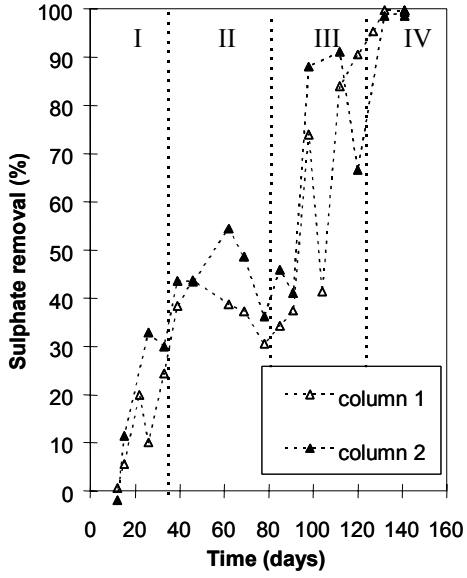


Fig. 21 Sulphate reduction in the anaerobic column treating the TCE containing groundwater.

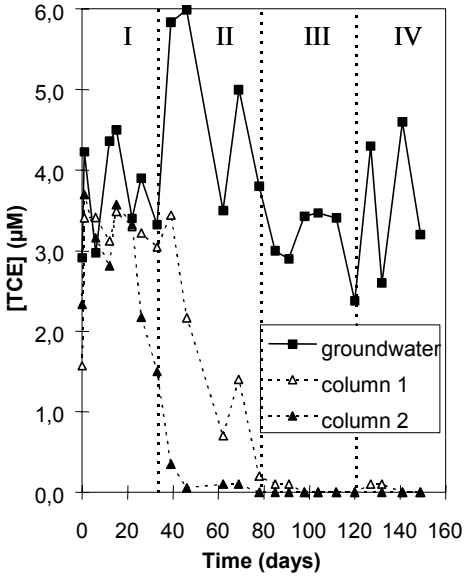


Fig. 22 Transformation of TCE in the anaerobic columns treating the groundwater from Bitterfeld.

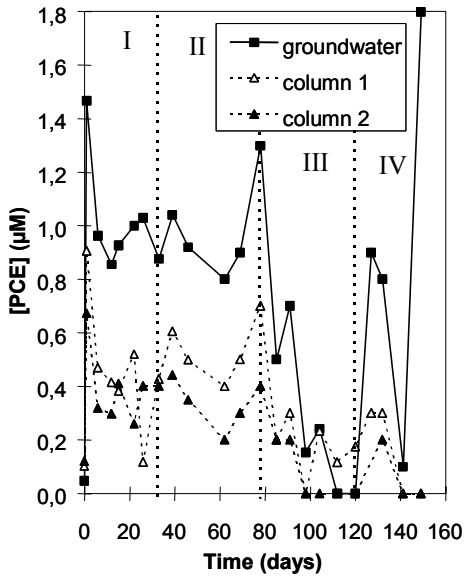


Fig.23. Transformation of PCE in the anaerobic columns treating the groundwater from Bitterfeld.

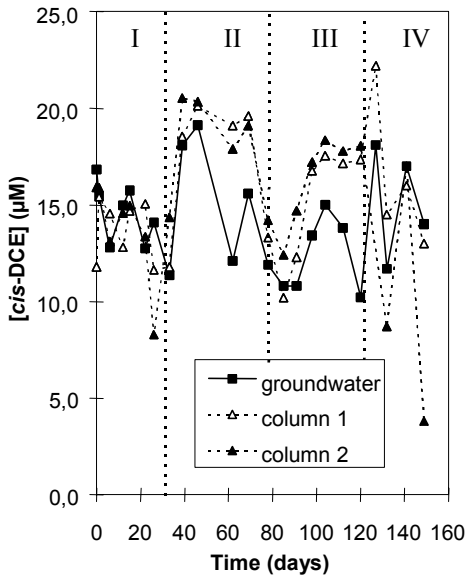


Fig.24 Transformation of cis-DCE in the anaerobic columns treating the groundwater from Bitterfeld.

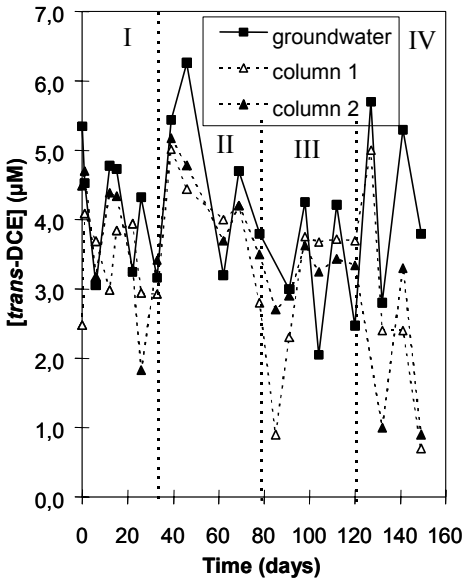


Fig. 25 Transformation of trans-DCE in the anaerobic columns treating the groundwater from Bitterfeld.

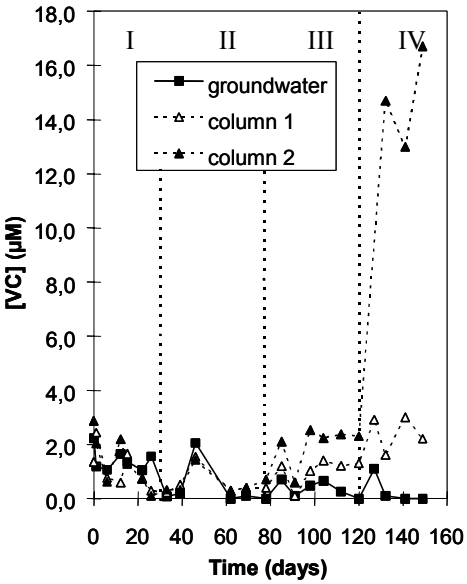


Fig. 26 Transformation of VC in the anaerobic columns treating the groundwater from Bitterfeld.

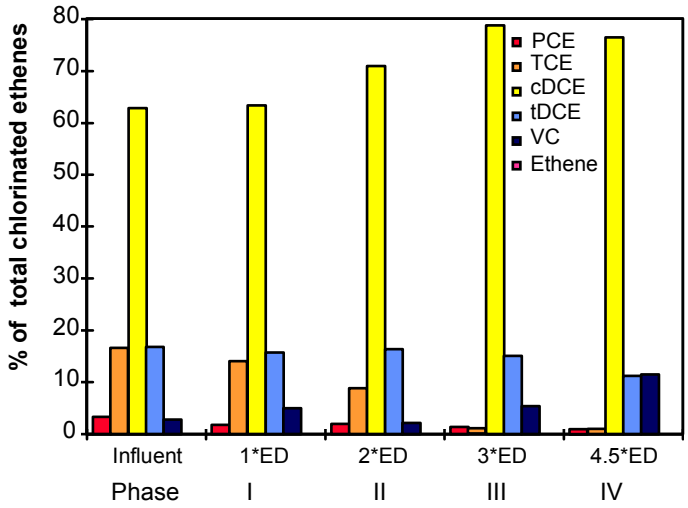


Fig. 27. The effect of increased electron donor concentration on the transformation of TCE in the Bitterfeld groundwater.

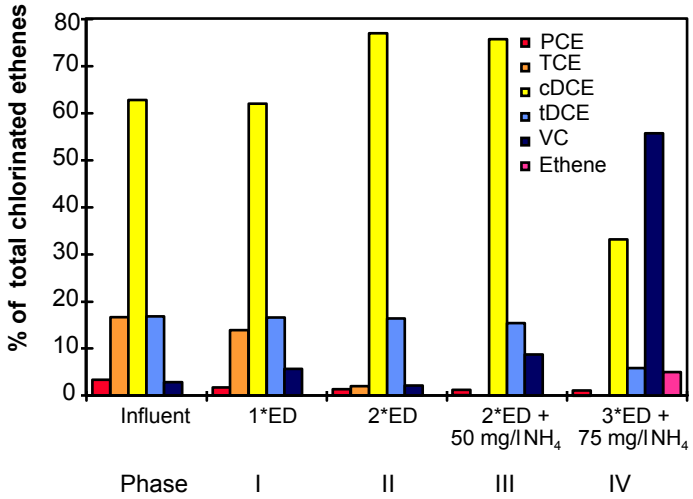


Fig. 28. The effect of increased electron donor concentration and the addition of nitrogen on the transformation of TCE in the Bitterfeld groundwater.

The electron donor was completely converted during every dosage regime. The fate of the electron donor is not completely clear yet. At least a part of the electrons generated from the VFA and lactate is used to reduce the sulphate present (25% and 32% in column 1 and 2, respectively). Around 53% and 69% of the electrons supplied to the column 1 and 2, respectively are accounted for (table 8). The remaining part of the electron donor is converted to unknown products. The electrons may be present as biomass, methane, unknown reduced products like alcohols, or may be used to reduce the aquifer material.
Other possible explanations, like leakage of oxygen through tubing or volatilisation of the hydrogen are unlikely because the column system is designed to be airtight and measures were taken to prevent the dissolution of oxygen in the groundwater.

Table 8. Fate of the electron equivalents during the first 149 days of operation of the columns.

Process	Column 1		Column 2	
	(mole)	(%)	(mole)	(%)
Electron donor supplied	5.3	100	4.1	100
Dechlorination	<0.01	<1.0	<0.01	<1.0
Sulphate reduction	1.3	24.5	1.3	31.7
Biomass[1]	0.25	4.7	0.25	6.1
Fe reduction[2]	1.5	28.3	1.5	36.6
Methane formation	0.03	0.5	0.03	0.7
Missing		42.0		24.8

[1] Assuming biomass yields of 0.80 g dry cells (mole eeq)$^{-1}$ for sulphate reducers [32, 45] and 2 g protein (mol eeq)$^{-1}$ for dechlorinating bacteria [19]. Biomass formula $C_5H_7NO_2$ [27].
[2] Assuming 10% of the aquifer material consists of Fe.

After 244 days, the electron donor of column one was changed to methanol at a concentration of 4*ED. At the same time, the VFA dosage of column 2 was decreased to 2*ED, while the ammonium addition remained unchanged.

Period V
During this period, the anaerobic columns were placed before two micro-aerobic columns to simulate the anaerobic-microaerobic *in situ* systems. The results from this period are described for both anaerobic and micro-aerobic columns in the next sections.

Period VI
In the final period, changes were made so that the anaerobic columns were uncoupled from the micro-aerobic columns again to run on their own. The anaerobic columns received the same influent as in period IV. On day 703 (March 2001), the electron donor addition to the VFA column was changed from once the amount of the needed reducing equivalents to reduce all sulphate and TCE (1*ED) to 10% of that amount (0.1*ED) to investigate the effect of a lower electron donor concentration on the dechlorination. By lowering the ED dosed to the groundwater, the extent of sulphate reduction was expected to decrease. The reason for this is that sulphate-reducing bacteria have a lower affinity to hydrogen (which is formed from VFA) as electron donor than dechlorinating bacteria. Thus, relatively more e-donor would be available for dechlorination. (see also figure 12). The operation conditions of the methanol columns remained unchanged with respect to period V. In the anaerobic columns, no significant removal of CB was observed, as expected.

The influent of column 1 was amended with electron donor to 2*ED (methanol 80%, G31 20%). G31 is a complex electron donor that also contains nitrogen. It was added during period V because with methanol alone, no dechlorination beyond *cis*-DCE was observed. With 20% G31, dechlorination to small amounts of ethene took place. In 2001, the performance of this column under these conditions was studied over a longer time period.
The results of this experiment are shown in figure 29. The relative amount of TCE found in the effluent decreases with time. This is mainly due to a more extensive dechlorination to *cis*-DCE, whereas the contribution of VC and ethene in the effluent remains constant. The sulphate reduction percentage ranged from 60-90% of the incoming sulphate.

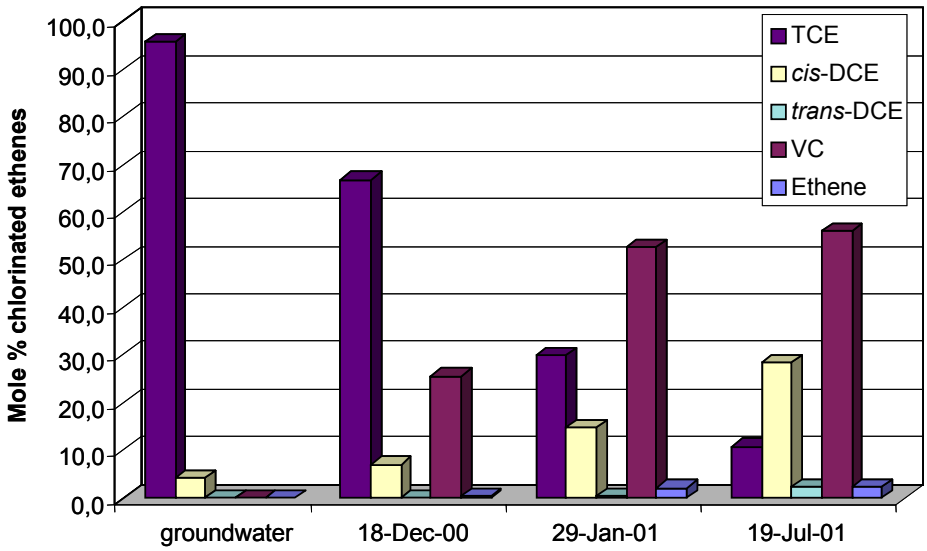


Fig. 29. Chlorinated ethenes contents of the influent (groundwater) and the effluent (on different dates) of the soil column with methanol/G31 as e-donor.

Column 2 was running in the previous periods for almost one year at 1*ED VFA, amended with 75 mg l^{-1} NH_4Cl. During this period, *cis*-DCE was the major product formed, with traces of VC. In period VI, the electron donor concentration was further decreased to 0.1*ED.
In figure 30 is shown that after the decrease of the VFA addition in March 2001, TCE was completely removed, with *cis*-DCE and VC as the main dechlorination products. Also the formation of ethene (ca. 5%) was observed. Sulphate and sulphide measurements showed that the sulphate reducing activity at 0.1*ED was considerably lower than at 1*ED (ca. 12% vs. 50%), which confirms the previously mentioned hypothesis.

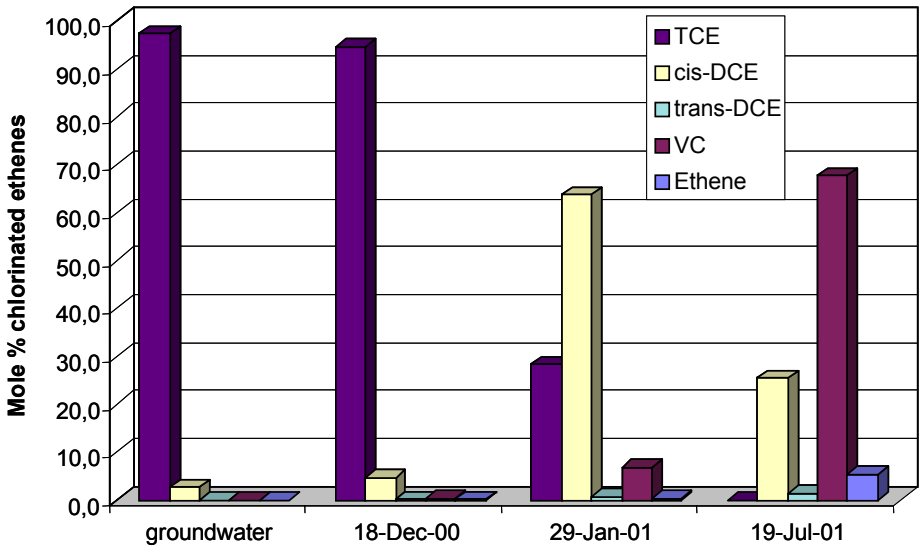


Fig. 30. Chlorinated ethenes contents of the influent (groundwater) and the effluent (on different dates) of the soil column with VFA/NH4Cl as e-donor/nutrient.

Micro-aerobic columns

The transformation of chlorobenzene during start-up of the microaerobic treatment was investigated with two laboratory column systems operated according to the scheme presented in table 9.

Table 9. Operating conditions of the two microaerobic columns.

Days	Influent conditions
0-28	Groundwater
29-56	Groundwater + 2.4 mM NO_3^-
57-113	Groundwater + 2.4 mM NO_3^- + 3 mg l^{-1} O_2

The mean chlorobenzene concentration found in the groundwater during the experiments was 5896 ± 1624 µg l^{-1}.
During the period, in which only nitrate was added, both columns already show a removal of chlorobenzene (figure 31). This is in contrast with the idea that complete chlorobenzene transformation under denitrifying conditions is not possible. After the addition of 3 mg l^{-1} oxygen, chlorobenzene removal was almost complete in both columns. After ca. 100 days, the chlorobenzene removal in column 30-98 L continued to be nearly complete, whereas chlorobenzene removal in the other column (30-98 R) slowly deteriorated. A clear indication of the cause of this discrepancy was not found. The operational conditions of both columns were similar. However, the difference in chlorobenzene degrading capacity went together with a striking difference in the colour of the columns. Column 30-98 L was clearly reddish suggesting the involvement of iron in the transformation process, while the other column (nr. 30-98 R) was black (figure 32). Therefore a total amount of 340 mg Fe(II), was added in the form of iron nitrate to the column system on day 118. An increase in the chlorobenzene transformation was not observed. This may have been due to the low amount of iron dosed to the reactor. Also, the fact that in that period, the anaerobic and microaerobic reactors were connected, may have had a deteriorating effect (see next section).

Between 50 and 100% of the nitrate was converted in the columns. The addition of the small amount of oxygen did not change these numbers.

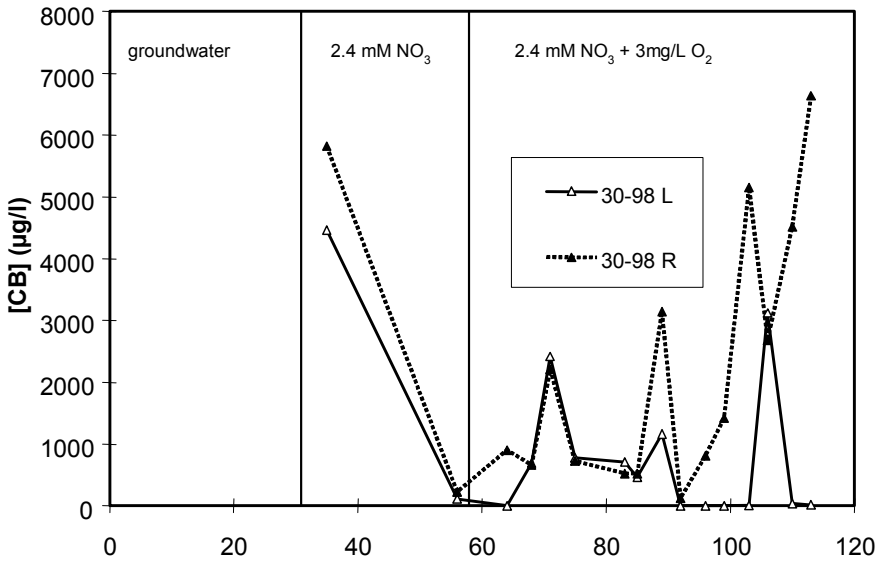


Fig. 31. Chlorobenzene removal in two micro-aerobic laboratory column systems.

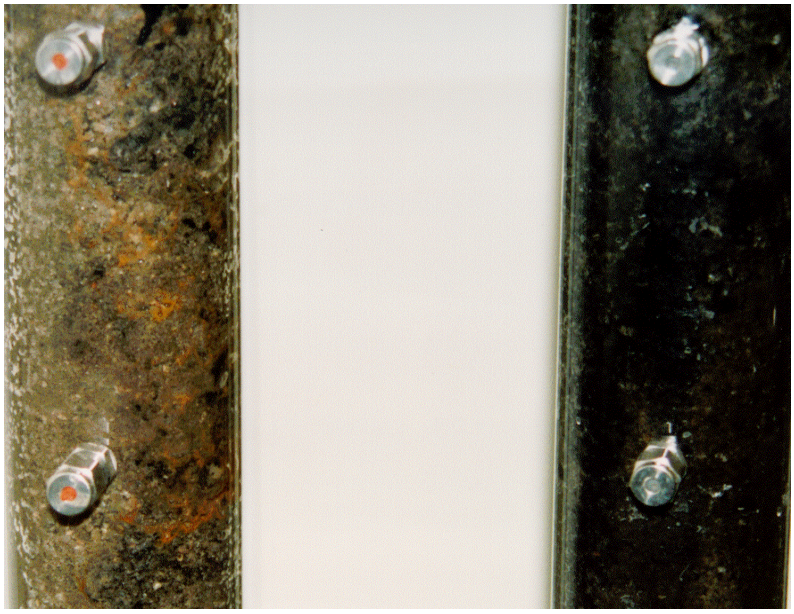


Fig. 32. Microaerobic columns 1 (left) and 2 (right).

The microaerobic columns were used to treat the effluent of the anaerobic columns for almost 1.5 years. The results of this period are described in the next section. After this period (in December 2000), the columns were disconnected from the anaerobic columns and from then on run as stand-alone reactors again. The oxygen concentration in column 30-98 L was 18 mg l^{-1} and in column 30-98 R this concentration was 3 mg l^{-1} (added as H_2O_2). Both columns received sodium nitrate to a final concentration of 0.24 mg l^{-1}. The degradation of CB was followed until the end of the experiment in August 2001. The CB removal in the period before and after the uncoupling of microaerobic column 30-98 L is shown in figure 33. The increase of the oxygen concentration in the influent on day 163 does not result in an increased CB removal. However, the figure shows clearly that the uncoupling on day 219 stimulated the CB degradation within three weeks: a removal of ca. 95% is reached. The last measurement shows that this removal capacity was sustained during the rest of the experiment. It is likely that after the column was disconnected, more oxygen became available for the degradation of CB, whereas before that time, oxygen was first used to oxidise the effluent of the anaerobic column. TCE, which was still added to the microaerobic influent was also removed. Lower chlorinated ethenes were no longer observed in the effluent.

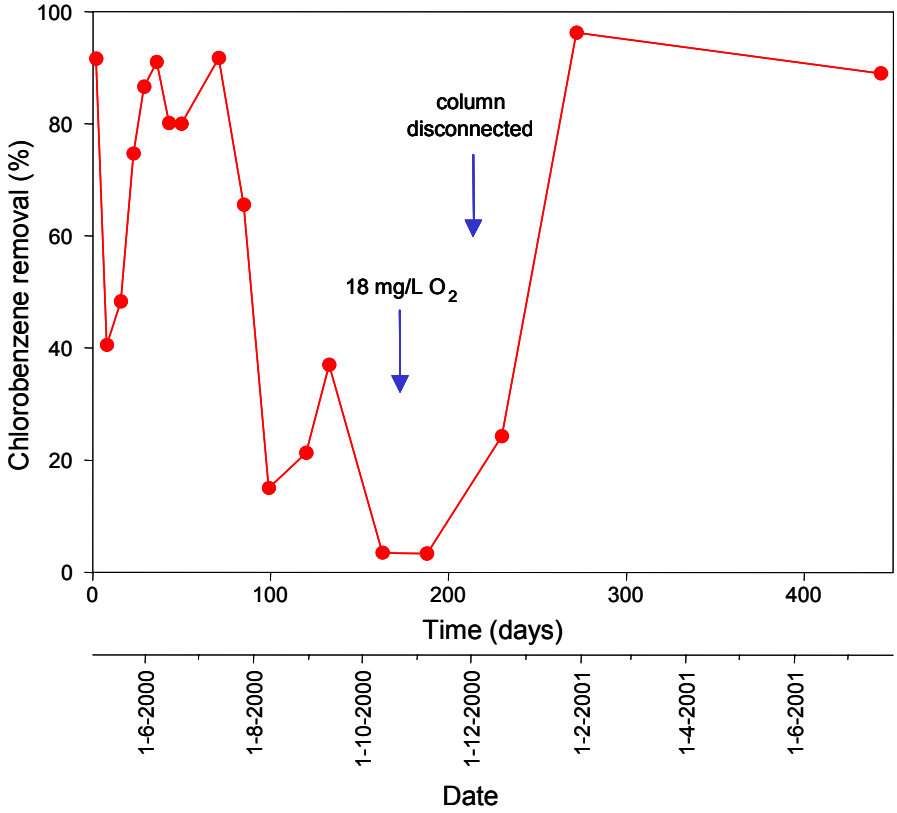


Fig. 33. Chlorobenzene removal in microaerobic column 30-98 L. The influent concentration fluctuated between 7-11 mg l^{-1}. On day zero, this column received 0.24 mg l^{-1} potassium nitrate and 3 mg l^{-1} oxygen in the influent. On day 169, the oxygen concentration was increased to 18 mg l^{-1}. On day 219, the column was disconnected from the anaerobic column.

Column 30-98 R was operated with 3 mg l^{-1} oxygen and 2.4 mM nitrate from day zero on during the whole period. Also here the CB removal increased after the disconnection of the columns. However, the removal rate stabilised at ca. 50% (data not shown). This indicates that more than 3 mg l^{-1} of oxygen is needed to remove CB completely from the groundwater.

Combined sequential anaerobic-aerobic columns

The microaerobic reactors were used to treat the effluent of the anaerobic columns described previously. In this way a sequential anaerobic - microaerobic system was created. The two microaerobic columns had different chlorobenzene removal capacities at the start of the sequential treatment. One column (column 1) was able to remove all the chlorobenzene in the groundwater while the other (column 2) did not remove any chlorobenzene.

The connection of the columns had a few side effects. Anaerobic conditions in the microaerobic column systems prevailed after a few weeks because sulphide and sulphate were entering the system. Initially, sulphide was converted to sulphate. However, around days 130 to 160, sulphate reduction and the formation of methane were observed. Throughout the research period, nitrate (2.4 mM) was converted in both columns. The fact that anaerobic processes prevailed in the microaerobic reactors was mainly caused by the reduced species in the influent of the microaerobic reactors. As a result, the chlorobenzene removal capacity in column 1 deteriorated (figure 34). The chlorobenzene removal in column 2 remained negligible (figure 35). By that time, some reductive dechlorination was occurring in the “micro-aerobic” columns. Both columns again got a more blackish appearance, presumably as a result of the presence of sulphides.

Also, precipitates were formed in the lower part of the column systems. These precipitates were analysed and calcite, sulphur and phosphates were found to be major components. This is not very surprising, given the fact that both the carbonate and calcium levels in the groundwater are exceptionally high, namely over 150 mg l^{-1}.

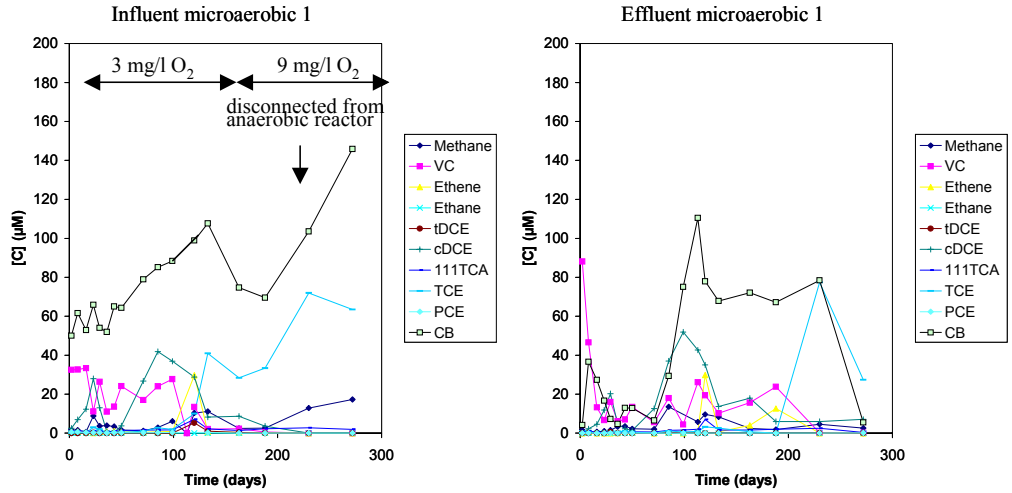


Fig. 34. Concentration of chlorobenzene and lower chlorinated ethenes in micro-aerobic column 1 (30-98 L).

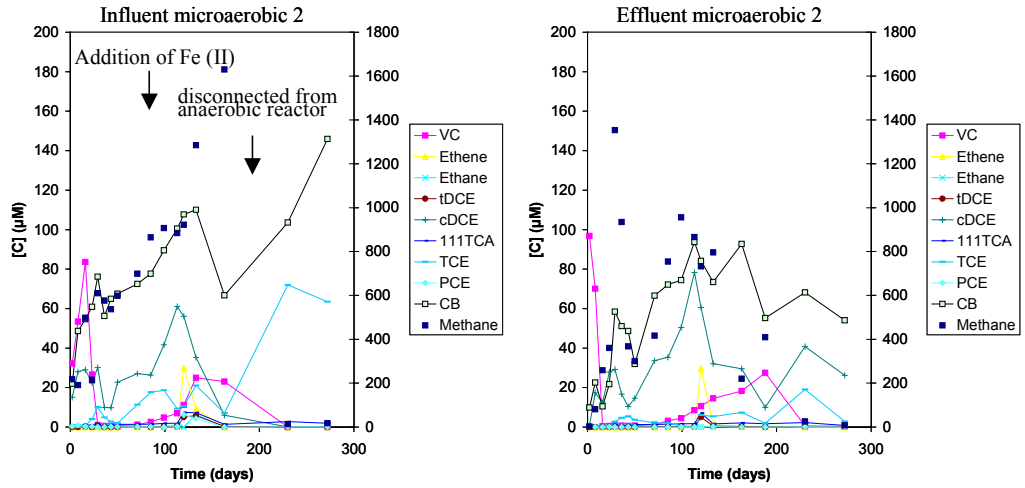


Fig. 35. Concentration of chlorobenzene and lower chlorinated ethenes in micro-aerobic column 2 (30-98 R).

2.3.3 *On-site (micro-)aerobic column experiments*

The column was operated for over 1200 days with groundwater containing ca. 20 mg l^{-1} chlorobenzene as the influent. During the first period of the experiment, during which only nitrate was added, no significant removal of chlorobenzene was observed. Probably this was due to a reduced state of the sediment, which consumes oxygen and therefore prevents biodegradation of chlorobenzene. Therefore, the oxygen concentration in the influent was dramatically increased to oxidise the sediment. After the application of aerobic conditions with 1 and 2 times the amount of oxidation equivalents, complete removal of chlorobenzene was achieved (resp. 88, and 176 mg l^{-1}, see also figure 36). However, chemical oxidation by hydrogen peroxide cannot be excluded. Then, the oxygen concentration was gradually decreased to operate again under micro-aerobic conditions with nitrate (2.4 mM) and 3 mg l^{-1} oxygen. However, chlorobenzene was not degraded

under these microaerobic conditions. Nitrate was only partially removed (10-20%). Therefore, the oxygen concentration was stepwise increased to 9 mg l^{-1} O_2.

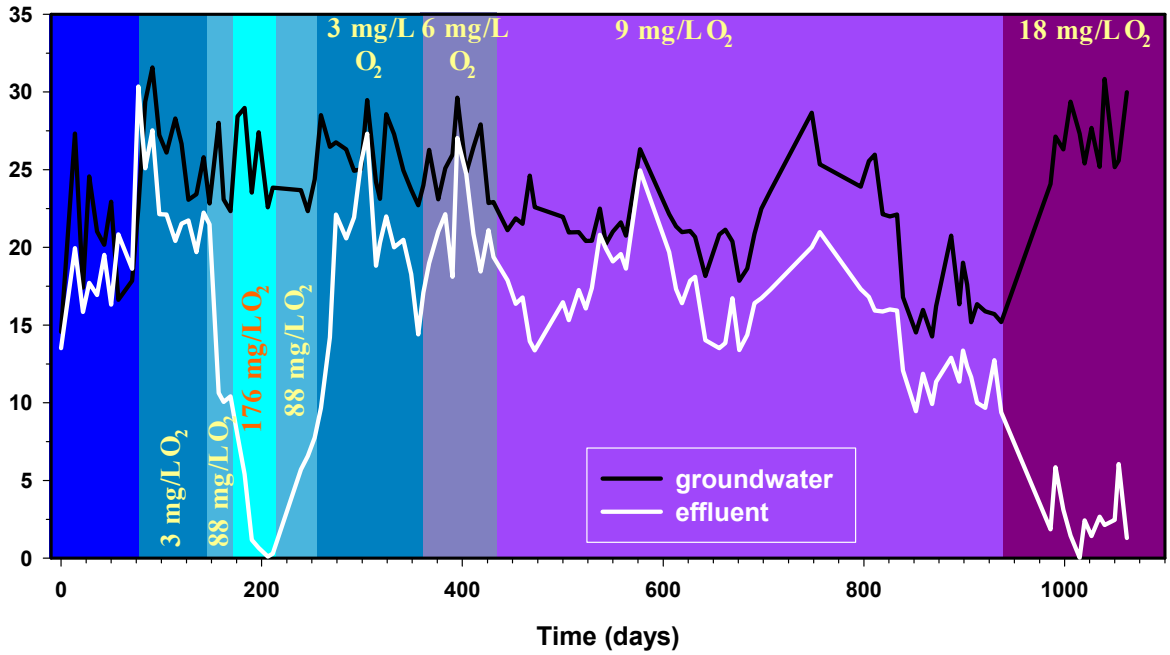


Fig. 36. Influent (groundwater) and effluent concentrations of the on-site micro-aerobic column. The column was operated with 2.4 mM NO3 in the influent and oxygen concentrations as indicated in the graph.

At the end of this period, the removal efficiency had reached a stable value of ca. 40%. Samples were taken from different heights in the column in order to make a concentration profile of CB. The data showed that CB was removed up to ca. 40% in the first part (0-25% of the column height) of the column. In the second part, no further removal was observed. This indicates that there was a lack of oxygen in the second part of the column. Therefore, the oxygen concentration was increased from 9 to 18 mg l-1, while the nitrate addition remained unaltered. This had as immediate effect that the CB removal efficiency increased to ca. 100% within two months. This complete removal was sustained for over six months. For unknown reasons, the CB concentration in the effluent of the column started to rise in August 2002 (not shown) and therefore the removal was decreased slowly to a value of 50% removal. This value remained stable over the last four months of 2002, after which the column operation was ceased.

2.3.4 *Laboratory column transfer to Bitterfeld*

Although almost similar environmental conditions were imposed on the Bitterfeld on-site column as in microaerobic column 1, only 40% of the chlorobenzene was removed in the on-site column. One of the reasons for this may be that the average temperature in the on-site column is 2-5 °C lower than that in the laboratory (20°C). To have a better comparison between the laboratory and the on-site columns, in August 2001, laboratory column 1 was transferred from Apeldoorn to Bitterfeld. Here, it was connected to the local groundwater that served as the influent, identical to the on-site column, which was already present. Oxygen and nitrate concentrations were set as in the laboratory as well as the other operating conditions. The CB concentration in the column was followed during the rest of the year. The results are shown in figure 37.

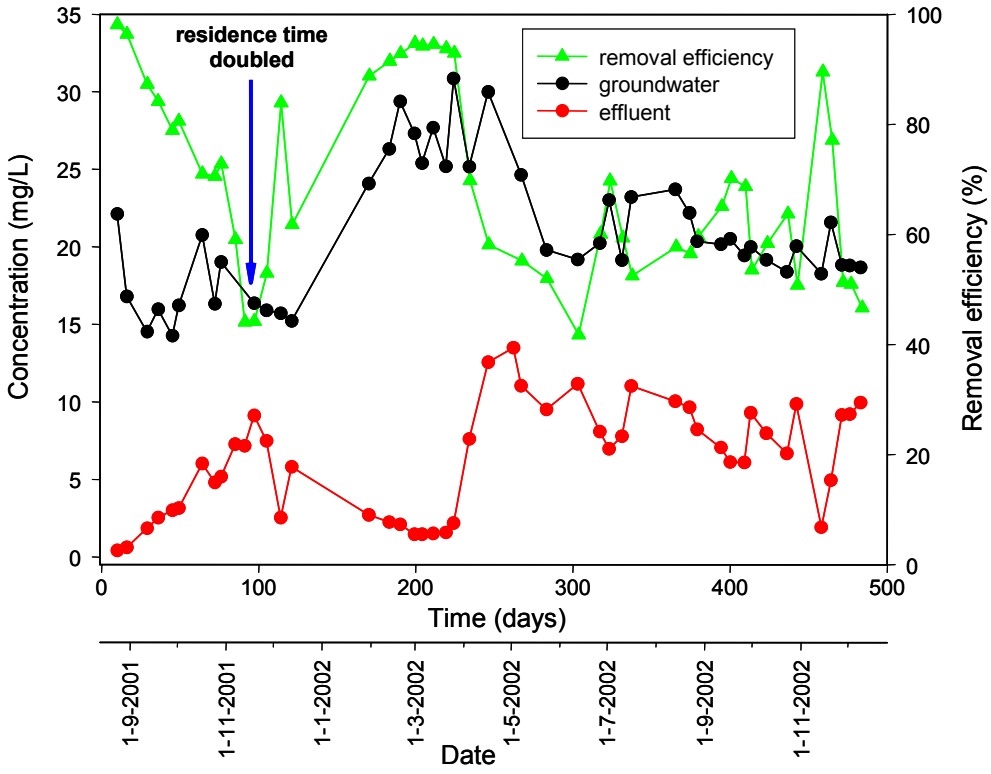


Fig. 37. Concentration of chlorobenzene and removal efficiency in microaerobic column 1 after its transfer to Bitterfeld. The residence time was doubled on day 99.

Ten days after the resumed operation of the column, the removal of CB was close to 100%. However, the removal efficiency slowly decreased during the following months to approximately 45% after 90 days of operation. This may indicate that the lower temperatures in the on-site facility (especially in the winter months) cause a reduced biological activity. Therefore, on day 99 the residence time of the groundwater in the column was doubled from 2 to 4 days. After this change, the removal efficiency increased again to a maximum of 95% removal. However, in April 2002, the CB concentration in the effluent started to increase rapidly, which resulted in a removal efficiency of ca. 50%. This value remained stable for the rest of the year 2002. The reason for the sudden decrease in CB removal is unknown. It is remarkable that this phenomenon occurred also in the large column that was previously discussed, although in that column it occurred four months later.

2.4 Summary of observations and conclusions

Transformation of chloroethenes under anaerobic conditions

- TCE is dechlorinated to *cis*-DCE, VC and ethene under anaerobic conditions in the presence of a complex electron donor;
- A decrease of the added amount of electron donor (applied as a mixture of VFA and lactate) to 0.1*ED leads to a complete dechlorination of TCE to VC as the main product and to a lower extent to *cis*-DCE and ethene;
- The application of a very low electron donor concentration seems to favour the dechlorination over sulphate reduction;
- Thus, dechlorination can be achieved, while sulphate reduction is minimised by adequate electron donor dosage.

Transformation of CB under microaerobic conditions

- Partial removal of CB occurs in the on-site column with 9 mg l^{-1} oxygen and 0.24 mg l^{-1} (2.4 mM) potassium nitrate. An increase of the oxygen concentration to 18 mg/L resulted initially in 100% removal of CB, although later, the removal decreased to approximately 50%;
- Almost complete CB removal has been observed in the laboratory experiments with 18 mg l^{-1} oxygen and 0.24 mg l^{-1} potassium nitrate;
- The laboratory column that has been transferred to the on-site facility, lost part of the removal capacity, presumably due to a lower ambient temperature. Doubling the residence time of the groundwater in the column resulted in almost 100% CB removal. Later this value decreased again to 50%.

CHAPTER 3

IN SITU REACTOR EXPERIMENTS

3.1 Introduction

In the *in situ* reactor systems, the sequential anaerobic/micro-aerobic treatment of the contaminated groundwater was investigated. The research comprises both the fate of the contaminants and sulphate. Following the earlier described NA+ concept, the chlorinated ethenes are dechlorinated in the first anaerobic step. Partially dechlorinated products present in the anaerobic effluent, together with chlorobenzene should be degraded in the second microaerobic step. Sulphide is most likely formed in high concentrations during the first anaerobic phase. Sulphide may precipitate in the anaerobic reactor, which in turn may lead to clogging problems. In the microaerobic reactor, sulphide may be oxidised under aerobic conditions both via chemical or microbiological pathways. Biological sulphide oxidation under denitrifying conditions is also known to occur.

During these *in situ* trials, more insight has been gained in the contribution of the different pathways to the transformation of the components in the groundwater.

3.2 Experimental set-up

Two sequential anaerobic-microaerobic reactor systems have been constructed in the shaft at the SAFIRA pilot facility in Bitterfeld in July 1999 (figure 38, see also section 1.3). In these reactors, the local groundwater, to which TCE was added, was treated in 4 reactors with a volume 4.4 m^3 each. This set-up guaranteed maximum flexibility and the possibility to change the reactor set-up at any time as a result of the outcome of the on-site experiments. The reactors were filled with aquifer material originating from the Bitterfeld test site.

Until the beginning of 2002, both systems consisted of an anaerobic reactor that was fed with groundwater amended with a mixture of volatile fatty acids (VFA) as electron donor (acetate, propionate, butyrate and lactate) and ammonium chloride as the nitrogen source. Because chlorinated ethenes are not present in the groundwater that is used for feeding the reactor systems, TCE was added to the groundwater from a water-saturated stock solution. The hydraulic retention time in the reactors was 2 days. The anaerobic effluent was led through the microaerobic reactor after addition of 3 mg l^{-1} oxygen (as hydrogen peroxide) and 2.4 mM sodium nitrate. For detailed operation parameters, the reader is referred to [14].

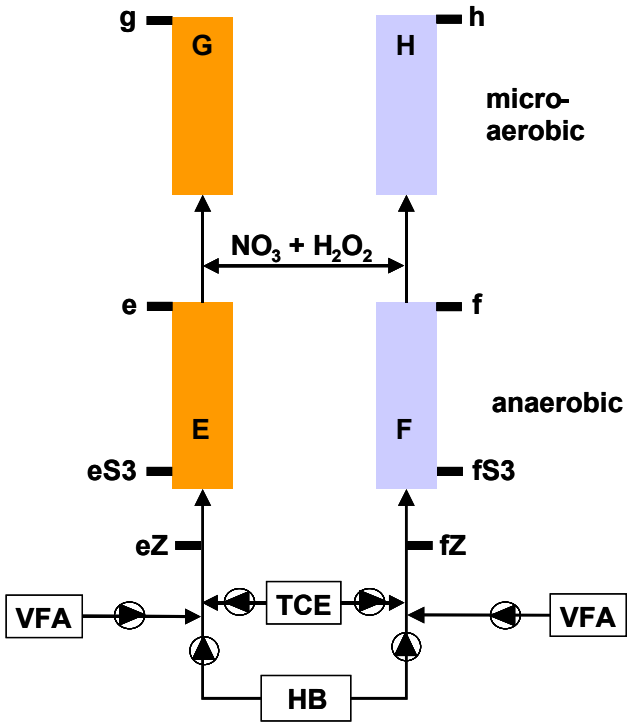


Fig. 38. Schematic set-up with additions and sample ports of the *in situ* reactor systems.

Figure 39 shows the operation history of the two reactor systems. The duplicate systems were started up in July 1999. The four reactors (4.4 m^3 each) have been washed with groundwater for almost a year to equilibrate the reactor systems. The addition of VFA and TCE to the systems was started in May 2000. After ± 6 months, a complete reduction of TCE to ethene was observed in reactor system II, while only partial dechlorination occurred in reactor system I.

The subsequent events and changes to the operating conditions are summarised in figure 39.

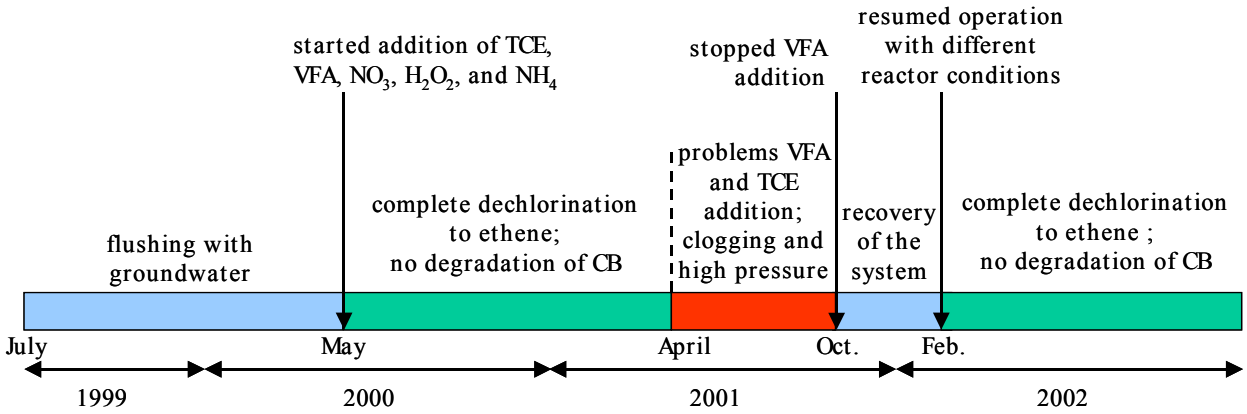


Fig. 39. History of the *in situ* reactors running at the SAFIRA pilot facility in Bitterfeld.

In February 2002, the operating conditions in both reactor trains have been changed. System I (reactor e-g) has been changed to operate under aerobic/nitrate-reducing conditions in order to study the degradation of CB under these circumstances. The TCE addition to these reactors was ended.
System II remained operating in the anaerobic mode. Due to promising results in laboratory experiments (section 2.3.2), the electron donor addition was reduced from 200% to 10% of the re-

ducing equivalents needed for complete reduction of sulphate plus TCE. Also, the hydrogen peroxide and nitrate addition to reactor h was discontinued. A schematic picture of the new operating conditions is shown in figure 40.

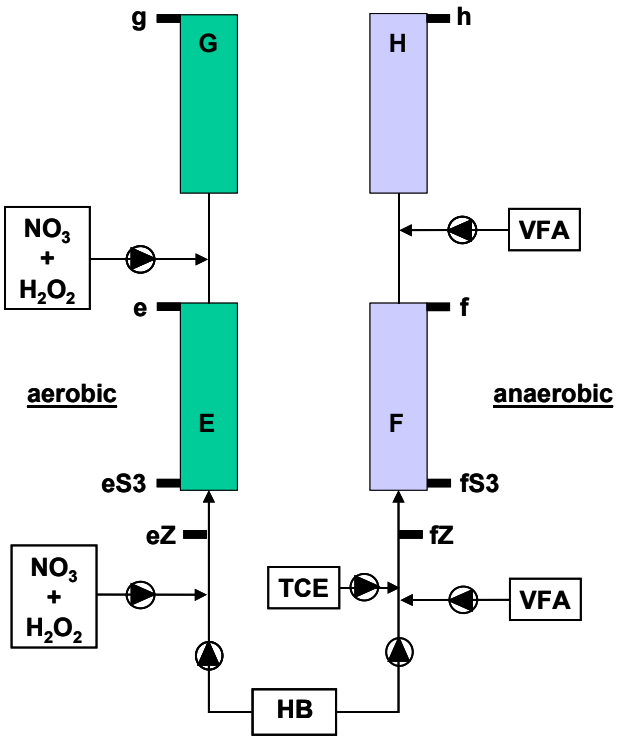


Fig. 40. Schematic setup of the in situ reactors from February 2002 on.

3.3 **Results of the *in situ* reactor experiments**

3.3.1 *Transformation of chlorinated ethenes*

Reductive dechlorination of the TCE added to the groundwater has been observed in both reactor systems over the first 9 months of operation. It was noticed that reactor system e-g received less electron donor as compared to reactor f-h, which resulted in a lower performance of the first system concerning the dechlorination of TCE. Measurements of VFA and TCE concentrations at the influent of the anaerobic reactors (e and f) revealed that the influent of reactor f contained 10 to 100 times elevated concentrations of both VFA and TCE as compared to the influent of reactor e. This had influence on both the dechlorination of TCE and the reduction of sulphate in the groundwater.

In September 2001, both systems had operational problems with the artificial TCE-addition, due to sulphide precipitation and excessive gas formation. To reduce the formation of sulphide, the VFA addition was discontinued in October.

The incoming groundwater of reactor system e-g contained ca. 40 µM TCE (5 mg l^{-1}, figure 41). Water samples taken from the first sampling point (eS) in the lower part of the anaerobic reactor contain mainly lower chlorinated ethenes like *trans*-DCE and VC. The extent of dechlorination in the effluent of the first reactor, however, is very low. It is likely that, although near sample point eS locally good conditions for dechlorination prevail, in other segments of the reactor little or no dechlorination takes place. This is presumably due to a not optimally functioning dosage system, causing unexpected low electron donor concentrations. In the effluent of microaerobic reactor g, no additional dechlorination products are observed.

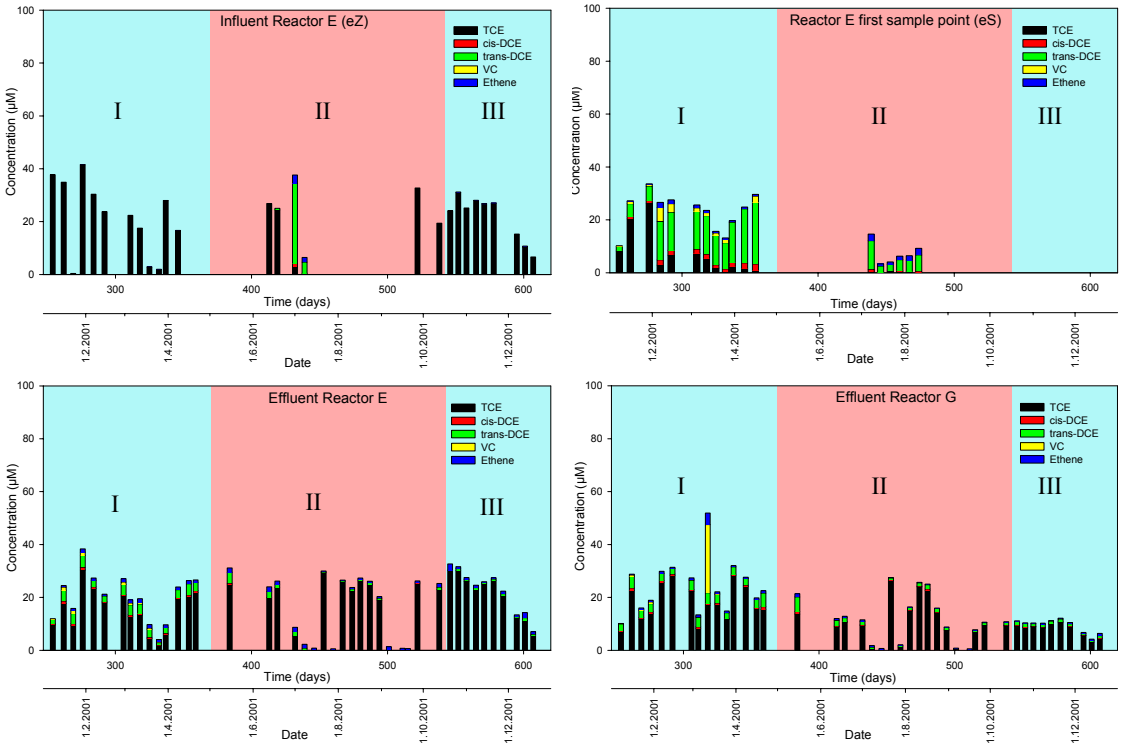


Fig. 41. Transformation of chlorinated ethenes in reactor system I: reactors e (anaerobic) and g (microaerobic). The colored time periods mark the normal operation of the reactors (I), operational problems (clogging, excessive gas production)(II), and the discontinuation of the electron donor supply (III).

Reactor system f-h performed well during the first year of operation and dechlorinated TCE to ethene mainly (figure 42). The incoming groundwater of this reactor system contained far more TCE than reactor system e-g, and the concentration of TCE was unstable. In January 2001, the influent contained very high TCE concentrations (ca. 90 mg l^{-1}) for two weeks. This had a clear negative effect on the dechlorination as measured at the first sample point (fS). The dechlorination activity at the beginning of reactor f has not been fully recovered since then. However, the effluent of reactors f and h contained unchanged amounts of dechlorination products. At the end of March, the effluent of reactor f suddenly contained mainly TCE instead of dechlorination products. In reactor h, which was in fact acting as a second anaerobic reactor, the dechlorination activity decreased also at the end of March. While the dechlorination recovered slowly in the latter reactor, no significant dechlorination was observed in reactor f from April on. In November, the dechlorination of TCE in reactor h ceased again.

The fluctuation in the dechlorinating activity in reactor system II is related to the constantly high and sometimes extremely high influent concentrations of TCE (up to 100 mg l-1). TCE concentrations, which have been found toxic to dechlorinating bacteria and consortia, are in the range of 60-70 mg l^{-1} [18 and 52]. The influent TCE concentration of reactor f repeatedly exceeded this toxic value, which has presumably caused an inhibitory effect on the dechlorination. Such concentrations prevail in source zones, but not in plumes, for which this technique is being developed. Therefore, the sensitivity of the reactor system is not problematic for this application.

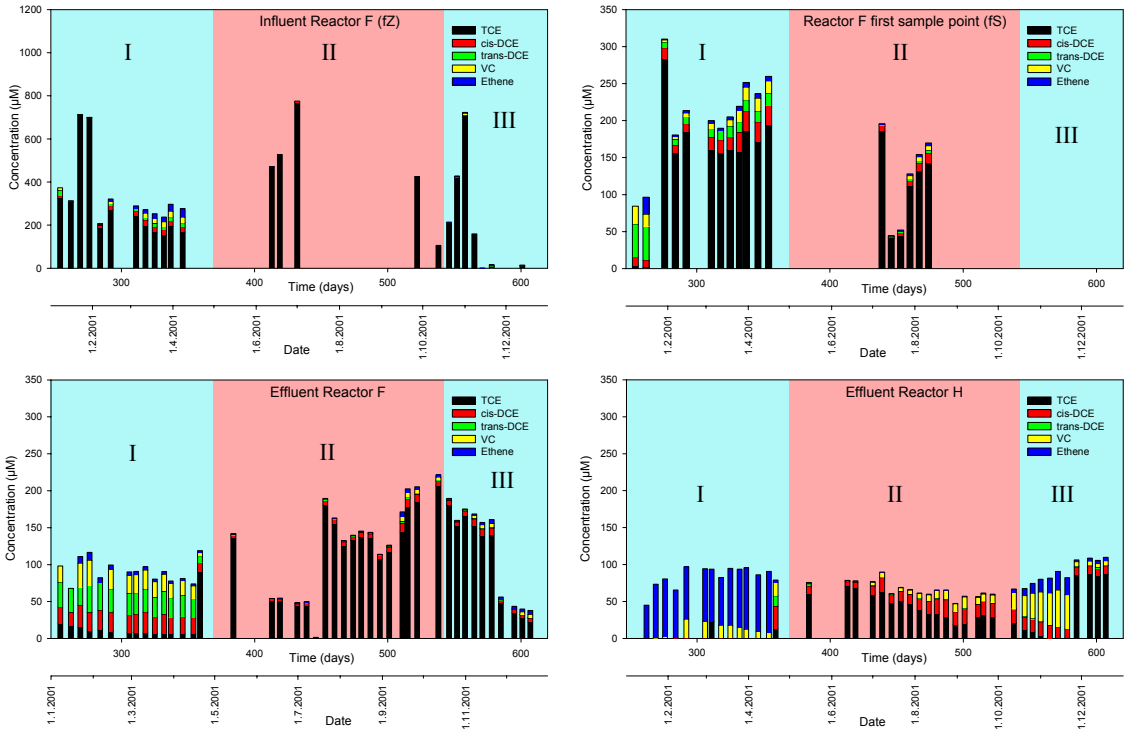


Fig. 42. Transformation of chlorinated ethenes in reactor system II: reactors f (anaerobic) and h (microaerobic). The colored time periods mark the normal operation of the reactors (I), operational problems (clogging, excessive gas production)(II), and the discontinuation of the electron donor supply (III). N.B. Please note the difference in concentration scale between the upper left graph and the other graphs.

Due to operating problems, the VFA addition to the groundwater was discontinued since mid October 2001 (see section 3.3.3). Besides a new high TCE influent concentration at the beginning of October, also the lack of VFA as electron donor may have caused the cessation of the dechlorination as observed in November in reactor h.

In February 2002, the reactors have been changed to their new mode (see section 3.2). From mid April on, both reactors of system II received VFA as the electron donor to achieve the following influent concentrations: Lactate 40 mg l^{-1}, acetate 23 mg l^{-1}, propionate 16 mg l^{-1}. From November 15 this dose was increased 1.5 times: Lactate 60 mg l^{-1}, acetate 35 mg l^{-1}, propionate 24 mg l^{-1}. The results of the low electron donor dosage are shown in figure 43. From the first graph of figure 43 it can be noted that again and repeatedly such high TCE influent concentrations were observed that the addition was temporarily stopped to let the concentration decrease to acceptable levels. The TCE-addition to the reactors improved significantly after the stock solution was changed from pure TCE in water, to water with a TCE concentration of half the saturation concentration. After the change, influent concentrations of TCE stabilised at approximately 100-200 µM (13-26 mg l^{-1}).

In reactor f, initially the effluent concentrations of TCE remain low, as compared to the influent concentrations in that period (fZ). Two months after the resumed electron donor addition, significant dechlorination of TCE to ethane was observed, and also an increase of the total (chlorinated) ethenes in the effluent to about 50 µM. This is only 25-50% of the chlorinated ethenes measured in the influent. In November 2002, the ratio of the different chlorinated ethenes seemed to stabilise and to ethene as a product of complete dechlorination was about 50-70% of the ethenes leaving reactor F. Therefore, the electron donor dosage was increased with 50%.

This resulted in an increase of the ethene concentration in the effluent and a decrease of the *cis*-DCE and VC concentrations. The sulphate concentrations in the effluent of reactor f were approximately 40% lower than those measured in the groundwater (not shown). This indicates that the sulphate reduction is clearly less than during the high electron donor addition in 2001 (ca. 90%). This is also reflected in the low hydrogen sulphide concentrations in the effluent of reactor f.

In the anaerobic reactor h, the effluent contained approximately 100 µM of chlorinated ethenes, of which the major part is TCE. These results are strange since there are less chlorinated ethenes and less TCE in the influent than in the effluent of reactor h. An explanation can be that during previous high TCE doses, pure phase of TCE has accumulated in the reactor, which is now dissolving again. Furthermore, more sulphate and nitrate is measured in the effluent (2500 mg l^{-1} and 20 mg l^{-1} respectively) than in the influent (600 mg l^{-1} and 0 mg l-1) of this reactor, and H_2S entering the reactor is not found in the effluent. The apparent explanation would be that somehow, still hydrogen peroxide and nitrate are added to the reactor, resulting in metal sulphide and ammonium (re)oxidation. However, personal verification of this with the crew of the test site showed that no such additions were actually made. Additional samples from other sample ports of this reactor were taken and analysed.

Analysis of these samples revealed that the redox potential in the first half of reactor h is increasing from –323 mV to –205 mV. However, in the effluent of reactor h, the redox potential has further increased to +121 mV. It is possible that during the previous aerobic conditions in the upper part of reactor h, Fe^{3+} has been formed. Reduction of this Fe^{3+} to Fe^{2+} can cause concomitant oxidation of sulphide to sulphate, coming from the anaerobic part of the reactor. This could also explain the high sulphate concentrations in the effluent of reactor h.

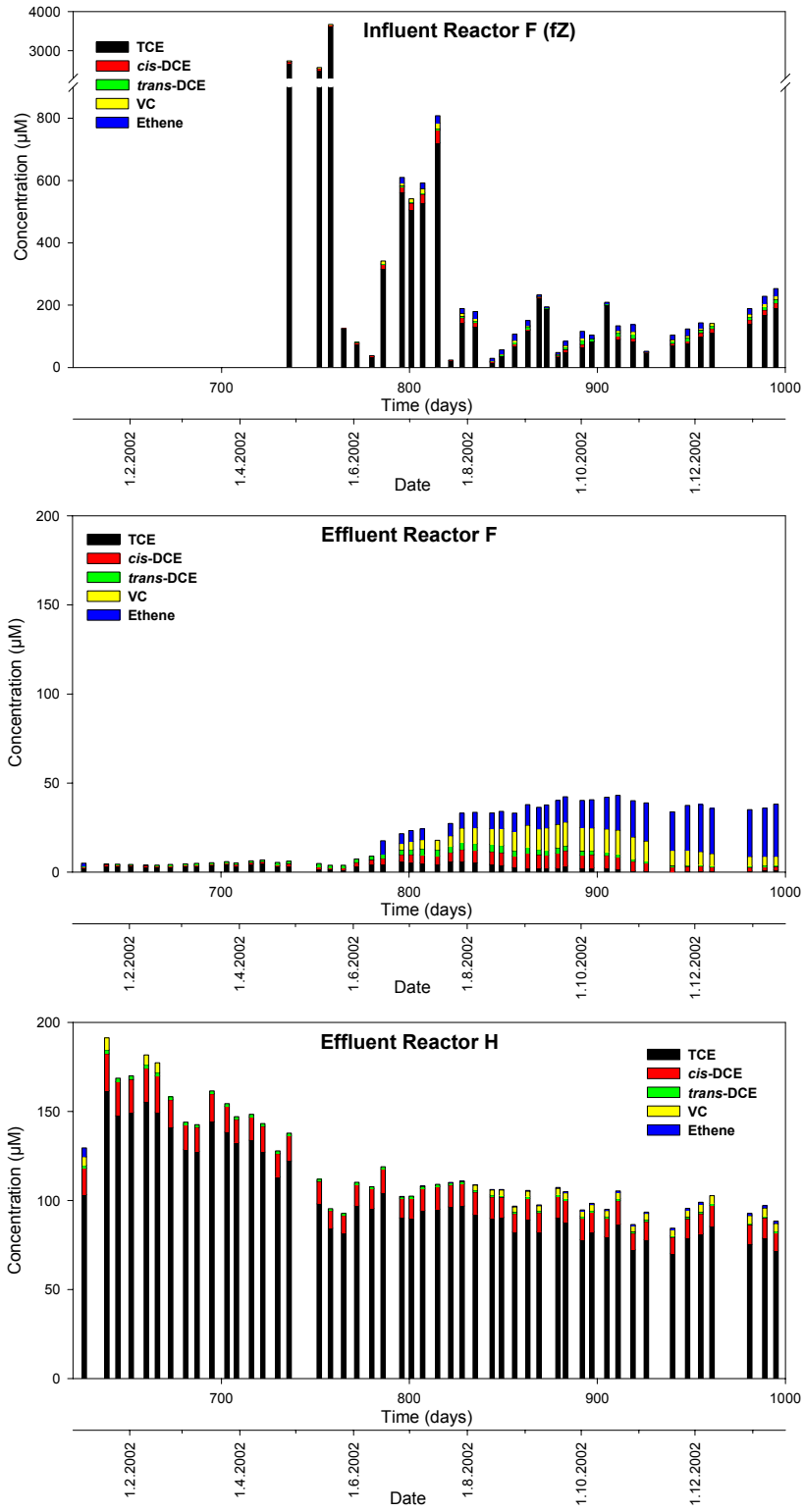


Fig. 43. Anaerobic transformation of chlorinated ethenes in reactor system II (reactors f and h) after the change of the electron donor addition in February 2002.

3.3.2 *Transformation of chlorobenzene*

The reactors g and h are meant to operate under microaerobic conditions. Therefore, oxygen and nitrate are added to the influent. However, due to the unstable operation of the anaerobic reactors e and f with respect to VFA and TCE concentrations, optimisation of the microaerobic reactors was not considered appropriate before this problem had been solved. Nevertheless, the

CB concentrations have been monitored in both reactor systems from the start-up of the reactor systems. Up to 600 days after the start-up of the system, no removal of CB has been observed in the reactor systems (figures 44 and 45). The apparent CB removal, which is observed during the first 4 months of 2001 in anaerobic reactor f (figure 45), seems to be due to an artifact since the CB concentration reaches “normal” levels again in microaerobic reactor h. Moreover, after April, the CB concentration in the effluent of reactor f rises suddenly to a level, similar to that of the influent and the effluent of reactor h. Possible reasons for this inconsistency are temporary preferential flow/heterogeneity in the soil, or errors in sampling and/or analysis.

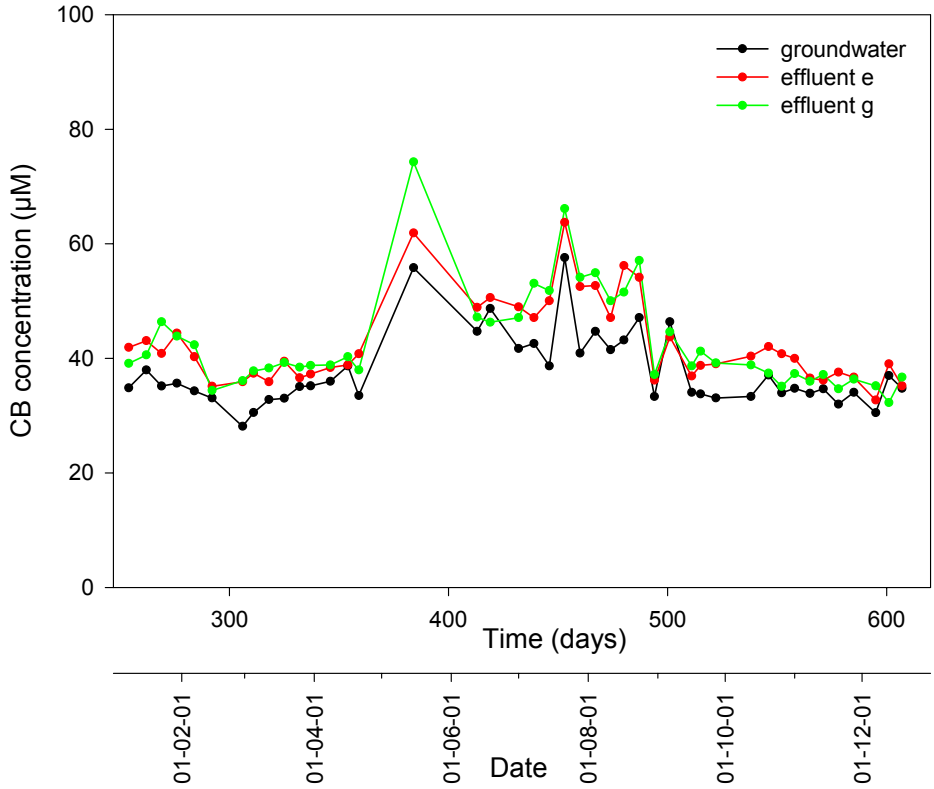


Fig. 44. Concentration of chlorobenzene in groundwater and anaerobic and micro-aerobic effluent (reactor system e-g).

The concentrations of other aromatic compounds like 1,2-dichlorobenzene, 1,4-dichlorobenzene, and chlorotoluene also remain constant in both reactor systems (data not shown).

The lack of CB degradation in the presumed micro-aerobic reactors g and h is most certainly due to anaerobic conditions prevailing in these reactors. Degradation of CB under anaerobic conditions has not been reported in the literature. The reason for the anaerobicity is probably the high concentrations of sulphide, which are formed by sulphate reduction in the anaerobic reactors e and f. The sulphide will consume all oxygen added to reactors g and h, thus creating anaerobic conditions again. This is confirmed by data on the chlorinated ethenes, which are subject to reductive dechlorination, an anaerobic reaction, in reactor h (see previous section).

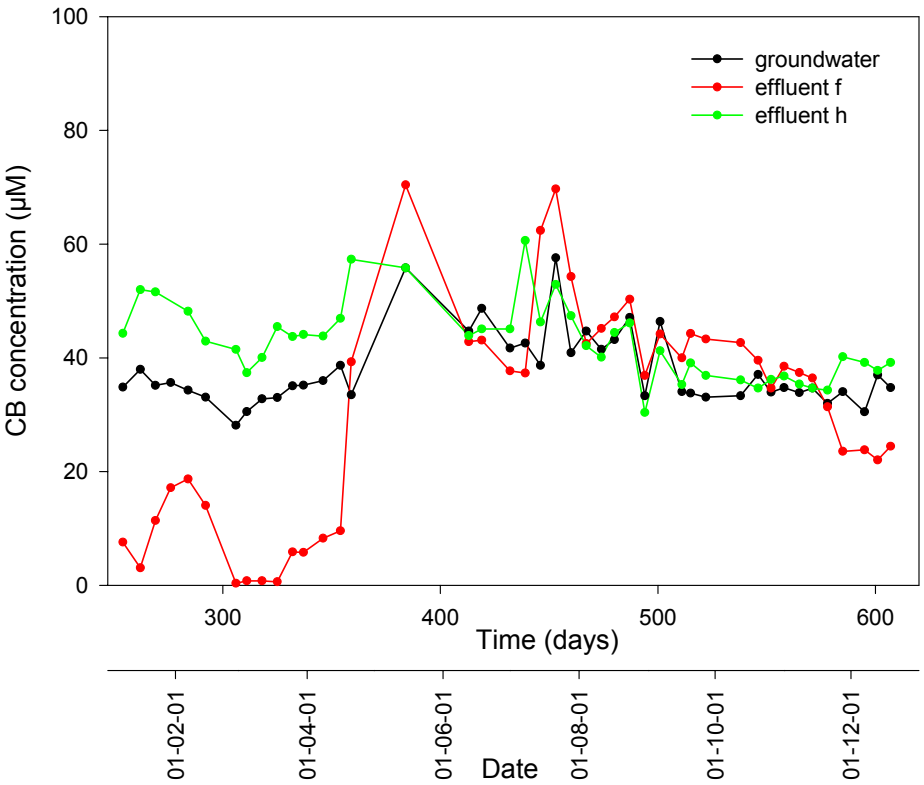


Fig. 45. Concentration of chlorobenzene in groundwater and anaerobic and microaerobic effluent (reactor system f-h).

In February 2002, the conditions in the two reactor trains were changed (see section 3.2). In reactors e-g, aerobic conditions were achieved similar as in the on-site columns (see section 2.2.3) by adding hydrogen peroxide (35 mg l^{-1}) and nitrate (2.4 mM) to the influent of both reactors. Figure 46 shows the concentration of CB in the reactors e and g. The CB concentration was not decreased in reactor e during the first 250 days after the increase of the peroxide addition. The CB concentration of the effluent of reactor g is about 10-20% lower than that of the effluent of reactor e. This decrease already occurred before the increase of the peroxide addition, but after the VFA addition to reactor e had been stopped. The reason for the fact that CB was not degraded in the previously anaerobic reactor e could be that there was still too much reducing power present in the form of precipitated sulphides that the conditions remaining too much reduced for CB degradation. Hence, the peroxide addition to reactor e was increased five-fold, equivalent to 100 mg l^{-1} oxygen. After this change, 25-30% of CB removal was observed in reactor e. It remains still unclear whether this is due to chemical or biological degradation. Remarkably is that after this change, the degrading capacity of reactor g seems not to contribute to further disappearance of the CB.

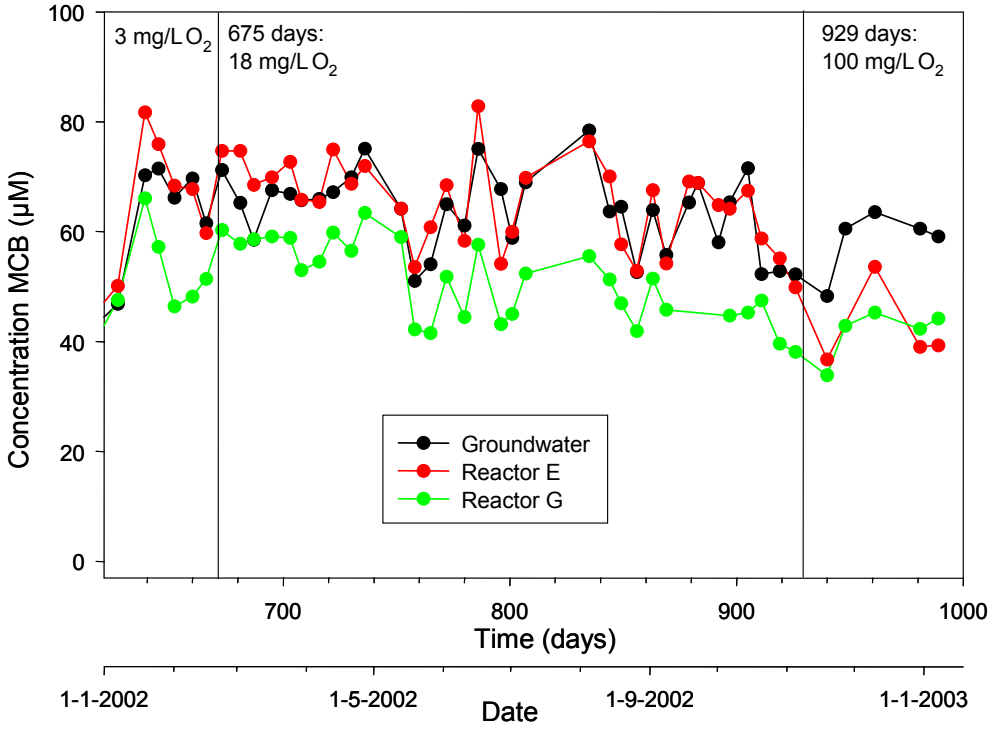


Fig. 46. Chlorobenzene concentrations in reactors e and g in 2002, after the hydrogen peroxide addition had been increased.

3.3.3 *Other factors determining reactor performance*

Partly oxidized aquifer material

Part of the aquifer material that was used for the on-site and in-situ experiments had been stored improperly (under aerobic conditions, which lead to low pH conditions) before being used in for the experiments. Therefore, laboratory experiments were carried out to gain insight in the specific effects.

The aquifer material which was initially oxidized and exposed to low pH was placed in upflow columns and allowed to be neutralized by feeding the columns with fresh gorundwater prior to the experiments. The effects of low pH exposure are summarised in table 10. The results were compared to the results obtained in the column experiments with unaffected aquifer material.

Overall it can be stated that low pH exposure affects both the anaerobic and the microaerobic processes. The anaerobic dechlorination of the chloroethenes started up much slower. Possible reasons for this effect are higher a higher electron donor demand of the oxidised aquifer material or an effect on the anaerobic microbiology. The microaerobic processes on the other hand started up much faster. A possible explanation may be the increased oxidation level of the sediment.

Table 10. Effect of low pH exposure on the performance of the biological processes in the column systems (compared to undisturbed systems).

Subject of research	Anaerobic processes	Microaerobic processes
Start-up performance	Slow	Faster
Additives	More electron donor needed for start-up	Process may be started up with NO_3^- and small amount of oxygen
Long term column performance	- reductive dechlorination capacity uncertain - sulphate reduction slower - stability of process unknown - longer period required for decreasing the amount of electron donor dosed	- chlorobenzene degrading capacity uncertain - stability of process unknown

Clogging

During the summer months of 2001, the first signs of temporary pressure build-ups at the effluent ports of the anaerobic reactor were observed. At the beginning of October the pressure build up started to approach the safety limits of the installation. As this was probably the result of sulphide precipitation, H_2S, methane gas and biomass formation in the system, it was decided to suspend the VFA addition to prevent growth of sulphate reducing bacteria and sulphide formation. Until October, more than 75% of the sulphate in the groundwater was reduced in the anaerobic reactors e and f. The sulphide concentrations measured confirm these results although not stoichiometrically. The latter is probably due to sulphide precipitations in the reactor, which cannot be measured. The sulphate concentration in the effluent of the micro-aerobic reactors g and h does not increase despite the oxygen dosage. After the VFA addition had been stopped, the sulphate reduction in both anaerobic reactors ceased rapidly. The pH in the reactor systems remained around normal levels (pH 6.5-7.5).

3.4 **Summary of observations and conclusions**

The following can be concluded from the *in situ* reactor operation:

- Chlorinated ethenes can be completely dechlorinated to ethene in the reactor system when low electron donor concentrations (0.1-0.2*ED) are provided;
- For the greater part of the research period, the artificial addition of TCE and VFA to the reactor systems was not stable. For TCE this has been solved by using a less concentrated stock solution;
- Toxic levels of TCE have entered system f-h, which reduced the dechlorinating activity almost completely. However, recovery of this activity was achieved after decreasing the TCE concentration;
- An *in situ* anaerobic bioreactive zone for chlorinated ethenes is technically feasible. It is limited by high TCE concentrations (>500µM or >66 mg), which has consequences for the positioning of the reactive zone in the plume. Optimisation of the required electron donor injection in space and time is needed;
- CB was not transformed in the (non-optimised) microaerobic part of the sequential anaerobic-microaerobic reactor system, probably due to a lack of oxygen;
- No significant degradation of CB has yet been observed in the new aerobic configuration of the reactors. The increase of hydrogen peroxide in the influent causes a slight disappearance of CB;

- After more than 1.5 years of operation with high electron donor dosage (2*ED), clogging and gas pressure problems occurred. The measure to stop feeding VFA to the influent proves to be effective in recovering the reactor system.

CHAPTER 4

INVENTORY OF ELECTRON DONORS

4.1 Introduction

Within the framework of the Bitterfeld Project (Phase III) Tebodin Consultants & Engineers have carried out an enquiry and desktop review on the availability of suitable electron donors for bio-remediation purposes. The enquiry was focused on a suitable and cost effective electron donor supply for chlorinated compounds, preferably without any increased contaminant levels. The following potential electron donor streams were found to be suitable:

- solids, liquids or easily soluble substances with COD > 10 000 mg l-1;
- waste waters, containing fatty acids, fats alcohols, acetates or sugars.

4.2 Calculated electron donor amount

The surface area involved is about 100 km². It is estimated that approximately 10 to 30% of the net rainfall is to be treated in order to provide sufficient electron donor supplies in the subsurface. The daily groundwater treatment volume therefore is 10 000 to 30 000 m³ or 3 650 000 to 10 950 000 m³ on a yearly base.

Under anaerobic conditions in the groundwater system chlorinated compounds are sequentially dechlorinated through PCE → TCE → c-DCE → VC → ethenes. Sulphate will be reduced into sulphide up to an estimated maximum of 250 g per m³ groundwater. The required amount of electron donor for the aerobic reactions was estimated:

- 850 ml/m³ for methanol;
- 450 g/m³ for G31 (developed by TNO-MEP);
- 500 g/m³ for fatty acids (e.g. acetate, lactate).

Calculated COD-load of methanol and ethyl acetate:

- $2\ CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$
  M = 64 g/mol o.m. M = 96 g/mol COD
  1 g MeOH ≅ 1,5 g COD
- $CH_3COOCH_2CH_3 + 5O_2 \rightarrow 4CO_2 + 4H_2O$
  M = 88 g/mol o.m. M = 160 g/mol COD
  1 g EtAc ≅ 1,8 g COD

On the basis of the reaction steps and physiochemical data of the different compounds, the required COD load was calculated at 900 to 1100 g/m³, which implicated a yearly COD load of $3.3*10^6$ to $12*10^6$ kg. As a nutrient addition about 75 g/m³ ammonium chloride should be dosed. Furthermore, the micro-aerobic degradation requires some addition of nitrate (200 g KNO_3/m^3) and oxygen (3 g O_2/m^3).

4.3 Suitable waste streams in Germany

Through the Chamber of Commerce, the Yellow Pages and Internet resources, a number of companies with potential suitable electron donors were selected (table 11). This search was focused on relevant industries, such as diary industry, breweries and distilleries, in the area of Bitterfeld, Leipzig and München. Furthermore, a recognised waste recycler and (for reference purposes) several selected Dutch industries were contacted. The inquiry was performed both by telephone and telefax.

Table 11. Contacted industries.

Company	Location	Type of Industry
Milch-Werke Frankische Rohn	Bad Kissingen	Dairy
ESKO	Beverungen	Dairy
Molkerei H. Strothmann GmbH	Guterloh	Dairy
Molkerei Eschede August	Eschede	Dairy
Molkerei Gebr. Rogge	Gronau Epe	Dairy
Frischli Molkerei Gifhorn	Gifhorn	Dairy
Molkerei Schwaighof	Allmanshofen	Dairy
Kasewerk Hoffman	Blievensdorf	Dairy
Bitburger Brauerei	Bitburg	Brewery
Paulaner Brauerei	Munchen / Leipzig	Brewery
Leipziger Brauhaus zu Reudnitz	Leipzig	Brewery
Bauer Ernst	Leipzig	Brewery
Wiltenaar Weinbrauerei	Wiltener	Distillery
Wilhelm Horn Brantwein	Leipzig	Distillery
Gross Gunter & Borner	Leipzig	Brewery
AVEBE	Lüchow	Food
AVEBE	Dallmin	Food
Ruckbau (waste collector)	Gronau	Waste management
Recycling Company		Waste management

The contacted dairy industry, breweries and distilleries do not have suitable (waste) streams with a COD > 10 000 mg l^{-1}. The German AVEBE potato processing plants have COD rich fluid waste streams (COD 30 000 mg l-1; 2 000 mg l^{-1} organic nitrogen) available. Currently these waste streams are used as a fertiliser in the local agricultural community (approx. 10 DM/m³). These waste streams, however, contain slightly increased contaminant levels, the availability is seasonal (limited to the period March – August) and AVEBE will not guarantee the availability nor quality aspects.

In general, German industrial facilities with high COD containing waste streams have waste treatment plants operational and are not interested in other outlets for the waste streams. Furthermore, from a liability point of view, many contacted industries do not want to be associated with contaminated land issues.

In comparison, in the Netherlands dairy industries have suitable waste streams (COD > 10 000 mg l-1) available. The costs of these electron donor supplies mount up to € 0.45 per litre. On the basis of the yearly COD load this would result in a yearly electron donor supply of € 75,000 to € 272,000.

4.4 **Alternative electron donors**

Alternative suitable electron donor supplies include the following options:
- (treated) compost percolate;
- pure compounds (e.g. methanol, acetate or molasses);
- solids (e.g. milk powder).

The costs of (treated) *compost percolate* (e.g. Percol+) are approximately € 1.02 per litre. The COD load of treated compost percolate is 20 000 mg l^{-1}. For the Bitterfeld case, this will result in a required amount of $166*10^6$ to $603*10^6$ litres and therefore estimated costs of € 170 to 615 million per year.

Compounds as *methanol* and *ethyl acetate* seem to be interesting electron donor supplies. The methanol dose is approx. 850 ml/m³ or 670 g/m³, which results in a yearly use of 2500 to 7300 tonnes (table 12). The required ethyl acetate concentration is 500 g/m³ and therefore 1800 to 5500 tonnes per year. The costs are included in the table below. These costs are dependant on the world market situation and will vary seasonally.

Table 12. Alternative electron donor supplies (source: Roland Nederland BV).

Compound	Costs per kg	Yearly use (tonnes)	Yearly costs
Methanol	€ 0.43	2 500 – 7 300	€ 1.1 – 3.1 mln.
Ethyl acetate	€ 1.03	1 800 – 5 500	€ 1.9 – 5.7 mln.

Alternatives may include *molasses* (approx. 0.30 € l-1) and *milk powder* (approx. 1.4 € l-1).
All costs are excluding equipment (e.g. dosing and infiltration), transport and additional ammonium chloride, nitrate and oxygen supplies.

4.5 **Conclusions**

The Bitterfeld project requires a yearly COD load of $3.3*10^6$ to $12*10^6$ kg. As a nutrient addition about 75 g/m³ ammonium chloride should be dosed. Furthermore, the micro-aerobic degradation requires some addition of nitrate (200 g KNO_3/m^3) and oxygen (3 g O_2/m^3). On the basis of current German waste management regulations and liability aspects, German industry in general has no interest in delivering suitable waste streams.

Since the application of specific waste streams seems to be no viable option, alternative electron donor sources are suggested. These alternative electron donor supplies include molasses, methanol and ethyl acetate. The yearly costs of the application of these compounds are € 1.1 to 5.7 million, excluding equipment and transport. Future research should address both technical and logistic aspects of these alternative compounds.

CHAPTER 5

DISCUSSION ON BATCH-, COLUMN- AND REACTOR EXPERIMENTS

The research carried out in the project “Bitterfeld: bioremediation of regional contaminated aquifers” was started up to bring clarity on several important unsolved issues:

1. *Optimisation of the electron donor dosage in the anaerobic stage of the process and the competition between dechlorinating and sulphate reducing bacteria for the electron donor*

For the reduction of TCE in the anaerobic reactors, there should be enough electron donor available to provide the necessary reducing equivalents. However, also sulphate will be reduced under these circumstances, which results in a possible competition for electron donor between sulphate-reducing and dechlorinating bacteria. In the first research period, the *in situ* reactors have received an excess of electron donor to reduce all sulphate and TCE. Due to the exceptional high sulphate content of the Bitterfeld groundwater (± 800 mg l^{-1}), this has led to operational problems, such as clogging and gas formation as described in section 3.3.3.
The actually used electron donor for dechlorination (and also for sulphate reduction), hydrogen, is biologically produced from the VFA dosed to the influent. From the literature, it is known that dechlorinating microorganisms have a higher affinity for hydrogen (i.e. are able to take up lower concentrations) than sulphate reducers. Others, however, reported that the dechlorination of *cis*-DCE to ethene would only occur when all sulphate is depleted. To test this, the electron donor concentration added to the laboratory column was gradually decreased from 2*ED to 0.1*ED. As compared to the previous higher VFA concentrations in the influent, this dosage led to significantly less sulphate reduction and an enhanced dechlorination activity. The dechlorination was also extended to VC and ethene, which indicates that sulphate reduction and dechlorination to ethene can take place simultaneously (section 2.3.2). Recently, this low electron donor dosage concept has been successfully extended to the *in situ* anaerobic reactor f.

2. *The coupling of the anaerobic and the microaerobic reactor systems*

Both in the laboratory column and the *in situ* reactor systems it was shown that a microaerobic system linked to an anaerobic dechlorinating system resulted in badly sustainable or no CB degrading performance of the latter. This is partly due to the high sulphide content of the anaerobic effluent, which causes a high oxygen demand for its oxidation. On the other hand, the degradation of CB without anaerobic pre-treatment requires far higher oxygen concentrations than expected (at least 18 mg l^{-1} instead of 3 mg l^{-1}, see section 3.3). As a consequence, we consider an increased peroxide addition to create complete aerobic conditions both from practical and economical point of view inefficient.
Therefore, the *in situ* reactor operation has focussed in the last period on separated anaerobic and aerobic systems to deal with chlorinated ethenes and CB respectively.

3. *The oxygen demand needed for complete chlorobenzene degradation; optimisation of the oxygen dosage*

As mentioned above, the oxygen concentration needed to achieve chlorobenzene degradation in the on-site reactor and the laboratory column were 9-18 mg l^{-1}. Therefore, we conclude that the degradation of chlorobenzene occurs under aerobic rather than microaerobic conditions.
The on-site micro-aerobic column showed in 2001 approximately 40% chlorobenzene removal. On the basis of chlorobenzene concentration measurements over the length of the column, an optimisation of the operation has been performed by doubling the oxygen concentration. This approach was initially effective to achieve full degradation of the chlorobenzene. After a prolonged period of time, the removal efficiency in this column dropped to 50%. The reason for this effect may be the depletion of certain essential macro- or micro-elements, due to the stimulated

biological activity and the relatively fast flow-through of the column. Within the time frame of the project, no assessment of this phenomenon has been made.
The approach of a high oxygen dosage has also been applied to the latest *in situ* reactor configuration for the aerobic train. However, this has not (yet) led to complete chlorobenzene removal in these reactors.

4. Operation of the in situ reactors

During the whole year 2001 it appeared impossible to achieve equal TCE and VFA influent concentrations in the two reactor systems. This caused a bad performance to system I (e-g), due to low concentrations of TCE and VFA. Until April 2001, we showed in system II (f-h) that a complete reductive dechlorination of TCE to ethene under *in situ* conditions is feasible (section 2.2). After April, extremely high TCE influent concentrations (up to 100 mg/L) were accidentally added to this reactor system. These (unintended) toxic concentrations caused a clearly negative effect on the dechlorination of TCE, which finally resulted in a complete inhibition around June 2001 (section 3.3.1). After a period of lower influent concentrations, the dechlorination activity was slowly recovered. The discontinuation of the VFA addition and a new high TCE influent concentration in October presumably caused the last decline in the dechlorination. Although the mentioned high TCE concentrations appear toxic to the dechlorinating microorganisms, such levels are expected only in the vicinity of pure phases of TCE (DNAPLs). These toxic levels of TCE are irrelevant to the intended application of the technique (plume management) since such concentrations are not expected to occur in VOCl plumes.
After almost two years of electron donor addition at high concentrations, the reactor systems showed clogging problems due to sulphide precipitation and excessive gas formation. The discontinuation of the VFA addition caused a rapid (within two weeks) improvement of the operation. Based on the positive laboratory column results of a low influent VFA concentration, during the last phase of the project, we have investigated, the effect of similar conditions in the *in situ* reactor systems. It appeared that this approach was also successful at such a large scale.

5. Large-scale application, with all the consequences involved (occurrence and prevention of clogging, costs, practical applicability) as a part of a regional plume management approach

Possibilities for large-scale application have been studied within the framework of a separate mission to the Bitterfeld region. The results of this mission have been presented in a separate report [39].

Based on the findings of the SAFIRA test site and study of available data, the mission team came to a concept on field scale. The concept is applicable at the site where concentrations are moderate. This means it is suitable for application in the plume and not in the source area. It is meant to prevent that contaminated groundwater is draining into the surface water system.
Along the flow lines, an area is selected to inject electron donors. Electron donors are necessary to enhance the first step in the process, anaerobic dechlorination of aliphatic compounds. Electron donors at a moderate price like protamylasse can be used as electron donor. Injection is done with special equipment in an area of about 20 m by a few m long, perpendicular to the flow lines, depending on the width of the plume.
Downstream of the injection zone, microorganisms, which are naturally present, are stimulated to start the dechlorination as proven in the SAFIRA test site.

Anaerobically, the degradation goes as far as total dechlorination to ethene.
Consequently, an aerobic step is needed. Zone 2, downstream of 1, can be an artificially created or natural wetland. Groundwater is seeping into a (created) wetland with an interface of anaerobic / aerobic conditions. It has been proven that this vegetation is creating specific conditions, such as bioturbation, which are positive for microbial activities. For example, the function of helophytic filters is well known. Also, the wetlands for the degradation of sewage water are well-

known systems. These wetlands are now being applied for the degradation of monochlorobenzene and the metabolites of the chlorinated hydrocarbons under (semi)aerobic conditions (Natural Attenuation at groundwater/surface water interfaces). Thus, the partly cleaned water then reaches the interception canal. This canal is a new or deepened existing drainage canal (Graben in German) in which the water is flowing into the direction of the Mulde, passing some cascades. The groundwater table, which is now normally at 2-3 bgl, might have to be lowered by pumping to capture enough contaminated groundwater. However, it may be also possible just to deepen the ditch in order to force the contaminated groundwater into the canal (possibly a gravel filled interception canal). If necessary, the interception drain will be kept lower than the average river system and water will be pumped out of this system in order to protect the river system and to create enough cascades for an optimal aeration and polishing of the treated groundwater.

Figures 47 and 48 show schematically the possible application of the 2-phase technology.

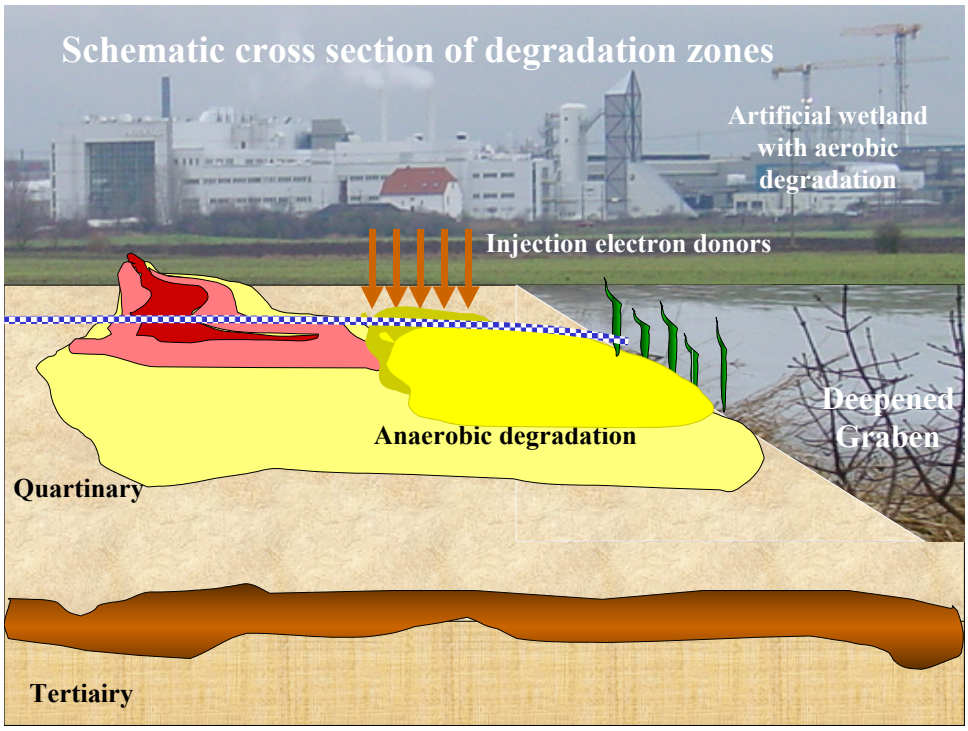


Fig. 47. Cross section of the anaerobic degradation zone with electron donor injection, and the artificial wetland in which aerobic degradation takes place.

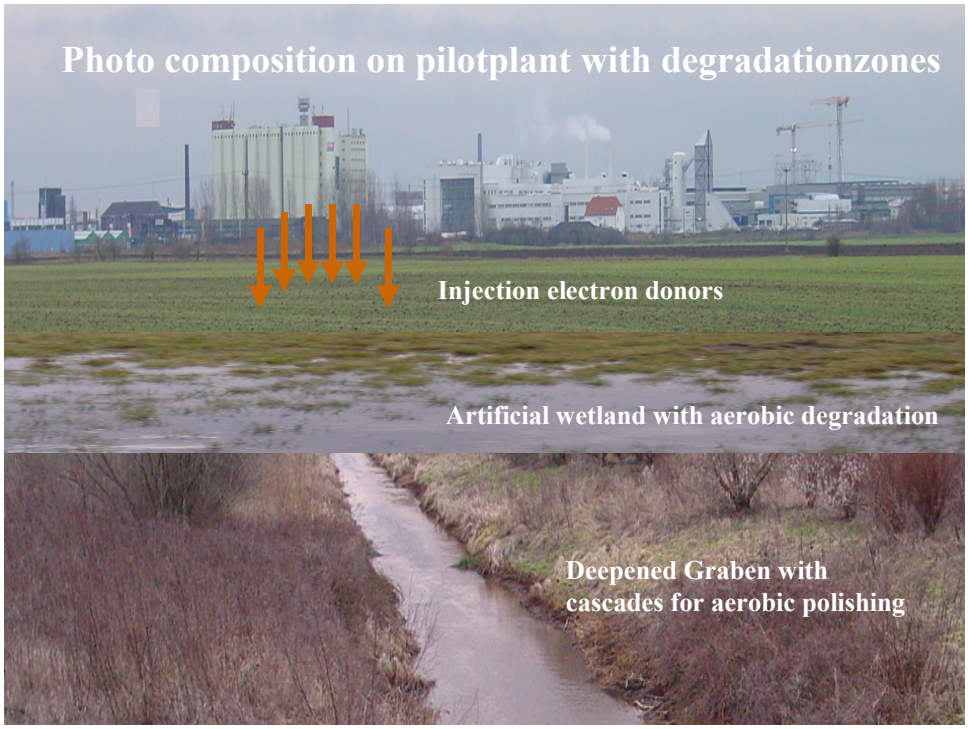


Fig. 48. Front view of the same system as in figure 47.

CHAPTER 6

SKB/SAFIRA TECHNOLOGIES: A COMPARISON

The SAFIRA project investigates the development and technological / economical feasibility of technologies that can be used in an integrated management approach for the groundwater contamination in the Bitterfeld area. This investigation is performed by testing the techniques at bench scale in on-site columns or in columns in the laboratory and in *in situ* reactors at a pilot plant at the test site in Bitterfeld.

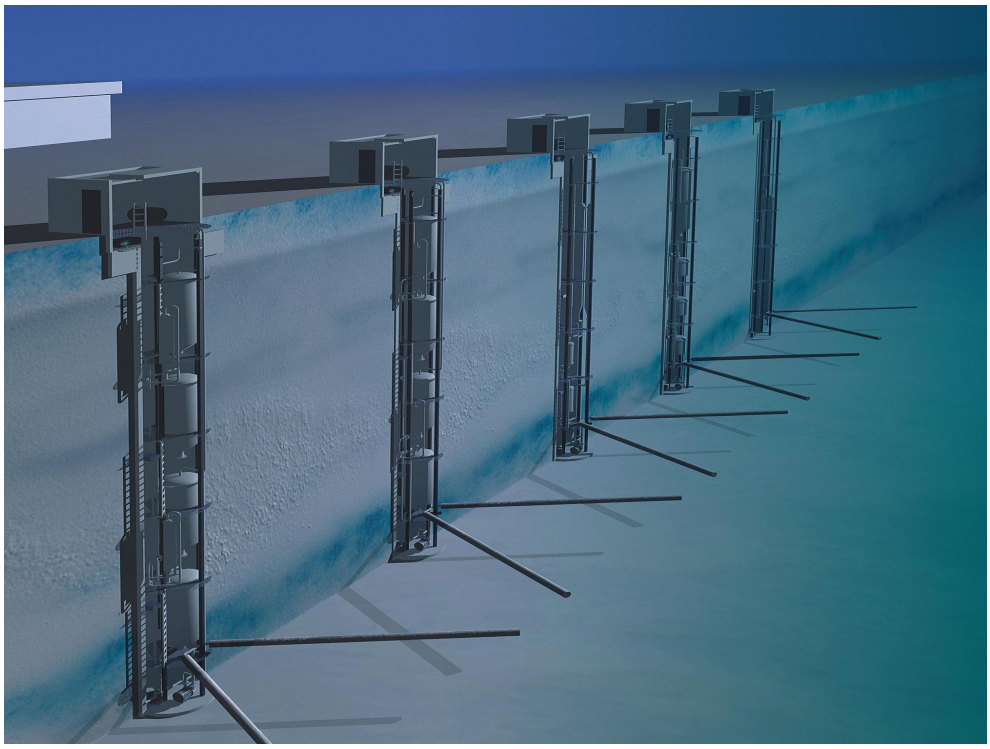


Fig. 49. Cross section of research shafts at the Bitterfeld test site.

In this chapter, the enhanced bioremediation technology tested by the TNO consortium will be compared with the other technologies in the SAFIRA project. Based on current information and knowledge and on realistic expectations gained from the project for each of the technologies, the presentation and comparison will focus on:

- technical possibilities and limitations;
- uncertainties and issues of ongoing research;
- remarks on costs (if and where possible and meaningful).

Due to the multiple sources related to the contamination in Bitterfeld and considering the size of the source area of about 25 km^2, a wide variety of nature and concentration levels of contaminants are present in the aquifers. Simplifying the contaminated plume to the extreme and focussing on the test site at Bitterfeld, chlorobenzene can be considered as the main contaminant found in the upper aquifer at characteristic levels of a few tens of mg l^{-1}. The lower aquifer mainly contains chlorinated ethenes at levels of several mg l^{-1}. A difficulty is posed by the high sulphate concentrations, varying from 600 to 1000 mg l^{-1}.

The aquifers in Bitterfeld bear lignite in concentrations, measured near the test site, of up to 12.5 mass %. So far this caused the initial equilibration of the reactors to take longer than expected and a slow response of the reactors to changes. The same will go for full-scale implementations later on: relatively long adaptation periods, slow responses and increasing concentrations after initial success due to desorption downstream of any reactor system.

All technologies in the SAFIRA project may be implemented using *in-situ* reactors, reactive walls, funnel-and-gate approaches or activated (bio-stimulated) zones. However, on-site application of the technologies becomes more likely when the control of the processes and required adjustments get more complicated. Currently the following technologies are tested:

Bioremediation technologies:
- Enhanced biodegradation of chloro-aliphatics and chloro-aromatics under anaerobic and micro-aerobic conditions (shaft I);
- Enhanced biodegradation of chlorobenzenes under anaerobic and aerobic conditions (shaft V);
- Simultaneous adsorption and microbial degradation using activated carbon (shaft II);
- Enhanced biodegradation using air sparging / oxygen walls; laboratory and on-site column and tank experiments only.

Physical / chemical technologies:
- Adsorption on activated carbon (shaft II);
- Zeolite-supported and membrane-supported palladium catalysts for reductive dechlorination (shaft III);
- Solid metal catalysts for oxidative de-chlorination (shaft III);
- Coupled *in situ* reactors (electrochemical processes combined with activated carbon filtration) with optimised geochemical processes downstream of the reactor (shaft IV).

The technologies 4 and 7 will be summarised briefly in this document for reasons of completeness but not compared to the other technologies. The information available is not detailed enough to allow for comparison.

In section 2 the technologies will be dealt with one-by-one, resulting in key findings and key qualifications of each of the technologies. In section 3 the qualifications of the technologies will be summarised in a table to present an overview and conclusions will be drawn.

6.1 Technologies one-by-one

6.1.1 *Enhanced biodegradation in anaerobic and aerobic conditions*

The TNO consortium uses shaft I for testing enhanced biodegradation in a two-phase system. The focus is on chlorinated ethenes and chlorobenzenes, two main groups of contaminants that require different conditions for degradation. As the withdrawn groundwater at the test site did not have appropriate concentrations of chlorinated ethenes, these were added in the required concentrations. As carrier material for the micro-organisms, the aquifer material from the Bitterfeld area was used in all experiments, resembling the (geo-) chemical environment in the field.

The first, anaerobic, step is to degrade the chlorinated ethenes by addition of an electron donor and of ammonium chloride as nitrogen source. Currently a mixture of volatile fatty acids (acetate, propionate, butyrate and lactate) is used as the electron donor but for future large-scale operations an electron donor at a moderate price like protamylasse can be used. In the experiments initially problems like clogging as a consequence of sulphide precipitation and excessive hydrogen gas formation were encountered, caused by preferential microbial reduction of sulphate over microbial reduction of chlorinated ethenes. These problems could be prevented by reducing the amount of electron donor to 10% of the amount of electron donor required to reduce all sulphate and chlorinated ethenes: the sulphate reducing activity was considerably lower and the reduction of chlorinated ethenes showed better results. Apparently the application of very low electron donor concentrations favours the de-chlorination over sulphate reduction, so adequate electron donor dosing is essential.

The second, micro-aerobic, step aims at a complete mineralisation of the chlorobenzenes by addition of hydrogen peroxide as oxygen source and potassium nitrate as nitrogen source. Partial to almost complete removal of chlorobenzenes has been found in the on-site column experiment and in the laboratory, using 9 (partial removal) to 18 mg l^{-1} of oxygen (almost complete removal). Thus the degradation of chlorobenzenes seems to require aerobic conditions instead of micro-aerobic conditions as anticipated. However, in the laboratory degradation of chlorobenzenes has been shown under micro-aerobic conditions. Additional research to optimise the peroxide supply is ongoing, aiming at full degradation of chlorobenzenes with a minimum of oxygen. Considering the future full-scale operation, the alternative will be to separate the anaerobic from the aerobic processes in the aquifers by a buffer zone of several tens of meters or to have the contaminated groundwater treated in an artificially created or natural wetland.

Key findings:
- chlorinated ethenes can be dechlorinated under anaerobic conditions in the presence of a complex electron donor, resulting in VC and ethene as the main end products;
- the application of a very low electron donor concentration seems to favour the dechlorination over sulphate reduction, thus dechlorination can be achieved and sulphate reduction minimized by adequate electron donor dosing;
- suitable waste streams to be used as electron donors are not readily available in Germany and alternative supplies like methanol and ethyl acetate are relatively expensive;
- the anaerobic and aerobic processes have to be separated spatially to prevent sulphide and methane from entering the aerobic system;
- complete degradation of chlorobenzenes occurs under aerobic rather than micro-aerobic conditions;
- natural and low-intensity engineered oxygen influx methods may be preferable above oxygen supply in the aquifer when it comes to large-scale field applications.

Key qualifications:
- *in situ* technology, characterised by low capital costs and relatively low operational costs;
- typical (edge of) plume technology, to be applied to protect objects of risk like surface water systems from draining contaminated groundwater;
- high sulphate contents, as typical for the Bitterfeld area, can be dealt with;
- potentially applicable to a wide range of contaminants: volatile aromatics like BTEX, MTBE, cresols and phenols, chlorinated pesticides, chlorobenzenes including hexa en penta chlorobenzene, chlorinated ethenes, chlorinated aliphatics, azo-dyes, TNT, chlorinated phenols and PCB's.

6.1.2 *Enhanced biodegradation of chlorobenzenes under anaerobic and aerobic conditions*

The Umwelt Forschungs Zentrum (UFZ) from Leipzig-Halle and the University of Dresden have tested microbial remediation of chlorobenzenes in shaft V under anaerobic (nitrate reducing) conditions and under semi-aerobic conditions. The focus in this research project is on chlorobenzenes only.

No degradation of chlorobenzenes was observed under anaerobic (nitrate reducing) conditions with only nitrate as additional electron acceptor. Nitrate was consumed completely but no decrease was observed in the concentration of chlorobenzenes during a 588 days test.

The experiment under (semi-) aerobic conditions used hydrogen peroxide and nitrate, first with 2.94 mM and later with 0.88 mM of hydrogen peroxide. Oxygen was rapidly released by the hydrogen peroxide, whereas biotic reactions (catalysed by enzymes) were almost four times faster than abiotic reactions (catalysed by inorganic compounds like Fe^{2+}). Chlorobenzenes were completely degraded in the experiment. Chemical degradation of chlorobenzenes mediated by hydrogen peroxide was not observed, suggesting that the degradation of chlorobenzenes was mainly based on an indigenous aerobic bacterial metabolism. The bacterial population was rather complex, using two different pathways for *in situ* degradation of chlorobenzenes.

Reducing the hydrogen peroxide resulted in rapidly increasing concentrations of chlorobenzenes, indicating that more than 0.44 mM is absolutely required for degradation.

Nitrate was uniformly reduced under all conditions whereas nitrite was as well reduced. The electron donor for nitrate and nitrite reduction is still unidentified and the role of nitrate is not understood; basically it is still possible that similar results can be reached without nitrate dosing. No sulphate reduction was observed.

Further research is going on with regard to the long-term stability, the main degrading bacteria under oxygen-limited conditions that have not been identified yet, the role of nitrate that is not understood yet and the biofilm structure that has not yet been established.

Key findings:

- no degradation of chlorobenzenes under anoxic conditions;
- chlorobenzenes can be degraded *in situ* with peroxide concentrations of 30 mg l^{-1} (and nitrate 134 mg l^{-1}), which represents aerobic conditions and is thus the same conclusion as the TNO consortium's finding mentioned earlier; the degradation seems complete as no accumulating compounds were determined;
- the oxygen released from the peroxide is almost completely consumed by bacteria for the degradation of chlorobenzenes and two different pathways are in use.

Key qualifications:

- *in situ* technology, characterised by low capital costs and relatively low operational costs;
- long-term degradation of chlorobenzenes with a limited dosing of oxygen and nitrate and without enrichment of intermediates.

6.1.3 *Simultaneous adsorption and microbial degradation using activated carbon*

A team of the University of Dresden is testing the adsorption on activated carbon with simultaneous microbial degradation of contaminants. The main goal is to identify the appropriate redox conditions and the addition of substrates to achieve the simultaneous microbial regeneration of the adsorbent and thus to considerably prolong the life span of the activated carbon filters.

Trichloroethene, chlorobenzene and benzene have been used as model pollutants in the column experiments and batch tests in the laboratory. The concept is anaerobic dechlorination followed by aerobic dechlorination, simulated in the laboratory as a sequence of an anaerobic and an aerobic column.

The initial removal process for TCE under anaerobic conditions is adsorption, followed later by biological dechlorination. The mass balance revealed that complete bioregeneration of the activated carbon was achieved, demonstrating a sufficient bio-availability of the presorbed TCE. Auxiliary substrates like sucrose and ethanol in concentrations of more than 1 mg l^{-1} DOC proved necessary but varying the concentrations in the range of 5 to 50 mg l^{-1} DOC did not improve the reductive dechlorination. VC and ethene occurred as breakdown products but formation of VC from *cis*-DCE was much slower than formation of *cis*-DCE from TCE. The reductive dechlorination processes proved stable although the microbial community varied significantly: methanogenic activity ceased completely whereas sulphate reduction was most pronounced in the initial phase but continued to exist during the experiment.

The aerobic stage aims to eliminate chlorobenzene and benzene as well as to further decompose the metabolites from the degradation of TCE. Hydrogen peroxide and nitrate were added as electron acceptors. Remaining organic compounds, added in the anaerobic column as auxiliary substrates, consumed the available oxygen at low peroxide dosing but aerobic dechlorination started from 40 mg l^{-1} on, with improved performance up to 100 mg l^{-1}. Chlorobenzene was removed by adsorption followed later by bio-regeneration, thus demonstrating a sufficient bio-availability of the presorbed chlorobenzene. Chloride formation as observed was predominantly from the degradation of chlorobenzene and the contribution from daughter products of TCE was low.

Specific tests have been run on the auxiliary substrates suitable for aerobic dehalogenation of *cis*-DCE and VC. Ethene (end product of reductive dehalogenation) performed best as auxiliary substrate, followed by aromatic compounds like chlorobenzenes, benzene and toluene. Also sucrose and ethanol (added as substrates in the anaerobic phase) proved to stimulate further dechlorination of *cis*-DCE in the presence of oxygen. All auxiliary substrates tested did better than the reference test without addition of an auxiliary substrate.

Key findings:

- the concept of sequential anaerobic / aerobic activated carbon barriers, using adsorption followed by microbial degradation and bio-regeneration of the activated carbon, proved feasible in laboratory tests;
- presorbed TCE and chlorobenzene have sufficient bio-availability to enable simultaneous regeneration of the activated carbon;
- both VC as intermediate product and ethene as end product of the anaerobic stage have been detected in the experiments under anaerobic conditions; ethene has been tested as the most successful auxiliary substrate for the aerobic phase, resulting in complete removal of *cis*-DCE within 48 days;
- the remaining presence of auxiliary substrates as sucrose and ethanol from the anaerobic phase affects the peroxide dosing in the aerobic phase (aerobic dechlorination started only at relatively high peroxide concentrations of 40 mg l^{-1}) but such substrates do stimulate further dechlorination of *cis*-DCE in the presence of oxygen;
- attention has to be paid to more hydrophilic metabolites as *cis*-DCE and VC that are formed by reductive dechlorination and can be eliminated in the second aerobic barrier in the presence of suitable auxiliary substrates like ethene.

Key qualifications:

- *in situ* technology, characterised by high initial capital costs and moderated operational costs due to the extended effective life-time of the activated carbon;
- the technology allows easy control and stimulation since pollutants and micro-organisms accumulate in a small volume;
- continuous or periodical regeneration of the activated carbon results in a longer operation period as compared to adsorption only; thus lower investment costs as compared to adsorption only;
- sequential anaerobic and aerobic dehalogenation allow for a wide range of contaminants and for cocktails of contaminants to be treated.

6.1.4 *Enhanced biodegradation using air sparging / oxygen walls*

UFZ and Dresdner Grundwasserforschungszentrum e.V. have conducted laboratory and on-site column and tank experiments to study the distribution of gas, saturation and mass transfer, with the goal of determining key parameters for air sparging: the rate constant and the microscopic transfer coefficient for oxygen mass transfer. Experiments have been concluded with a one-component gas (pure oxygen) only; future research should include multi-component gasses.

The research team has not yet interpreted the tests and calculations with respect to the applicability and feasibility for the Bitterfeld area so no key findings and key qualifications will be presented.

However, it is clear that the technology applies to aerobic degradation of compounds like chlorobenzene only and will not be effective for anaerobic degradation of compounds like chlorinated ethenes. As an alternative for dosing hydrogen peroxide and nitrate into the aquifer, the technology of air sparging / oxygen walls may qualify in situations where a relatively low oxygen supply will boost the aerobic microbial degradation of the contaminants. As an alternative for extensive aeration in landscape-integrated approaches, the technology may qualify in situations where an earlier start of the aerobic degradation is preferred due to conceived risks to the receiving surface water like in natural reserves or in situations where the urban infrastructure will not allow landscape-integrated approaches.

6.1.5 *Adsorption on activated carbon*

The University of Tübingen focuses on activated carbon filtration, aiming at the identification of the relevant inherent groundwater parameters which might influence an economic long-term operation of a granulated activated carbon (GAC) *in situ* barrier, the prediction of the longevity of a GAC reactor under *in situ* conditions and quantification of particle related contaminant release from GAC reactors. The team further addresses the long-term contaminant release from lignite seams as a continuous source of contamination and the maximum concentrations from such diffusive contaminant release.

The long-term stability of the contaminant removal mechanisms is crucial for the economically successful application of any technology. Although activated carbon filtration is a standard method in drinking and wastewater treatment, little is known about the long-term performance of this technology for contaminant removal under *in situ* conditions in groundwater. The team has now run four GAC reactors for over two years, using three different types of GAC. So far the treatment is successful and efficient for the removal of hydrophobic, low solubility contaminants such as chlorobenzene. In none of the *in situ* operated activated carbon filters clogging, chemofouling or biofouling has been observed; investigations using methodologies like REM and BET confirmed the same. The physical and chemical parameters of the groundwater (anions, cations, pH etc.) remained unchanged. The loading of the GAC with the contaminants agrees very well with expectations from modelling. However, the technology does not deal with all different con-

taminants as effectively and efficiently, especially not with hydrophilic, high solubility contaminants like phenols.

The investigations have shown that after an initial high release of uncontaminated particles from the reactor, a decrease and stabilisation of the released particles takes place followed by the release of contaminated particles. However, this release is minor compared to the slow and lasting release of contaminants from the lignite in the aquifer.

Key findings:
- in testing for over two years no clogging, chemofouling or biofouling have been observed;
- physical and chemical parameters of the groundwater (anions, cations, pH etc.) remained unchanged;
- good match between the results of modelled and measured breakthrough curves, using isotherm parameters and kinetic parameters from laboratory tests;
- technology is successful for long-term removal of hydrophobic, low solubility contaminants like chlorobenzene, with test results suggesting stable long-term performance and predictable behaviour with regard to loading and adsorption characteristics.

Key qualifications:
- as technology for treatment of contaminated groundwater on-site, proven, widely used, low tech and often cheap;
- *in situ* low-tech technology, characterised by lower initial capital costs than the high-tech application of simultaneous adsorption and microbial degradation using activated carbon but possibly higher operational costs due to the shorter effective life-time of the activated carbon.

6.1.6 *Zeolite-supported and membrane-supported palladium catalysts*

In shaft III the Umwelt Forschungs Zentrum (UFZ) from Leipzig-Halle and the University of Tübingen have been testing different types of palladium catalysts.

Pd-catalysts have been chosen as the subject for research because of qualities like being effective for a wide range of contaminants, being a speedy process and leaving the natural processes in the groundwater basically unchanged. Pd-catalysts have a high reactivity for dechlorination of aliphatics and aromatics, using hydrogen as reduction agent. The main issue in the research was how to prevent de-activation of the catalyst due to sulphides and other compounds. The catalytic active component Pd needs to be protected from de-activating ionic compounds either by embedding the Pd into hydrophobic polymer membranes or by generating Pd-clusters in the pores of hydrophobic zeolites. However, in the SAFIRA project both catalysts reached only short life times, caused by the formation of H_2S and possibly other sulphur compounds by microbiological sulphate reduction. Though the catalysts could be regenerated by treatment with hypochlorite, poisoning re-occurred after short periods of operation. In conclusion, the team concluded that the utilization of noble-metal catalysts directly in the water phase of the Bitterfeld groundwater was problematic and changed the research concept. However, the use of Pd-catalysts for groundwater remediation in general should not be neglected as at a site in Stuttgart with a less complicated groundwater composition the team has succeeded to realise stable processes for a period of months, using Pd-catalysts in the water phase just as in Bitterfeld. In Stuttgart a commercial full-scale plant based upon Pd-catalysts is being negotiated now.

The new approach chosen is to pass the groundwater through a zero-valent iron-reactor, to remove any sulphides that could poison the catalyst and to enrich the groundwater with hydrogen that comes from iron corrosion. Further, the zero-valent iron will start the de-chlorination of susceptible aliphatic compounds. Specifically for 1,1,2,2-tetrachloroethane, abundantly present in the Bitterfeld aquifers but difficult to be removed from the groundwater, NaOH is added to raise

the pH and the groundwater is led through an activated carbon reactor, thus causing partial hydrolysis to TCE. TCE can be easily removed together with most other contaminants, including chlorobenzene. The activated carbon is not used but just functions as temporary adsorber. For the treatment nitrogen gas is used as the agent in a so-called full-phase membrane unit. An absorber with zinc oxide pellets protects the Pd-catalyst, removing any formed sulphur compounds like H_2S. Next, the gasses are effectively and efficiently treated with the Pd-catalysts, allowing a small catalyst unit, capable of handling a wide range of contaminants, including VC.

Key findings:
- in the specific situation in Bitterfeld with high sulphate concentrations, the Pd-catalysts used in the water phase reached only short life times and efforts to protect them sufficiently from being de-activated failed;
- treatment of 1,1,2,2-tetrachloroethane (and components with similar physical/chemical properties) requires a separate step;
- applicable for a wide range from VC to chlorobenzene (criterion is stripping efficiency).

Key qualifications:
- on-site technology due to the multi-stage, complex technology: different pre-treatment techniques in the water phase, vacuum stripping of contaminants and catalytic hydro-dechlorination over Pd-catalysts in the gas phase;
- effective and efficient removal of contaminants from the gas phase;
- effective for a wide range of contaminants, including VC, and for a wide range of concentrations;
- probably most cost-effective in hot spots in the absence of 1,1,2,2-tetrachloroethane.

6.1.7 *Oxidative solid metal catalysts (no detailed information available)*
The University of Leipzig is testing the oxidative solid metal catalysts in shaft III.

The report on the mission in January 2002 [39] mentions the use of nickel catalysts to oxidise chlorobenzene, and its main findings: oxidation did take place but it could not be decided whether the disappearance of chlorobenzene was the result of biodegradation or of catalytic processes; the former being the most likely. The solid metal catalyst is a wire mesh specially treated to give it a catalytically active surface coating. Hydrogen peroxide is used as the oxidising agent. The brief periodic application of ultrasound regulates the catalytic activity and hence increases service life.

No further information is available.

6.1.8 *Coupled in situ reactors with optimised (geo-)chemical processes downstream*
The University of Kiel in shaft IV investigates a coupled set of a redox-reactor, aerobic reactor (ORCs; Oxygen Release Compounds) and activated carbon reactor, having concluded earlier that a reactive barrier with one single filling cannot treat the complex mixture of contaminants. Using metallic or zero-valent iron reducible substances such as trichloroethene can be converted into ethene and chloride; microbial anaerobic degradation processes will consume the hydrogen that is produced in this process. Non-reducible organic compounds such as chlorobenzene do not react with iron and are adsorbed on activated carbon. Bacteria degrade biodegradable compounds such as benzene or ethene, resulting from the reaction with iron. The research is designed to ascertain how the various remediation processes affect one another and the sequence in which the reaction chambers must be installed so that the pollutants can best be removed from groundwater over longer periods of time.

The team has concluded from its research that the two most promising combinations are iron and activated carbon in sequence and iron and ORC in sequence. It has investigated the possibility

and process of precipitation of iron minerals in the reactor, the de-activation of the zero-valent iron due to adsorption of chlorobenzene and the pH increase connected to zero-valent iron and ORC-reactors. The groundwater flowing out of a zero-valent iron-reactor has an increased pH and a smaller buffer capacity, causing a slower oxygen release from the ORC. This high pH causes a slow and unstable microbial degradation. The team also investigated the relation between oxygen production and chlorobenzene inflow. With an overproduction of oxygen, zero-valent iron will be de-activated, with a surplus of chlorobenzene there will be an incomplete removal.

The costs for monitoring, planning and construction of the barriers are similar but the combination of iron and activated carbon is generally cheaper than the combination of iron and ORC, due to material costs. The combination of iron and activated carbon can be cheaper than activated carbon alone if the concentrations of the substances degradable by iron are high and if the type of groundwater does not affect the lifetime of the iron adversely.

The second part of the research investigates the (geo-)chemical processes downstream of different barrier systems. The composition of the groundwater at the outflow of the barriers is less relevant than the composition of the groundwater after having flown through some distance of aquifer material. The high pH at the outflow of iron- and ORC-barriers is buffered in the aquifer material to a neutral value; and in the activated carbon if a coupled reactor is the case.

Further research is going on with regard to the base neutralisation capacity to be able to predict the break through velocity of the pH and with regard to the mechanisms responsible for pH buffering.

Key findings:
- ORC and zero-valent iron in a sequence will de-activate the iron in case of an overproduction of oxygen;
- so best combinations are zero-valent iron with activated carbon in a sequence and with ORC in a sequence;
- groundwater flowing out of a zero-valent reactor has an increased pH and a smaller buffer capacity;
- oxygen release from ORC is less with higher pH so best results are gained in the case of a high natural buffer capacity of the groundwater;
- oxygen release should be balanced carefully with the chlorobenzene concentration to ensure complete degradation;
- pH is buffered sufficiently by the aquifer material (and the activated carbon, if it is the case) but initially the high pH causes a slow and unstable microbial degradation.

Key qualifications:
- *in situ* technology, characterised by high initial capital costs;
- in situations with high contaminant loads and where the zero-valent iron is granted a long lifetime due to the composition of the groundwater, a combined iron / activated carbon barrier may be cheaper than a barrier of activated carbon only.

6.2 **SKB SAFIRA technologies: overview and conclusions**

6.2.1 *Overview*

The key qualifications of the technologies, as elaborated in the earlier section, are summarised in Appendix D. Technologies 4 and 7 are excluded from this table, as insufficient information is available.

6.2.2 *Conclusions*

Addressing the situation in Bitterfeld

SAFIRA has shown that multi-stage technologies are basically capable of dealing with the mix of contaminants present at the mega-site. Bitterfeld is, to say the least, a challenging test site due to the complex mix of contaminants, the variation in concentrations, the size of the area and the short distances to objects of risk.

Abiotic multi-stage technologies have successfully passed the laboratory, bench-scale and reactor-scale testing phases. The technologies are applicable in reactive walls, funnel-and-gate approaches or as on-site technology. Due to spatial variations, variations in time and other types of variations, the technologies will require a strict process control and a stretched flexibility to be able to adjust to variations. It has not been defined yet what flexibility is required and to what extent this flexibility can be realized in large-scale applications. Prolonged reactor tests and pilot tests will be needed to assess the flexibility of each of the technologies, to be able to include flexibility into the design and to build and operate large-scale applications effectively and efficiently.

Biotic multi-stage technologies have passed the laboratory and bench-scale testing phases and are in good progress with regard to the reactor-scale phase. The technologies are applicable in activated (bio-stimulated) zones in aquifers or in intermediate zones.

The one single-stage technology tested (adsorption on activated carbon) has been found low-tech, proven and effective for long-term removal of hydrophobic, low solubility contaminants only. Thus this technology itself cannot fully deal with the mix of contaminants found in Bitterfeld.

Generally it can be stated that during the SAFIRA research period a paradigme shift occurred within most of the SAFIRA research groups: in most cases, not a single technology, but a smart combination of technologies will lead to the most efficient approach to the contaminated groundwater.

Addressing more common situations

Most contaminated sites are essentially less complicated than the Bitterfeld case. With regard to these contaminations, SAFIRA has presented new multi-stage technologies that add to the technologies at hand. The knowledge and experience gained on the SAFIRA innovative technologies may facilitate and boost pilot-scale applications in The Netherlands, by carefully matching the merits of each of the technologies to the specific situation and requirements of the case. In most situations the required flexibility will be easier to assess and incorporating flexibility into pilot and large-scale applications may well be within reach.

CHAPTER 7

A FIRST STEP TOWARDS PLUME MANAGEMENT FOR THE BITTERFELD REGION

7.1 Introduction

The past few years, research on the Bitterfeld contamination has aimed at the application of *in situ* technologies. The technologies tested are to be used in large-scale remedial concepts for the Bitterfeld region, such as reactive barriers or funnel-and-gate systems. At the start of the project, however, no 'official' large-scale remediation concept for the Bitterfeld region had been developed yet. Evaluation of the techniques under development within the SAFIRA project should therefore be placed in a broader view of possible large-scale applications, and optimal use of available possibilities and technical/infrastructure resources. The techniques to be developed eventually should be applicable at a regional scale. Some technologies may be applicable to some specific areas of the Bitterfeld region, whereas other concepts may be required to provide a solution for the whole region. To contribute to the development of a cost-effective pollution control concept for the Bitterfeld region in addition to more technically orientated research, the NOBIS/SAFIRA team has carried out this first brief evaluation in 1999.

The basis of the current evaluation is management of the risks of the 'plume' of contaminated groundwater and is further called 'plume management'. In order to develop a concept for plume management, 'objects' at risk have to be identified and ordered to priority. The Bitterfeld region is contaminated at such a large scale that a complete clean up is not feasible. Instead, the objective of plume management is to reduce risks for selected objects to an acceptable level. Questions like "which objects should be selected" and "what level is acceptable" are to be dealt with by the authorities (Landesamt Sachsen-Anhalt, Büro für Bodemökologie, Bodemkartierung, Bodenschutz) and are not discussed here. What will be discussed are possible measures that can be used for interception of contaminated groundwater. The amount and the quality of the water to be treated are key issues for estimation of treatment costs and the identification of problems arising when scaling up.

In this paragraph the hydro(geo)logical system of the Bitterfeld region is analysed in relation to the contaminant situation and possible intervention scenario's (as pieces of the total jigsaw puzzle) are described aiming at protecting different potential objects at risk. From the hydrological analysis and intervention scenario's key figures for up scaling could be derived. The combination of these key-figures with technologies currently being developed provides possible limitations for these technologies for scaling-up.

The analysis of the hydrological system of the Bitterfeld region and the contaminant situation are based on a broad review of data made available to the project team. This first effort does not provide complete solutions but aims at identification of possible limitations and gaps in technologies and concepts encountered in scaling-up to a remediation plan for the whole Bitterfeld region. Some of the interception measures have been discussed at the SAFIRA workshop held at Bitterfeld the 17th and 18th of November 1999.

7.2 Source-path-object approach for risk based corrective actions

According to the previous paragraph, identification and ordering of potential objects at risk form the basis for the design of a concept for plume management. Identification of objects at risk and especially prioritising them is a subjective matter. Without doubt the main object at risk is the vil-

lage of Bitterfeld itself. Evacuation of buildings within the village, to avoid exposure to dangerously high contaminant concentrations, has recently been reported.

Due to a closure of groundwater extraction for mining purposes, it is to be expected that the groundwater level will rise under the village into the cellars of the houses. This closure of groundwater extraction will also cause a part of the contaminated groundwater to discharge in the river Mulde instead of in the groundwater extraction wells. Therefore the ecosystem of the wetland of the river Mulde is at risk as well. Furthermore, water from the Mulde is diverted into the former mining pit. The pit will be filled within a year or two. Due to termination of the groundwater extraction and creation of an artificial lake in the former mining pit, the direction and magnitude of the groundwater flow will change. Less or no contaminated groundwater will flow towards the former pit, as the filled pit does not act as a drainage system. The groundwater that used to flow towards the pit will either infiltrate towards the deeper aquifer or will discharge into the river Mulde.

The Bitterfeld area can be characterised as an infiltration area. On regional scale, water that infiltrates will partially flow through the Quaternary aquifer towards the Mulde and discharge in this river, another part will infiltrate even deeper to the underlying tertiary aquifer [47]. In fact two hydrogeological systems exist (apart form groundwater extractions and man made drainage systems). A relatively shallow system (the Quaternary aquifer) consists of an area around the river Mulde and a deeper system (the Tertiary aquifer) consists of an area bordered by the watershed upstream of the village Bitterfeld (to the west) and the border between the deeper and shallow system (figure 50).

The lateral extend of both systems and the volume of groundwater flowing through these systems are dependant on the relative permeabilities of both aquifers and the confining layer (Braunkohl), the distance from the watershed east of Bitterfeld to the Mulde, the drainage characteristics of the Mulde and the groundwater recharge. The extent of both systems can be estimated, if those parameters have been properly assessed and evaluated.

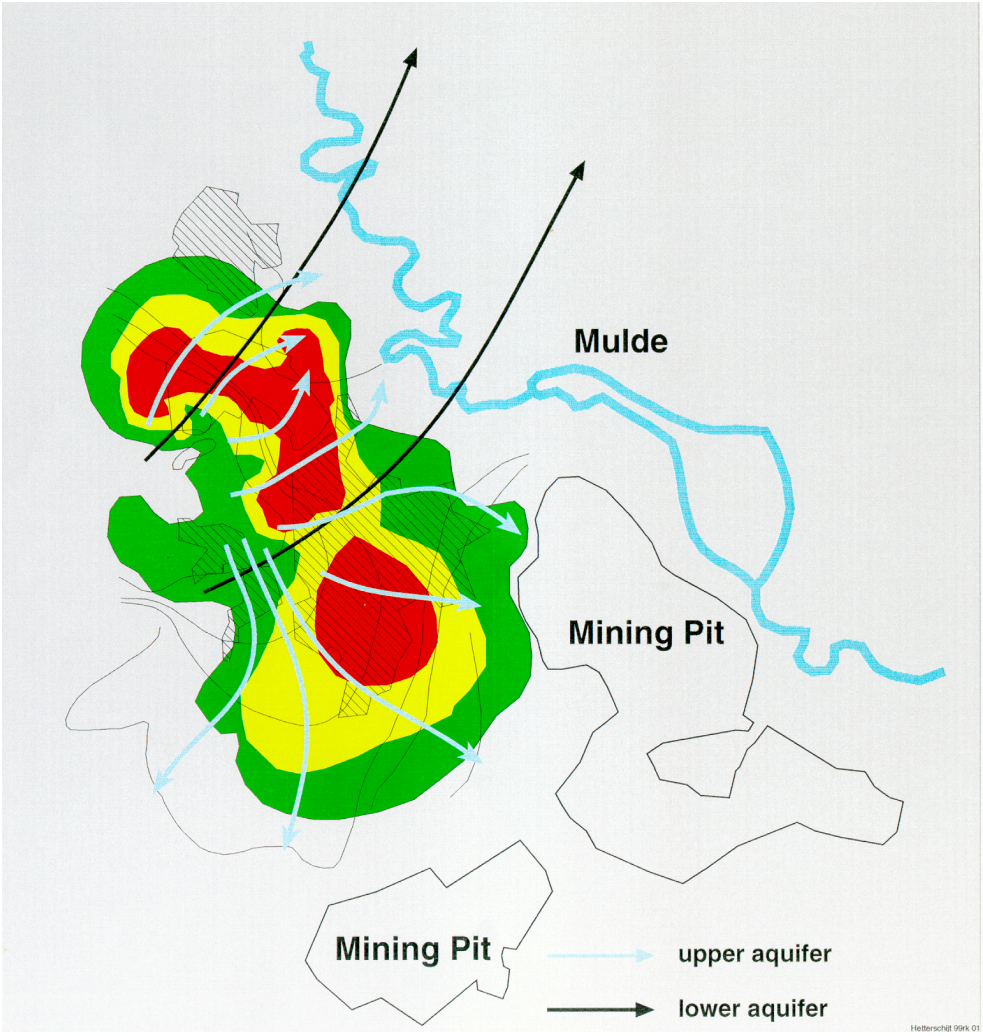


Fig. 50. The current contaminant situation, the isohypses, from which the direction of the groundwater flow can be deduced, and the pit and river Mulde. When the pit is replenished, the general groundwater flow will be from west to east in the direction of the Mulde.

7.3 Jig-saw pieces for scaling-up

The currently identified potential objects at risk to be protected are the following:
- river Mulde;
- deeper aquifers;
- former mining pit (artificial lake);
- the village of Bitterfeld.

The primary aim of SAFIRA is to develop groundwater contamination interception approaches to protect down gradient objects at risk. Although the village of Bitterfeld is also a serious object at risk too, it is not a part of the SAFIRA programme. Therefore it is not discussed further here.

River Mulde: active or passive treatment
One of the objects at risk is the river Mulde. This has been the case even before closure of the mining wells, although the flux of contaminated groundwater towards the river was less at that time. Prevention of exposure of the river ecosystem can be achieved by *in situ* treatment of the contaminant groundwater travelling towards the river. Groundwater discharging into the river Mulde originates from the shallow Quaternary aquifer. The interception and treatment of ground-

water travelling towards the river Mulde should focus on the Quaternary aquifer and the main contaminants in the shallow aquifer.

There are several options for interception of contaminated groundwater travelling towards the Mulde:
- groundwater extraction and *ex situ* treatment;
- funnel-and-gate, SAFIRA-technologies implemented in gate-reactor;
- reactive wall, together with additional funnelling;
- reactive wall;
- reactive wall and diversion of clean groundwater as funnel;
- no wall, no funnels, using Mulde flood plain as bio-reactor;

These remedial options have been ranked by decreasing extent to which the contaminated groundwater is actively collected before it is treated.

The most active way to collect the groundwater for treatment would be pump-and-treat. Treated groundwater has to be discharged on the river Mulde or injected into the subsurface. Both possibilities have to deal with geochemical and biological processes hindering injection or surface water discharge due to ex-situ treatment. The different redox status between the effluent and the receptor (the subsurface or the river Mulde) forms a specific research item. Problems like for example possible clogging and precipitation of oxides are related.

The concept of funnel-and-gate seems more feasible to protect the river. The gate can be placed parallel to the river downstream of the contaminated groundwater plume. In this way groundwater is treated in-situ. The volume of groundwater that has to be treated in the 'gate' depends on the degree of funnelling. To assure that all contaminated groundwater is trapped and treated in the gate, some pumping may be necessary. A cost optimum has to be found between the effort of funnelling and the volume of groundwater to be pumped towards the gate. If pumping has to be avoided by all means, a reactive wall could act as gate. Again a cost optimum has to be found between the degree of funnelling and the required extent of the gate. Funnelling could be done by hydrological means (groundwater extraction), sheet piling or physical or chemical isolation. These funnel systems are probably even or more expensive than the gate and will have to be replaced in due time.

A more cost-effective solution would be a reactive wall or biological treatment zone, optionally in combination with groundwater extraction systems. Groundwater may be funnelled towards a biological treatment zone by groundwater extraction downstream of the wall. The extracted groundwater originates from the wall and doesn't need further treatment. This 'clean' groundwater could be injected upstream between reactive walls in order to create a hydrological barrier. In this way the extent of the active zones could be largely reduced, no funnels are required and groundwater is passively treated in situ within the walls.

A similar extensive approach is to use the natural hydrological discharge to funnel contaminated groundwater towards the floodplains along the river. Biodegradation of contaminants could be facilitated by using degradation capacity of those wetlands (helophytic filters). This approach requires careful management of those areas.

For all the options mentioned above, the summed volume of contaminated groundwater to be treated and or extracted is the same. However, the options differ with respect to the effort put in the funnel & gate or reactive walls. If the cost of funnelling groundwater is less than the cost of the gate, options with the emphasis on large funnels and small gates should be preferred. This is the case if clean groundwater extraction downstream of the reactive wall is used as a funnel. The

cost of this hydrological funnel is low compared to traditional downstream groundwater extraction or sheet piles as funnel because the extracted groundwater is clean and doesn't have to be treated. As already mentioned a proper estimation of the volume of contaminated groundwater to be treated can only be made when the hydrological system is characterised. A hydrological model is most useful for this purpose. Based on a rough estimate of the contaminated area of 100 km^2, one millimetre recharge per day and the educated guess that 10-30% of water infiltrating in this area will discharge into the Mulde, about 1.10^4 till 3.10^4 cubic meters a day have to be treated. The rest of the infiltrating groundwater within the 100 km^2 penetrates the Tertiary aquifer.

Deeper aquifer: few or no objects at risk
Probably the largest part of the contaminated groundwater will infiltrate towards the deeper, tertiary aquifer, due to the small capacity of the river Mulde to discharge deeper groundwater. Contaminants in the deeper aquifer will migrate over large distances (>100 km) before they eventually discharge to surface water. Due to adsorption and degradation it may take thousands of years before surface water (e.g. river Elbe) is contaminated by this deeper groundwater. Within this time frame risks for exposure of humans to this contaminated groundwater are small. Exceptions are of course extraction of groundwater from the deeper aquifer for drinking water purposes. The migration of contaminants could be monitored to support planning and future risk assessment. Treatment of the deeper aquifer seems not cost-effective due to the absence of objects at risk and other priorities.

Former mining pit (artificial lake): funnel &gate
Groundwater extraction around the former mining pit forced groundwater originating from the village of Bitterfeld towards the mining pit, where it was extracted. Contaminated groundwater travelled towards the extraction wells. The situation has changed drastically, as the groundwater extraction has been ceased and the pit has been filled with surface water from the Mulde. The groundwater flow will eventually resemble the 'natural' flow regime before mining started. This implies that the groundwater formerly flowing towards the pit will infiltrate towards deeper aquifer and flow towards the river Mulde. The extent of exchange of groundwater between the water of the artificial lake could be assessed using a hydrological model of the area. At this moment the extent of exchange is not known and it is not certain if and to what extends the lake is at risk.

When the lake would be at risk, a funnel-and-gate system could be installed between the front of the contaminant plume and the lakeshore. The same options could be applied as mentioned in the section 'Mulde', although extraction of groundwater as a funnel would extract a lot of water from the lake. An alternative for this particular case could be stimulated degradation of chloroaromatics and VC within the natural redox-transition zone groundwater-surface water (enhanced bioremediation).

7.4 Possible limitations of current technologies for plume management

Within the funnel-and-gate or the reactive wall approach as described in the previous paragraphs, an *in situ* treatment process should be implemented. Most viable alternatives seem to be:
- complete (enhanced) *in situ* bioremediation (combined anaerobic and aerobic stages);
- physiochemical methods (zero valent iron, catalysts, activated carbon) in combination with enhanced bioremediation.

Limitations of the proposed funnel-and-gate systems could be both technical and financial. Besides technical limitations of the treatment technologies currently under investigation, technical problems could also arise when groundwater has to be infiltrated after extraction and treatment (e.g. clogging effects). Especially combined hydrological funnel-and-gate systems seem to be susceptible for these kinds of technical problems. Passive techniques like biological treatment

zones or reactive walls are less susceptible for clogging, because groundwater passes those walls at natural flow rate (except if groundwater is funnelled towards the wall).

Decreasing the extent of the required gate by funnelling can reduce financial limitations of treatment technologies currently being developed. A cost-effective way to do this is by hydrological funnelling of groundwater by extraction downstream of the gate. At this moment no estimate of the volume of groundwater to be treated is known, so an evaluation of the cost-effectiveness of the different treatment technologies or bioreactors is not made at this stage.

7.5 Concluding remarks on plume management

The SAFIRA research projects have focussed on development of in-situ treatment technologies, which could form a part of a funnel-and-gate or reactive wall solution for the Bitterfeld region.

The funnel-and-gate concept seems feasible for protection of objects at risk downstream from the contaminant plume like the river Mulde and the artificially created lake. It is to be expected that shallow groundwater will contribute the most to contamination of the river and the lake. Development of treatment technologies should focus on the shallow groundwater contaminants.

Several concepts for funnelling and gate can be designed for protection of the Mulde and the artificial lake. Passive treatment techniques like reactive walls are preferred, because risks of technical failure of passive systems are smaller than for active systems. Funnelling groundwater towards these gates could be necessary to reduce the cost of the gate systems. Extraction of groundwater behind a small reactive wall could be a cost-effective funnel. The extracted groundwater is clean and doesn't need further treatment. An even less intensive concept for funnel-and-gate is to use natural discharge points instead of active funnels. The floodplain of the river Mulde could be used to collect and treat contaminated groundwater, because contaminated groundwater will naturally discharge in those plains. The treatment systems should be adapted to this type of natural funnel-and-gate.

The largest part of the water infiltrating in the Bitterfeld area won't discharge into the Mulde, but will penetrate the deeper Tertiary aquifer. The same funnel-and-gate options could be applied to this deeper aquifer, although the required effort to do so would be twice or three times higher. With no apparent objects at risk, monitoring the migration of the contaminants and careful planning of groundwater extractions seems more appropriate.

It is recommended to assess the flux of contaminated groundwater towards gates. The volume of groundwater to be treated at the gate and its contaminant load are key figures for estimation of the remediation costs and design. These costs are necessary to decide on the feasibility of the proposed concepts for plume management for the Bitterfeld contamination. Special attention should be given to subsurface heterogeneity [50].

CHAPTER 8

KNOWLEDGE EXCHANGE

An important aspect of the Bitterfeld project was the exchange of knowledge gained in the NOBIS/SKB project and within the SAFIRA framework.
This exchange of results of research among the partners in the NOBIS/SKB consortium and the KEG as well as SAFIRA partners and others has been brought about in several ways:

- The FZK/TNO Consoil conference was held in Leipzig on 18-22 September 2000. Separate sessions were dedicated to the Bitterfeld area, namely, the SAFIRA project and the Spittelwasser case;
- Knowledge exchange meetings were held throughout the project on a semi-annual basis;
- Workshop Microbiology in the SAFIRA project held in Leipzig, 14 November 2000;
- Within the framework of the Bitterfeld mission in January 2002 [39], a KEG delegation visited the Bitterfeld region. An implementation plan was set up for the region, using the knowledge applied at the SAFIRA test site. Besides that, also the upscaling of the enhanced Natural Attenuation Technology in the field was prepared;
- A SAFIRA-broad Workshop, held June 4-5, 2002 in Leipzig, including presentations of the organisations involved and an excursion to the Bitterfeld region. Before this Workshop in Leipzig, a summarising update was produced for the KEG;
- The abstracts of the workshops of November 2000 and June 2002 have been published and distributed among interested parties [40 and 49]
- A poster, entitled: “A two-phase anaerobic/aerobic *in situ* treatment zone system for the Bitterfeld region” was presented at the European Conference on Natural Attenuation, Heidelberg, 15-17 October, 2002.

CHAPTER 9

CONCLUDING REMARKS AND RECOMMENDATIONS

9.1 Introduction

This chapter summarizes the most important conclusions and recommendations from the Bitterfeld project.
As an overview, figure 51 shows the significance of the project phases for the development of a full-scale applicable field system. It also shows the results that have been obtained in each phase.

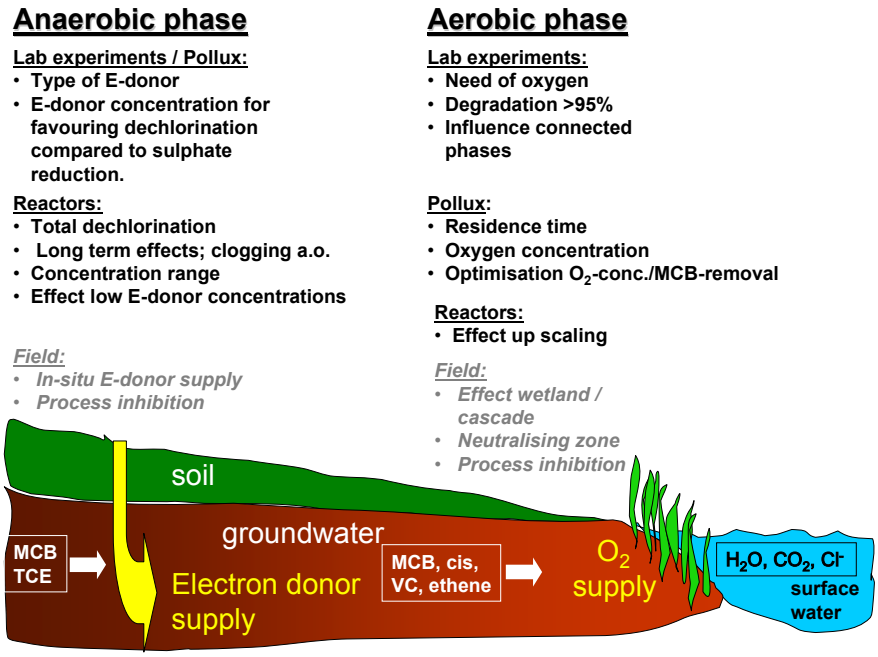


Fig. 51. Contribution of different research phases to a full-scale applicable system (in italics the issues that could not yet be addressed).

In the following paragraphs, concluding remarks and recommendations will focus on respectively the research at the Bitterfeld test site and on upscaling / implementation.

9.2 Research at the Bitterfeld test site

Phase 1: Transformation of chloroethenes under anaerobic conditions
TCE has been dechlorinated to *cis*-DCE, VC and ethene under anaerobic conditions in the presence of a complex electron donor (applied as a mixture of volatile fatty acids and lactate) both in the column and the reactor systems.

Optimisation of the electron donor dosage in the anaerobic stage of the process and the competition between dechlorinating and sulphate reducing bacteria for the electron donor
For the reduction of TCE in the anaerobic reactors, there should be enough electron donor available to provide the necessary reducing equivalents. However, also sulphate will be reduced under these circumstances, which results in a competition for electron donor between sulphate-reducing and dechlorinating bacteria.

It turned out to be possible to gain increased dechlorination combined with a decrease of sulphate reduction at low electron donor concentrations (the quantity was decreased from 2 to 0.1* the total amount needed for a reaction with both the chlorinated hydrocarbons and the sulphate). The dechlorination was also extended to VC and ethene, which indicates that sulphate reduction and dechlorination to ethene can take place simultaneously (section 2.3.2).

Despite the high sulphate concentrations present in the groundwater at the Bitterfeld test site, the results from the research carried out in the *in situ* reactors have shown very promising results for the anaerobic removal of chlorinated ethenes.

After almost two years of electron donor addition at high concentrations, the reactor systems showed clogging problems due to sulphide precipitation and excessive gas formation. However, the discontinuation of the VFA addition caused a rapid improvement (within two weeks) of the operation, showing the system's robustness because it can soon recover from temporary high contaminant concentrations.

Phase 2: Transformation of monochlorobenzene under aerobic conditions
Oxygen concentrations of 18 mg/L resulted in 100% removal of monochlorobenzene in the aerobic (rather than microaerobic) stage in the column systems. This removal efficiency was maintained for over half a year, after which it dropped to ca. 50% without apparent changes in the operation conditions. This raises questions on the sustainability of the stimulated biodegradation process, which we have not been able to address within this project.
CB was not transformed in the (non-optimised, originally named) "microaerobic" part of the sequential anaerobic-microaerobic reactor system, most likely due to a lack of oxygen.

Phase 1 and 2: The coupling of the anaerobic and the microaerobic reactor systems
Both in the laboratory column and the in situ reactor systems was shown that an aerobic system linked to an anaerobic dechlorinating system resulted in badly sustainable or no CB degrading performance of the second phase.
Therefore, the *in situ* reactor operation has focussed in the last research period on separated anaerobic and aerobic systems to deal with chlorinated ethenes and CB respectively.
Also in the field, a buffer zone should be created to prevent negative effects from the effluent of the anaerobic phase to the aerobic phase.

Experiences with the in-situ reactor infrastructure at the Bitterfeld test site
Typical for the SAFIRA research was the opportunity to investigate clean-up systems in in-situ reactors in shafts of 22 m depth and 3 m diameter. Although the reactor systems basically form a perfect stage for upscaling systems from column studies to pilots in the field, the flexibility turned out to be limited.

As an example, the artificial addition of TCE to the influent of the in-situ reactors (the pumped up groundwater at the Bitterfeld test site did not contain sufficiently high TCE-concentrations) was a structural problem for the infrastructure at the test site.

Most essential is that the research is carried out with site specific groundwater and aquifer material. In future occasions, direct up scaling from columns to field pilots should be considered. When applicable, an intermediate stage could be a more flexible reactor system above ground.

In any case, the SAFIRA research has strongly been focussed on the in-situ reactor systems and did not yet enable research groups to upscale their system to field pilots.

Different SAFIRA technologies for the Bitterfeld region
SAFIRA has shown that (multi-)stage technologies are basically capable of dealing with the mix of contaminants present at the mega-site (see appendix A**)**.
(Multi-)stage technologies have successfully passed the laboratory, bench-scale and reactor-scale testing phases. The technologies are applicable in reactive walls, funnel-and-gate approaches or as on-site technology. Prolonged reactor tests and pilot tests will be needed to assess the flexibility of each of the technologies, to be able to include flexibility into the design and to build and operate large-scale applications effectively and efficiently.
The one single-stage technology tested (adsorption on activated carbon) has been found low-tech, proven and effective for long-term removal of hydrophobic, low solubility contaminants only. Thus, this technology itself cannot fully deal with the mix of contaminants found in Bitterfeld.

During the SAFIRA research period a paradigm shift occurred within most of the SAFIRA research groups: in most cases, not a single technology, but a smart combination of technologies will lead to the most efficient approach to the contaminated groundwater.

9.3 **Up scaling and implementation**

Large-scale application as a part of a regional plume management approach
Possibilities for large-scale application have been studied within the framework of a separate mission to the Bitterfeld region. Based on the findings of the SAFIRA test site and study of available data, the mission team came to a concept on field scale. The concept is applicable in the plume and not in the source area. It is meant to prevent that contaminated groundwater is draining into the surface water system.
Along the flow lines, an area is selected to inject electron donors. Downstream of the injection zone, microorganisms, which are naturally present, are stimulated to start the dechlorination as proven in the SAFIRA test site.

Anaerobically, the degradation in the 2-phase system goes as far as total dechlorination to ethene. Consequently, an aerobic step is needed. This aerobic zone, downstream of the first one, can be an artificially created or natural wetland. Groundwater is seeping into a (created) wetland with an interface of anaerobic / aerobic conditions. The wetlands can be applied for the degradation of monochlorobenzene and the metabolites of the chlorinated hydrocarbons under (semi)aerobic conditions (Natural Attenuation at groundwater/surface water interfaces). Thus, the partly cleaned water then reaches the interception canal. This canal is a new or deepened existing drainage canal in which the water is flowing into the direction of the Mulde, passing some cascades. Figure 52 shows schematically the possible application of the 2-phase technology.

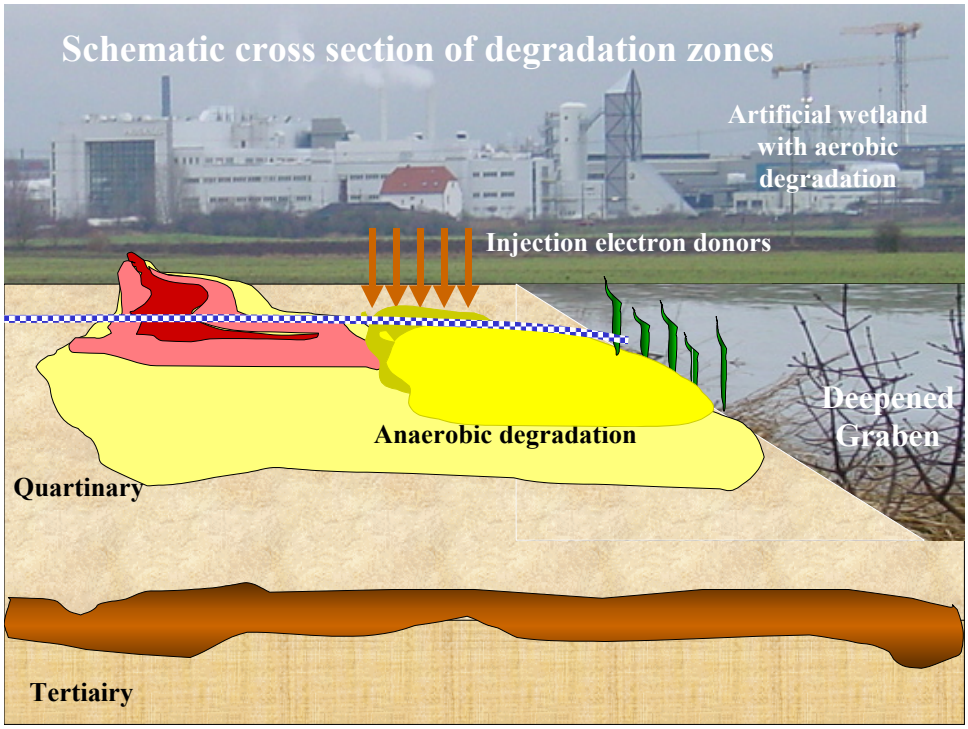


Fig. 52. Cross section of the anaerobic degradation zone with electron donor injection, and the artificial wetland in which aerobic degradation takes place (picture B. Satijn).

Field study and implementation

Field measurements were planned to get insight in the actual occurrence of NA in the Bitterfeld area. Also, the possibilities for the implementation of the sequential anaerobic-microaerobic processes were planned to be assessed.

To date, sufficient results have been gained from the column and reactor systems for up scaling to the field. Besides, after about four years of research in the in situ reactors and the possible occurrence of defiencies in the aquifer material, it is considered no longer useful to continue the research in the present systems.

Due to the flooding catastrophe in the Bitterfeld region in August 2002, but also the specific conditions in the Bitterfeld area, it has not yet been possible to carry out field measurements as a preparation for a pilot test on field scale.

However, this research has shown that the 2-phase system is ready for up scaling in the field and that this in fact is the most logic way to find useful application for this low intensity, low cost method.

Research continuation within other frameworks

Solutions for the Bitterfeld region are currently also being investigated within the framework of the EU-WELCOME (Water, Environment, Landscape management at COntaminated MEgasites) project. This project focuses on a megasite approach and includes natural attenuation in the groundwater and in the groundwater / surface water interface.

Continuing research in the Bitterfeld region has also been planned within the framework of the EU-AQUATERRA project, which is expected to be started early 2004. The work will focus on interaction fluxes of the groundwater with the surface water. The emphasis will lay on the survey of transport processes with the seepage water from soil surface via the vadose zone to the groundwater and further in to the surface water body.

Importance of SAFIRA technologies for the Netherlands
Most contaminated sites are essentially less complicated than the Bitterfeld case. With regard to these contaminations, SAFIRA has presented new (multi-)stage technologies that add to the technologies at hand. The knowledge and experience gained on the SAFIRA innovative technologies may facilitate and boost pilot-scale applications outside of the Bitterfeld region, including The Netherlands, by carefully matching the merits of each of the technologies to the specific situation and requirements of the case.

Application of the 2-phase system at more common situations
Apart from the Bitterfeld area, the investigated 2-phase system can also be applied at other areas or sites, either large or small scale, with a combination of chlorinated aliphatic and aromatic compounds or other (cocktails of) contaminants that need a 2-phase approach. A recent example is the successful field pilot of a site contaminated with hexachlorocyclohexane (HCH) in Hengelo, the Netherlands.

It is worthwhile to put effort in a search for a substantial number of applications for the system that was subject of research within this project.

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APPENDIX A

GEOCHEMICAL ANALYSIS OF THE BITTERFELD GROUNDWATER

Geochemical analysis of the groundwater used in the on-site mobile test unit. Concentrations are given in mg l^{-1} unless stated otherwise. The "June-August 1998" data are for the groundwater that was used in the on-site test unit. Data from June 1998 and 1997 are ranges measured in different sampling wells (different depths).

Parameter	June-August 1998	June 1998/1	June 1998/2	1997
pH	6.8	6.5-7.7	6.6-7.3	
Temperature (°C)		12.6-15.5		
Redox potential (mV)	-160	(-97)-(+263)		
Conductivity (mS/cm^2)	2.13	1.4-4.05	1.4-3.5	
TOC		3.1-30.0		
AOX	9	0.02-20.2		7.40-30.1
1,2-cis-DCE		0-21.6		
1,2-trans-DCE		0-10.1		
Chlorobenzene	15-45	0-29.6		0.09-50.7
1,1,2,2-TeCA	up to 0.04			
O_2	< 10µg/l	0-0.1		
HCO_3^-	203-500			
Cl^-	430-500	52.0-800	48.6-814	64.0-1266
NO_3^-	<0.1		1.04-37.8	0.05-37.8
NO_2^-	<0.05		0-0.99	
NH_4^+	0.34		0.01-4.98	
P_{total}			0.21-4.2	
PO_4^{3-}	3-15		0.04-17.3	
S_{total}			205	
SO_4^{2-}	380-800		351-975	554-975
Fe_{total}	<0.02			0.01-3.52
Mn	0.08		0-1.03	0.15-2.10
Ca	300		187-405	222-619
Mg	35		26.0-61.6	27.0-74.5
Al			0-0.45	
K	170		10.5-145.4	15.0-134
Na	170		21.8-202	32.0-253
As			0	
B			0.25-1.35	0.2-1.35
Br			0.13-2.54	
Zn			0.01-0.18	
Pb			0	
Hg			0.0001-0.001	
Co			0	
Cr			0	
Cu			0	
Ba			0.018-0.196	
Ni			0-0.03	

APPENDIX B

SET-UP OF BATCH EXPERIMENTS - TRANSFORMATION OF CHLOROETHENES UNDER ANAEROBIC CONDITIONS

The experiments were carried out in 120-ml serum flasks with 25 ml effluent of the anaerobic reactor fed with a mixture of Methanol and G31 and groundwater (75 ml) from the contaminated site in Bitterfeld, which was amended with 10 mg l^{-1} TCE. The final TCE concentration in the serum flasks was 6 mg l^{-1}. Electron donors were dosed in concentrations which, based on electron equivalents (eeq), were equal to 0.1, 1 or 10 times the amounts needed for complete reduction of the TCE and the sulfate present in the groundwater.

Lactate, acetate or a mixture of methanol and G31 (ratio 80%/20%) were used as the electron donors. The batches were incubated on a rotary shaker at 20°C.

The following combinations were investigated:

Batch no.	E-donor	x * ED
1,2	Lactate	0.1
3,4	Lactate	1
5,6	Lactate	10
7,8	Acetate	0.1
9,10	Acetate	1
11,12	Acetate	10
13,14	MeOH/G31	0.1
15,16	MeOH/G31	1
17,18	MeOH/G31	10

Chloroethenes and VFA, H_2 and sulfate were measured on a regular basis as described in reference [2].

Amendments:
Lactate: 386 g l^{-1} Na-acetate (0.02 ml, 0.2 ml or 2ml)
Acetate: 1.05 g/ml (0.01 ml, 0.1 ml, or 1 ml)
MeOH/G31: 411 ml l^{-1} methanol and 200 g l^{-1} G31 (0.01 ml, 0.1 ml, or 1 ml)

APPENDIX C

SET-UP OF BATCH EXPERIMENTS - TRANSFORMATION OF CHLOROETHENES UNDER MICRO-AEROBIC CONDITIONS

originating from the microaerobic columns and 20 ml effluent of the microaerobic reactor 1 and groundwater (80 ml) from the contaminated site in Bitterfeld containing around 15 mg l^{-1} (133 µM) chlorobenzene. The final concentration of CB in the serum flasks was 12 mg l^{-1} (106 µM). Co-substrates were added in similar concentrations compared to chlorobenzene. The batches were prepared in the anaerobic chamber to avoid "contamination" with oxygen. After an equilibration phase of 3 days the chlorobenzene concentrations were measured. At this point in time the auxiliary compounds (cosubstrates, nitrate, iron, oxygen) were added.

The following combinations were investigated:

Batch nr.	Condition	Cosubstrate/Addition
1,2		no additions
3,4	Denitrifying	nitrate
5,6	Denitrifying	nitrate, toluene
7,8	Denitrifying	nitrate, benzoate
9,10	Denitrifying	nitrate, phenol
11,12	Microaerobic	nitrate and 3 mg l^{-1} oxygen
13,14	Microaerobic	nitrate and 3 mg l^{-1} oxygen, toluene
15,16	Microaerobic	nitrate and 3 mg l^{-1} oxygen, benzoate
17,18	Microaerobic	nitrate and 3 mg l^{-1} oxygen, phenol
19, 20	Iron reducing	iron reducing conditions
21,22	Iron reducing/denitrifying	iron, nitrate
23,24	Iron reducing/denitrifying/microaerobic	iron, nitrate and 3 mg l^{-1} oxygen

Batches were incubated on a rotary shaker at 20 °C. Oxygen was added weekly (when appropriate). Chlorobenzene and cosubstrates (toluene only), and nitrate were measured biweekly as described earlier [2].
Auxiliary compounds were replenished after they had been depleted.
Nitrate was added at day 0, 14, and 46.
Iron was added at day 0, 14, and 46.
Toluene, benzoate and phenol were added at day 0, 14, and 46.

Amendments:
Nitrate: 2 times overdose: 1,2 mM (as Na-nitrate)
Iron: 2 times overdose: 1,2mM (as Fe(III)Cl3
O_2: 3 mg l^{-1} weekly (as 6 mg l^{-1} H_2O_2)
Toluene: 106 µM
Benzoate: 106 µM as Na-benzoate
Phenol: 106 µM

APPENDIX D

SUMMARY OF KEY QUALIFICATIONS OF SAFIRA TECHNOLOGIES

	1/2. Enhanced biodegradation in anaerobic and aerobic conditions	3. Simultaneous adsorption and microbial degradation using activated carbon	5. Adsorption on activated carbon	6. Zeolite-supported and membrane-supported palladium catalysts	8. Coupled in-situ reactors with optimised (geo-) chemical processes downstream
Short description	- in-situ technology for activated (bio-stimulated) zones in the aquifer or in transition or borderline zones, where biodegradation is enhanced in a two-phase system - first anaerobic step is to degrade chloro-ethenes (and others) by adding electron donor and nitrogen source - second aerobic step is landscape-integrated approach like cascades, basically increasing oxygen content using ambient air - alternative second step, as tested extensively by one of the German teams, is to degrade mono chloro-benzene (and others) by adding hydrogen peroxide and nitrate	- in-situ technology for barrier using granulated activated carbon, where biodegradation is enhanced in a two-phase system - first anaerobic step is to adsorb and degrade chloro-ethenes (and others), by dosing auxiliary substrates like sucrose and ethanol - second aerobic step is to adsorb and degrade mono chloro-benzene (and others), by dosing auxiliary substrates like ethene, chloro-benzenes, benzene and toluene - result is extended active life-time of activated carbon barrier	- in-situ low-tech technology for barrier using granulated activated carbon, with adsorption of contaminants as dominant process - no substrates or chemicals added	- on-site technology due to the multi-stage, complex technology - several pre-treatment techniques in the water phase: zero-valent iron to remove sulfides, enrich groundwater with hydrogen and start de-chlorination of aliphatic compounds, NaOH dosing to deal with 1,1,2,2-tetrachloro-ethane, activated carbon - vacuum stripping of contaminants, gas flow to pass absorber with zinc oxide to protect catalysts - hydro-de-chlorination over Pd-catalysts in the gas phase - de-ironing of the groundwater is NOT required	- in-situ technology for barrier - two types have shown best results - sequential zero-valent iron and activated carbon: volatile, less adsorbing substances removed by iron, other substances by activated carbon, thus increasing the life-time of the carbon - sequential zero-valent iron and ORC: reducible substances removed by iron, bio-degradable substances in ORC barrier - no (other) substrates or chemicals added
Status of technology development	- laboratory and reactor tests with synthetically contaminated groundwater concluded successfully for first step and alternative second step; low-tech second step of landscape integrated approach has not been tested extensively; type and costs of substrates and chemicals to be established	- laboratory tests with synthetically contaminated groundwater concluded successfully; information from reactors available but not yet published; type and costs of substrates and chemicals to be established	- laboratory and reactor tests concluded successfully; ready for pilot project as results suggest stable long-term performance and predictable behaviour with regard to loading and adsorption characteristics	- laboratory and reactor tests concluded successfully; details still being tested	- laboratory and reactor tests concluded successfully; issues regarding the optimisation of downstream processes still being tested
Applicability and suitability	- plume technology, to protect objects of risk like surface water systems from draining contaminated groundwater - high sulphate contents, as typical for the Bitterfeld area, can be dealt with - potentially effective for a wide range of contaminants: volatile aromatics, MTBE, cresols and phenols, chlorinated pesticides, chloro-benzenes incl. hexa en penta, chloro-ethenes, chlorinated aliphatics, azo-dyes, TNT, chlorinated phenols and PCB's	- potentially effective for wide range of contaminants incl. cocktails of contaminants	- long-term removal of hydrophobic, low solubility contaminants like mono chloro-benzene - not applicable for hydrophilic, high solubility contaminants	- effective for wide range of contaminants incl. vinylchloride, and for wide range of concentrations - probably most cost-effective in hot spots in the absence of 1,1,2,2-tetrachloroethane	- potentially effective for a wide range of contaminants
Costs	- low capital costs and low operational costs	- high initial capital costs and moderated operational costs due to the extended effective life-time of the activated carbon	- lower initial capital costs than the high-tech application of simultaneous adsorption and microbial degradation using activated carbon but possibly higher operational costs due to the shorter effective life-time of the activated carbon	- unknown	- high initial capital costs; operational costs depend upon the extended effective life-time of the activated carbon vs. ORC and on the lifetime of the iron