NOBIS 98-1-01

BITTERFELD: BIOREMEDIATION OF REGIONAL CONTAMINATED AQUIFERS

Phase I and II

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Samenvatting

Dit rapport beschrijft het onderzoek dat in fase I en II van het project "Bitterfeld: Bioremediation of regional contaminated aquifers" is uitgevoerd. Dit NOBIS project is uitgevoerd binnen het raamwerk van het (Duitse) SAFIRA project. Het NOBIS project behelst onderzoek naar de toepassing van een gestimuleerde bioremediatie variant voor de reiniging van grondwater dat op grote schaal is verontreinigd met alifatische en aromatische chloorverbindingen. Het grondwater wordt in een sequentieel anaëroob-microaëroob systeem behandeld. De aandacht richt zich hierbij op de anaërobe afbraak van de alifatische verbindingen na stimulering van de omzetting door toediening van elektronendonor, terwijl afbraak van de aromatische verbindingen wordt bewerkstelligd onder microaërobe omstandigheden na toevoegen van nitraat en een geringe hoeveelheid zuurstof. Het onderzoek is enerzijds in "bench-scale" en laboratorium kolomexperimenten uitgevoerd en anderzijds in grootschaliger (4,4 m^3) in situ reactoren in Bitterfeld.

Naast deze biologische variant worden in SAFIRA verband op de proeflocatie door andere onderzoeksgroepen ook fysisch-chemische technieken onderzocht. De voorlopige resultaten van deze technologieën, alsmede de mogelijke implicaties van het onderzoek voor de verwijdering van de verontreiniging op regionale schaal worden eveneens in dit rapport beschreven.

Trefwoorden

Gecontroleerde termen:	**Vrije trefwoorden:**
biologische afbraak, bodem, chloorkoolwaterstoffen, in-situ	alifatische chloorkoolwaterstoffen, aromatische chloorkoolwaterstoffen, reductieve dechlorering, sequentieel anaëroob-microaëroob, sulfaatreductie

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Titel project Bitterfeld: Bioremediatie van regionaal verontreinigde aquifers - Fase I en II	**Projectleiding** TNO-MEP (dr. ir. M.H.A. van Eekert, 055-5493474)

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Abstract

The research is this report deals with phases I and II of the project "Bitterfeld: bioremediation of regional contaminated aquifers". This NOBIS project was carried out within the framework of the (German) SAFIRA project. The NOBIS project focusses on the feasibility of a stimulated bioremediation technology for the treatment of groundwater that is contaminated with aliphatic and aromatic chlorinated compounds at a regional scale. The groundwater is treated in a sequential anaerobic-microaerobic treatment system. The aim of the research is the anaerobic degradation of the chlorinated aliphatics after the addition of electron donor to the groundwater, while the chlorinated aromatics are removed under microaerobic conditions in which case nitrate and traces of oxygen are dosed to the groundwater. The research is carried out in on site "bench scale" and laboratory column systems and in large scale (4.4 m^3) in situ reactors.

Besides biological remediation, several physicochemical technologies are also being tested by other research groups at the Bitterfeld location. The preliminary results that are obtained with those techniques, and the possible implications of the research as a whole for the removal of the contaminates at a larger scale are also discussed in this report.

Keywords
Controlled terms:
bioremediation, chlorobenzene, chloroethenes, in situ, on-site

Uncontrolled terms
chlorinated aliphatic compounds, chlorinated aromatic compounds, contaminated groundwaters

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Project title
Bitterfeld: Bioremediation of regional contaminated aquifers - Phase I and II

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FOREWORD

All over Europe sites can be found that are contaminated at a regional scale. One of these sites is located near Bitterfeld in former Easter Germany. Due to mining activities and the presence of chemical industry an area of around 25 km^2 is polluted with a variety of chemical compounds.

This report comprises the results of phase I and phase II of the NOBIS project "Bitterfeld: Bioremediation of regional contaminated aquifers" that aimed at finding a biological technology to treat the polluted groundwater. The NOBIS project was carried out in the framework of the SAFIRA (SAnierungs Forschung In Regional kontaminierten Aquiferen) project, which comprises the activities of several German universities and UFZ (Umwelt Forschungs Zentrum – Leipzig) to find a physical-chemical or biological method to remediate the large contaminated aquifer.

The NOBIS project was carried out by a consortium that consisted of TNO MEP, TNO NITG, Tebodin, HBG/HWZ and Shell. During the first two phases on site and in situ reactor experiments were carried out both in Bitterfeld and in Apeldoorn. The consortium would like to acknowledge UFZ for their co-operation and assistance in carrying out the experiments.

December 2000

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SUMMARY

Bitterfeld: Bioremediation of regional contaminated aquifers
Phase I and II

Description of the Bitterfeld-Wolfen contamination situation

Large scale areas contaminated with xenobiotic compounds can be found all over Europe due to industrial activities. One of the areas with these problems is the Bitterfeld-Wolfen region near Leipzig in former East Germany. This used to be a center of lignite open-pit mining and, later, a center of chemical industry. In Bitterfeld the groundwater table was kept at a low level to make lignite mining possible. Chemical industries discarded hundreds of thousands of tons of chemical waste in the subsurface and in old mining pits. As a result the groundwater became heavily polluted. At present, an area of 25 km^2 is heavily contaminated to a depth of several tenths of meters with high concentrations of chlorinated aliphatic and aromatic compounds and more complex compounds like hexachlorocyclohexane (HCH), PCBs and dioxins. At the edges of this large scale source area, plumes of mobile chemicals and natural degradation products can be found in very high concentrations.

Currently, severe changes in the groundwater situation are occurring. Recently, the pumps that kept the groundwater regionally at the low (artificial) level were shut down. As a result the groundwater table is rising and the groundwater flow will change to its original natural direction and velocities. These changes in the groundwater situation urge the development of approaches to protect potentially endangered environmental receptors in the region. Therefore, it was decided to start the SAFIRA (SAnierungs Forschung In Regional kontaminierten Aquiferen) research project (with a 17 Million DM budget) with the aim to develop and test technically and economically feasible technologies that can be used in an integrated plume management approach for the region.

SAFIRA and the NOBIS-participation in this international multi-research group project

The SAFIRA project develops and tests several groundwater treatment technologies in a large underground testing facility, at a site in Bitterfeld, at the edge of the heavily contaminated source area. The project and the test facility are managed by UFZ Leipzig (Umwelt Forschungs Zentrum). Several research-groups have been invited to participate in SAFIRA.
A NOBIS consortium, managed by TNO, with Tebodin, HBG-HWZ and Shell as partners, was invited to participate to test an in-situ biological technology for enhanced attenuation (NA^+ = Natural Attenuation plus) of mobile chlorinated ethenes and aromatics (NOBIS project nr. 98-1-01: "Bitterfeld: Bioremediation of regional contaminated aquifers"). The large scale test facilities were made available for this team for the period 1999 to 2002.
Eight different physicochemical and biological technologies are being tested by eight research groups in total, and most of the technologies have entered the phase of testing under large scale underground conditions at the SAFIRA testing site.

The NOBIS-TNO-UFZ team has started their part of the project in December 1998 with an on-site column test program (Phase I), followed by the initiation of the underground reactor testing program (Phase II).

Aim and significance of the project

The aim of the SAFIRA project framework and the NOBIS 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 overall aims were:

- To select suitable techniques (in terms of technical feasibility, efficiency, reliability and costs) for such situations, by testing under real-scale situations. The SAFIRA partners tested physicochemical techniques. The specific aim of the NOBIS contribution was to test a suitable biological alternative (i.e. bioactivated zone and funnel-and-bioreactor approach) under real-scale conditions and to compare this method to the other physicochemical approaches tested.
- To develop a smaller scale mobile on-site testing unit for assessing suitable containment measures at other large polluted areas. The specific aim of the NOBIS participation was to develop the biological test unit in such an installation.
- In the near future, follow-up initiatives are planned to use this mobile on-site treat-unit at other large sites contaminated with mixtures of chloroaliphatic, chloroaromatic and pesticide (i.e. HCH) compounds.

Information/results obtained in the NOBIS-SAFIRA co-operation (Phase I and II)

The groundwater at the Bitterfeld location contains both chlorobenzene and chlorinated ethenes. Chlorobenzene is the main contaminant found in the upper aquifer at Bitterfeld, whereas the lower aquifer contains mainly chloroethenes. The removal of these contaminants was investigated with a sequential anaerobic-microaerobic system. In the anaerobic phase chloroethenes are dechlorinated, whereas chlorobenzene is aimed to be degraded under microaerobic conditions. A difficulty in the composition of the groundwater is posed by the high sulphate concentrations (up to 750 mg/l) in the groundwater (in view of the electron donor supply and the sulphide formed). The research has been carried out in two phases: on-site and laboratory column tests and in situ reactor tests.

Phase I: on-site and laboratory column tests

In phase I of the Bitterfeld project the transformation of the contaminants was investigated with bench-scale on-site (volume 7.9 l) and laboratory columns (volume 880 ml) using groundwater and aquifer material from the Bitterfeld location. Under anaerobic conditions TCE was dechlorinated to ethene (figure S1). Electron donor (a mixture of lactate, acetate, propionate and butyrate) had to be supplied to the anaerobic columns at high dosages. The addition of nitrogen (as NH_4^+) was found to be necessary to drive dechlorination beyond cDCE to ethene. Sulphate reduction was taking place in the anaerobic columns. The results obtained in phase I did not make clear to what extent sulphate needs to be reduced before dechlorination can take place. A complete reduction of sulphate may be required. In that case, the amount of electron donor needed for the reduction of sulphate is 500-1000 times higher than the amount needed for complete dechlorination of the chloroethenes present.

It is also possible that, after addition of the nitrogen source, sulphate needs to be reduced partially. In that case lower amounts of electron donor are required. Additional experiments elucidating this are currently performed, and are not yet reported here.

Until now, sulphate reduction started before the first dechlorination of TCE was observed. Nevertheless, it could also be that an initial reduction of the aquifer material (together with the addition of a N-source) is enough to improve the environmental conditions for the dechlorinating bacteria. If that is the case, there would be no further sulphate reduction and the amount of electron donor thus could be reduced.

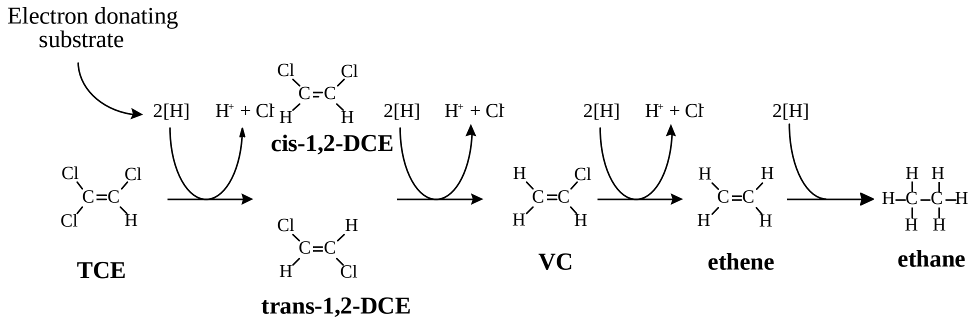


Fig. S1. Reductive dechlorination of TCE and lower chlorinated ethenes.

The degradation of chlorobenzene was initially tested under denitrifying conditions. Removal of the aromatic compound was not observed under these conditions, while nitrate was only partially used by the bacteria present. Since it was known from literature that small amounts of oxygen present in the groundwater may enhance the transformation of aromatic compounds under anaerobic conditions (according to the reaction scheme presented in figure S2), 3 mg/l was dosed to the groundwater together with the nitrate. This, however, did not result in the degradation of chlorobenzene. Finally, after increasing the oxygen concentration to twice the amount needed for complete removal of chlorobenzene, complete transformation was observed. The fate of chlorobenzene is still unknown. Currently, attempts are made to obtain complete removal of chlorobenzene at lower oxygen concentrations. The oxygen concentration will be reduced as far as possible.

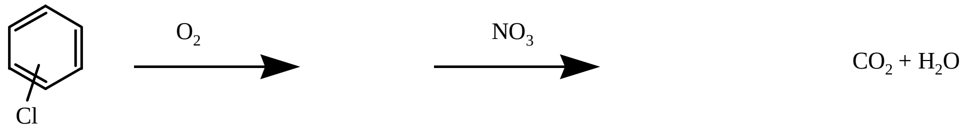


Fig. S2. Microaerobic degradation of chlorobenzene.

Phase II: in situ reactor tests

The *in situ* reactors (volume ± 4m^3) in the underground shaft have been started up (phase II) in two parallelly run anaerobic-microaerobic reactor systems. The anaerobic reactor is being operated with two times the electron donor needed for complete reduction of sulphate and the chlorinated compounds together with ammonium. In this way, the sediment will be reduced more quickly than in the on-site column experiments, while environmental conditions for the dechlorinating bacteria are better. The second reactor is operated under microaerobic conditions with nitrate and 3 mg/l oxygen. At the time of writing this report, preliminary results were not yet sufficiently available.

SAFIRA technologies and plume management in the Bitterfeld region

The results obtained so far with the different technologies tested in the SAFIRA project indicate that the physicochemical technologies (e.g., adsorption on activate carbon, palladium catalysis, electrochemical processes) alone are not able to remove all the contaminants present in the Bitterfeld groundwater. The combination of contaminants present (chlorinated aliphatic and aromatic compounds) requires at least a partial biological treatment. The biological methods used are in principle able to degrade the contaminants completely. Several bottle-necks in optimisation still need to be resolved.

The primary aim of SAFIRA is to develop groundwater contamination interception methods to protect down-gradient objects at risk in a plume management approach.

With regard to the Bitterfeld groundwater problem, the identified objects of risk are:

- the river Mulde, and the Spittelwasser;
- deeper aquifers;
- a former mining pit "the Goitsche", which becomes an artificial lake.

The village of Bitterfeld is an object at risk due to the rising water table. It is a problem for which SAFIRA initially was not meant to bring a solution. Nevertheless, although this is not discussed in this report, the developed concepts may also be used for this problem.

Funnel-and-gate concepts seem feasible for the protection of objects at risk downstream from the contaminant plume, like the river Mulde and the former mining pit. Passive systems, such as treatment zones incorporated in the present landscape and infrastructure, are probably easier to implement and are less subjective to technical failure. Such systems are therefore considered to be more powerful than active high energy-demanding barrier systems.

Recommendations for future research in the future

The topics for further research in the project should include:

- Optimisation of the electron donor dosage in the anaerobic stage of the process.
- Competition between dechlorinating bacteria and sulphate reducers for the electron donor. Can dechlorination occur while only little or no sulphate reduction takes place? High sulphate concentrations may interfere with the anaerobic process (competition for electron donor, dechlorinators must be able to sufficiently compete with sulphate reducers; otherwise high electron-donor demand due to sulphate reduction
- The coupling of the anaerobic and the microaerobic reactor systems and the effects of the composition of the groundwater (chlorinated compounds, sulphate) on the electron donor and electron acceptor demand in and the performance of the complete system.
- Sulphide formed in the anaerobic step, influencing the aerobic step (increased oxygen demand due to sulphide oxidatio
- The high oxygen demand thus far needed for complete chlorobenzene degradation, which can probably be reduced to microaerobic levels after the initiation phase; optimisation of the oxygen dosage.
- 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.

SAMENVATTING

Bitterfeld: Sanering van regionaal verontreinigde aquifers
Fase I en II

Beschrijving van de verontreinigingssituatie in Bitterfeld/Wolfen

In heel Europa worden grootschalige verontreinigingen gevonden, die daar terecht zijn gekomen door industriële activiteiten. Eén van de gebieden met dit soort problemen ligt in de Bitterfeld/Wolfen regio nabij Leipzig in voormalig Oost-Duitsland. In Bitterfeld werd gedurende tientallen jaren de grondwaterspiegel kunstmatig laag gehouden om zodoende de bruinkoolwinning ter plaatse mogelijk te maken. Chemische industrieën hebben de oude mijngroeves en de ondergrond gedurende deze tijd gebruikt om honderdduizenden tonnen chemisch afval in te storten. Dit resulteerde in een grootschalige vervuiling van het grondwater. Momenteel is ongeveer 25 km^2 zwaar verontreinigd tot een diepte van enkele tientallen meters met hoge concentraties gechloreerde alifatische en aromatische verbindingen zoals hexachloorcyclohexaan (HCH), PCBs en dioxines. Op de rand van deze grootschalige verontreinigingen kunnen verontreinigde grondwaterpluimen worden gevonden, waarin hoge concentraties van mobiele chemicaliën en hun natuurlijke afbraakproducten worden gevonden.

Op dit moment vinden er grote veranderingen plaats in de grondwatersituatie. Recentelijk zijn de pompen, die het grondwaterniveau regionaal op een (kunstmatig) laag niveau hielden, stopgezet. Hierdoor stijgt de grondwaterspiegel en zal de grondwaterstroom zijn natuurlijke loop en snelheid weer aannemen. Deze veranderingen maken de ontwikkeling van nieuwe technologieen die de potentieel bedreigde gebieden in de regio kunnen beschermen noodzakelijk. Om dit te bewerkstelligen is het SAFIRA (SAnierungs Forschung In Regional kontaminierten Aquiferen) onderzoeksproject (met een budget van 17 miljoen D-Mark) gestart met als doel om technisch en economisch haalbare technologieën, die mogelijk in een geïntegreerde pluimbenadering voor de regio kunnen dienen, te ontwikkelen en te testen.

SAFIRA en de deelname van NOBIS in dit internationale onderzoeksproject

Het SAFIRA project ontwikkelt en onderzoekt op een locatie in Bitterfeld op de rand van het zwaar verontreinigde gebied verschillende grondwaterbehandelingstechnologieën in een grote ondergrondse faciliteit. Het project en de onderzoekslocatie worden beheerd door UFZ Leipzig (Umwelt Forschungs Zentrum). Verscheidene onderzoeksgroepen zijn uitgenodigd om deel te nemen in SAFIRA. Een NOBIS consortium, onder penvoering van TNO, met Tebodin, HBG-HWZ en Shell als partners, is gevraagd deel te nemen en een in situ gestimuleerde biologische natuurlijke afbraakvariant te testen (NA$^+$ = Natuurlijke Afbraak plus) van mobiele gechloreerde ethenen en aromaten (NOBIS project 98-1-01: Bitterfeld: Bioremediation of regional contaminated aquifers). De grootschalige onderzoeksfaciliteit werd voor dit project beschikbaar gesteld voor de periode 1999-2002. Acht verschillende fysisch-chemische en biologische technieken worden onderzocht door acht onderzoeksgroepen.

Het NOBIS-TNO-UFZ project team is in december 1998 met een on-site kolommen test programma (Fase I) aangevangen. Dit wordt gevolgd door een onderzoek in de grootschalige in situ reactoren in de ondergrondse testfaciliteit (Fase II).

Doel en belang van het project

Het doel van het SAFIRA project en het daarin opgenomen NOBIS project was verschillende reactieve wanden en andere *in situ* saneringstechnieken te onderzoeken en met elkaar te vergelijken op de toepasbaarheid als methode om grootschalige gebieden, die vervuild zijn met mengsels van organische verbindingen, te reinigen. Hierbij is aandacht besteed aan:

- Selectie van geschikte technieken (met betrekking tot technische toepasbaarheid, efficiëntie, betrouwbaarheid, en kosten) voor zulke gebieden, door het testen op ware grootte. De SAFIRA partners onderzoeken voornamelijk fysisch-chemische technieken. Het specifieke doel van het NOBIS project was om een geschikt biologisch alternatief (i.e. een biologisch geactiveerde zone en een "funnel-and-bioreactor" variant) te testen op ware grootte en om deze technologie te vergelijken met de fysisch-chemische methoden.
- Het ontwikkelen van een kleinschaliger mobiele *on-site* test unit, waarmee geschikte beheersvarianten voor ander grootschalig vervuilde gebieden zouden kunnen worden vastgesteld. Het specifieke doel van de NOBIS deelname is om de biologische test unit in zo'n installatie te ontwikkelen.
- In de nabije toekomst, zijn initiatieven gepland om deze mobiele unit te gebruiken op andere grote locaties die zijn vervuild met (mengsels) van chlooralifaten, chlooraromaten en pesticiden (i.e. HCH).

Resultaten verkregen in de fases I en II van het NOBIS en SAFIRA samenwerkingsproject
Het grondwater in Bitterfeld bevat zowel chloorbenzeen als gechloreerde ethenen. Chloorbenzeen wordt voornamelijk gevonden in het bovenste aquifer, terwijl het tweede aquifer voornamelijk vervuild is met gechloreerde ethenen. De afbraak van de verontreinigingen is onderzocht in een sequentieel anaëroob - microaëroob systeem. Onder anaërobe omstandigheden worden voornamelijk chloorethenen gedechloreerd, terwijl chloorbenzeen vooral onder de microaërobe condities moet worden gemineraliseerd. De van nature hoge sulfaatconcentratie in het grondwater (tot 750 mg/l) zou hierbij tot moeilijkheden kunnen leiden (in verband met de vraag van de elektronendonor de gevormde sulfide). Het onderzoek is in twee fasen uitgevoerd: on-site en laboratoriumonderzoek en in situ reactoronderzoek.

Fase I: kolommen onderzoek, on-site en in het laboratorium
In fase I van het Bitterfeld project is de omzetting van de contaminanten onderzocht in bench-scale on-site (volume 7.9 l) en laboratorium-kolommen (volume 880 ml). Hierbij werd gebruikt gemaakt van grondwater en sediment van de Bitterfeld locatie. Trichlooretheen (TCE) werd onder anaërobe condities gechloreerd onder vorming van etheen (figuur S1). Om dit te bewerkstelligen moest een relatief hoge concentratie elektronendonor (een mengsel van lactaat, acetaat, propionaat en butyraat) worden toegevoegd aan het grondwater. De toevoeging van stikstof (als NH_4^+) bleek noodzakelijk te zijn om de dechlorering van cDCE tot etheen te laten verlopen. Er vond sulfaat reductie plaats in de anaërobe kolommen.

Uit de resultaten van fase I blijft echter onduidelijk of het noodzakelijk is eerst alle sulfaat te reduceren voordat dechlorering kan plaatsvinden. Voordat de eerste dechlorering van TCE naar cDCE werd waargenomen vond namelijk al sulfaatreductie plaats. Het zou ook kunnen dat een initiële reductie van het aquifeer materiaal (samen met de toevoeging van een N-bron) voldoende is om de omstandigheden voor dechlorering gunstig te maken voor de dechlorerende bacteriën. Als dat het geval is, zou volledige sulfaatreductie niet langer noodzakelijk zijn en zou de hoeveelheid elektronendonor gereduceerd kunnen worden. De hoeveelheid elektronendonor noodzakelijk voor de reductie van het sulfaat is namelijk 500 tot 1000 maal hoger dan de hoeveelheid die gebruikt wordt voor complete dechlorering van de aanwezige chloorethenen.

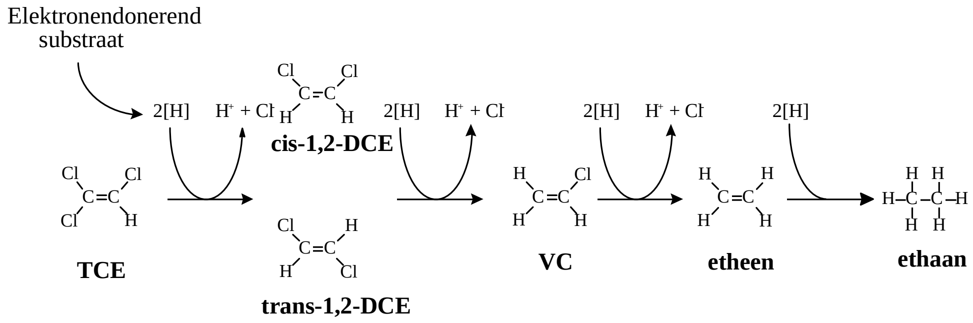


Fig. S1. Reductieve dechlorering van TCE en lager gechloreerde ethenen.

De afbraak van chloorbenzeen is in eerste instantie onderzocht onder denitrificerende omstandigheden. De omzetting van de aromatische verbindingen werd niet waargenomen onder deze omstandigheden en het toegevoegde nitraat werd slechts gedeeltelijk verbruikt. Omdat uit voorgaand onderzoek gebleken is dat het toevoegen van kleine hoeveelheden zuurstof de omzetting van aromatische verbindingen onder anaërobe omstandigheden kan verbeteren (zoals weergegeven in het reactieschema in figuur S2), werd vervolgens 3 mg/l zuurstof samen met het nitraat aan het grondwater toegevoegd. Dit resulteerde echter ook niet in de gewenste afbraak. Uiteindelijk werd afbraak van het chloorbenzeen bewerkstelligd na toevoeging van twee maal de hoeveelheid zuurstof die nodig is om alle chloorbenzeen te mineraliseren. Het is nog onbekend in hoeverre daadwerkelijk volledige mineralisatie van chloorbenzeen plaatsvindt. Momenteel wordt getracht de toegevoegde hoeveelheid zuurstof weer te verlagen.

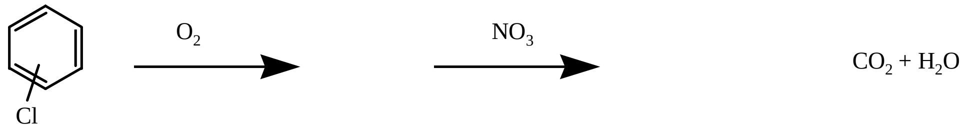


Fig. S2. Microaërobe afbraak van chloorbenzeen.

Fase II: in situ reactor tests

De *in situ* reactoren (volume ± 4m^3) in de ondergrondse schachten zijn opgestart. Ze worden bedreven als twee parallel geschakelde anaëroob - microaërobe straten. The anaërobe reactor wordt opgestart met twee maal de hoeveelheid elektronendonor nodig voor de complete reductie van sulfaat en de chloorethenen, en een N-bron. Op deze manier wordt het aquifeer materiaal in de reactoren wellicht sneller gereduceerd en zijn de omstandigheden voor dechlorering gunstiger. Later zal de hoeveelheid elektronendonor worden gereduceerd om zodoende de sulfaatreductie in het systeem te minimaliseren. De tweede reactor wordt bedreven onder microaërobe condities. Door onvoorziene omstandigheden zijn de in situ reactoren later opgestart dan gepland en is het niet mogelijk om nu reeds resultaten te geven.

De SAFIRA technologieën en een integrale beheersing van de pluim in de Bitterfeld regio

De resultaten van het onderzoek met de diverse SAFIRA technologieën lijken erop te wijzen dat fysisch-chemische technieken (bijvoorbeeld adsorptie op actieve kool, palladium gekatalyseerde conversie, elektrochemische processen) alleen niet in staat om alle contaminanten die in het grondwater van Bitterfeld aanwezig zijn te verwijderen. De eerste SAFIRA-brede onderzoeksresultaten geven aan dat, mede gezien het mengsel van verontreinigingen, verwacht mag worden dat biologische methoden een bijdrage zullen leveren aan te minste een deel van de problematiek in Bitterfeld.

Het voornaamste doel van SAFIRA is om methoden te ontwikkelen om grondwatervervuiling te beheersen en benedenstroomse aan risico blootgestelde objecten te beschermen.
De objecten die aan het risico dat ze vervuild raken, zijn blootgesteld, zijn:

- de rivier de Mulde en de daarin uitkomende Spittelwasser;
- dieper liggende watervoerende pakketten;
- een voormalige mijngroeve de "Goitsche", die langzaam wordt omgevormd naar een kunstmatig meer.

Het dorp Bitterfeld, dat als zodanig wel risico loopt ten gevolge van de grondwaterstijging, was oorspronkelijk niet het probleem waar SAFIRA een oplossing voor zou dienen aan te dragen. Mogelijk kunnen de ontwikkelde concepten ook voor dit probleem aangewend worden. Dit valt echter buiten de context van dit rapport.

Funnel-and-gate concepten lijken geschikt te zijn om de bedreigde objecten die benedenstrooms van de vervuilde grondwaterpluim liggen, zoals de rivier de Mulde en de voormalige mijngroeve, te beschermen.
Passieve systemen, zoals behandelingszones die worden ingepast in de huidige landinrichting en infrastructuur, zijn gemakkelijker toe te passen en zijn minder gevoelig voor technisch falen. Daarom wordt aan dergelijke systemen de voorkeur gegeven boven veel energie verbruikende en kostbare actieve schermen.

Toekomstig onderzoek
De volgende onderwerpen staan nog open voor verder onderzoek in een later stadium:

- Optimalisatie van de elektronendonor dosering in de anaërobe trap van het proces.
- Competitie om de elektronendonor tussen de dechlorerende en sulfaatreducerende bacterien. Kan dechlorering plaatsvinden terwijl er slechts weinig of geen sulfaat wordt gereduceerd? Hoge sulfaatconcentraties zouden kunnen de anaërobe dechloreringsprocessen kunnen belemmeren o.a. via competitie op het gebied van de elektronendonor. De dechloreerders moeten de competitie van de sulfaatreduceerders kunnen winnen, anders is de vraag naar elektronendonor zeer hoog.
- De koppeling van het anaërobe systeem aan het microaërobe systeem en de effecten van de samenstelling van het grondwater (gechloreerde verbindingen, sulfaat) op de hoeveelheid elektronendonor en elektonenacceptor, die nodig zijn in het systeem.
- Sulfide, gevormd in de anaërobe reactor, beïnvloedt de zuurstofvraag in de aërobe reactor.
- Optimalisatie van de zuurstofconcentratie. Er is een hoge zuurstofconcentratie nodig voor de omzetting van chloorbenzeen. De benodigde hoeveelheid zuurstof kan waarschijnlijk worden teruggebracht naar microaërobe niveaus na de opstart van het biologische proces.
- Toepassing op grote schaal, met alle consequenties van dien (vóórkomen en voorkómen van verstopping, kosten, praktische toepasbaarheid) als onderdeel van het management van de verontreinigingspluim op regionale schaal.

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 can not be achieved via the application of conventional not effective pump-and-treat methods because of the large amounts of contaminated soil and groundwater involved. Natural or enhanced remediation are 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 project "Bioremediation of regional contaminated aquifers" the feasibility of barrier and *in situ* techniques has been studied in co-operation with a German initiative, the SAFIRA (SAnierungs Forschung in Regional kontaminierten Aquiferen) project. The SAFIRA project is managed by UFZ (Umwelt Forschungs Zentrum) at Leipzig, 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, 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-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 will be 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.
- Electro-chemical 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 SAFRIA project are focussing on chlorinated aromatic compounds alone. NOBIS has participated in the project by testing and evaluating an enhanced bioremediation (Natural Attenuation (NA)$^+$ approach) method for the removal of both chlorinated aliphatic and chlorinated aromatic compounds.

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

This final report comprises the results of the first two phases of the NOBIS project (December 1998 - February 2000). In phase one, bench scale on-site and laboratory column tests were carried out. Large scale *in situ* reactor tests were scheduled for phase two. The results obtained so far are described here.
The contaminated region and the test site are described in Chapter 2. The knowledge regarding the biodegradation of the contaminants found is summarised in Chapter 3. This chapter also contains the rationale behind the set-up of the NA$^+$ process in the sequential anaerobic-microaerobic process. The results of the laboratory and on-site column tests are discussed in detail in Chapter 4. Chapter 5 comprises the results of the *in situ* reactor test obtained so far. The results obtained by other SAFIRA project members and the possible measures and consequences for the plume management of the area are described in Chapter 6 and 7, respectively. Concluding remarks and recommendation for further research are described in Chapter 8.

Fig. 1. Location of the experimental site.

The research is planned to be continued (phase III) in the years 2000 and 2001. This phase will focus on present bottle necks and the long term performance of the reactor system and first efforts on the translation of the results to field-scale remediation.

CHAPTER 2

THE CONTAMINATED REGION AND THE TEST SITE

2.1 The contaminated region

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 build in these (former) mining areas with artificially low groundwater levels resulting in large sub surface 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 [1]).

The need for containment and remediation of this area has been foreseen because of the planned changes in the hydrogeological situation in the region. The mining activities have ceased and plans to shut down large scale groundwater extraction wells have been made. 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 down stream 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 [1].

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 [1].

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 monochlorobenzene (DCB and CB) and benzene).

The contamination levels vary among the upper and lower aquifers. The lower aquifer was mainly contaminated with chlorinated aliphatics and benzene; whereas the upper aquifer contains primarily chlorinated benzenes [2].

This stratification trend can be observed both in soil and groundwater samples (table 1). The groundwater was also geochemically analysed (Appendix A). Next to the compounds mentioned in the tables 1 and A1 (Appendix A), also trace amounts of bromobenzenes, perchloroethene (PCE), and other compounds like HCH, higher chlorinated benzenes and dioxins were found in the groundwater. AOX and chlorobenzene concentrations differ among the groundwater samples. However, currently, the highest concentrations measured are 9 and 45 mg/l for AOX and chlorobenzene, respectively.

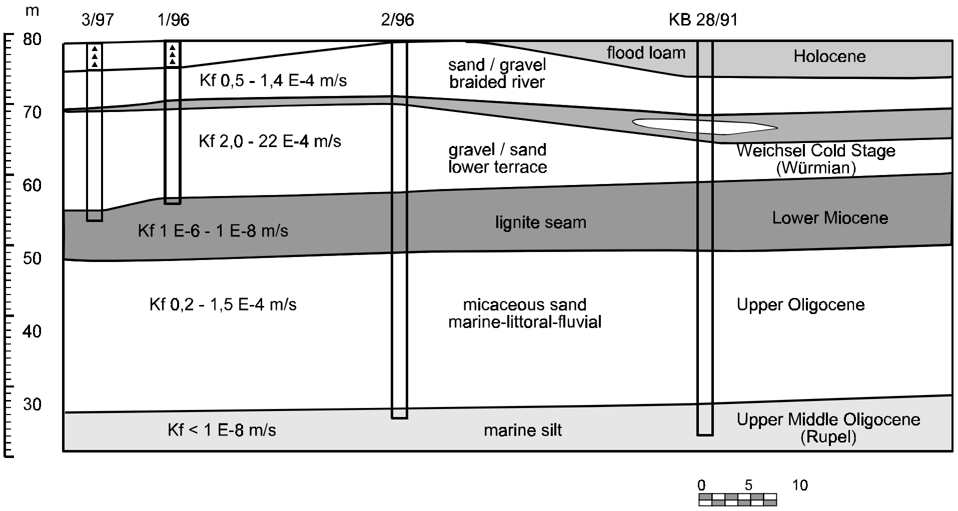


Fig. 2 Geological section of the Bitterfeld Wolfen area [1].

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. Although this is more negative than the values given for the different sampling wells measured in the same period, it is clear that the groundwater is not completely anaerobic.

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

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)	550-1000	740	
chloride (mg/l)	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, which could cause a problem under sulphate reducing conditions because of the sulphate concentration (550-1000 mg/l), which could lead to calcium and magnesium precipitation as sulphide salts. With the exception of sodium and potassium, all other compounds measured are present in minor amounts only.

2.2 Design of the test-site

The SAFIRA project is carried out in two phases. Most of the research is carried out at a test site 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 reactors. All the research groups in the SAFIRA project were given the opportunity to carry out the small scale experiments in an on-site mobile test unit (figure 3).

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

This mobile test-unit is located at the test site and is continuously supplied with groundwater from the test-site (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 4.

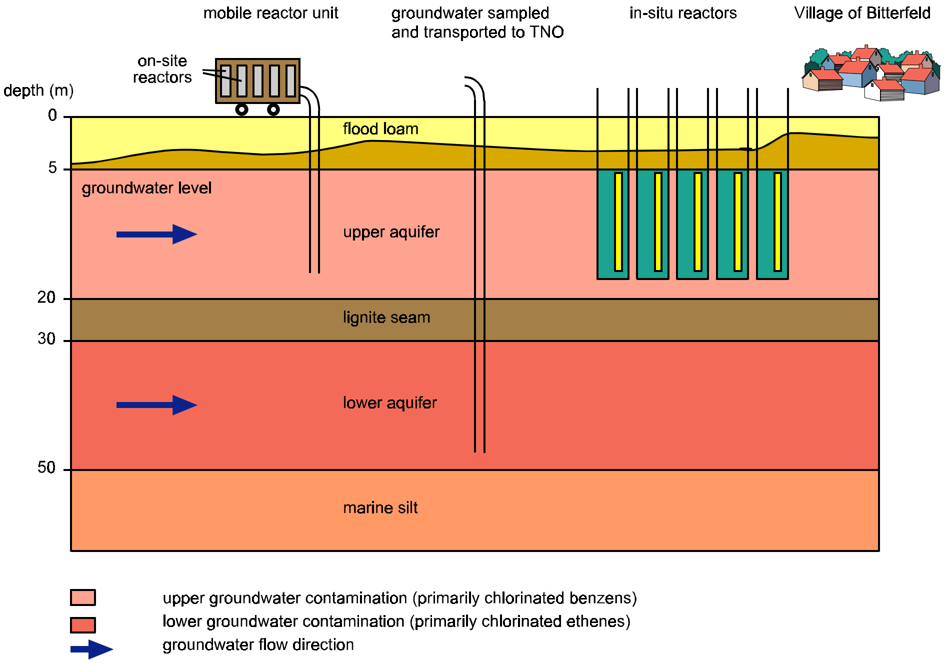
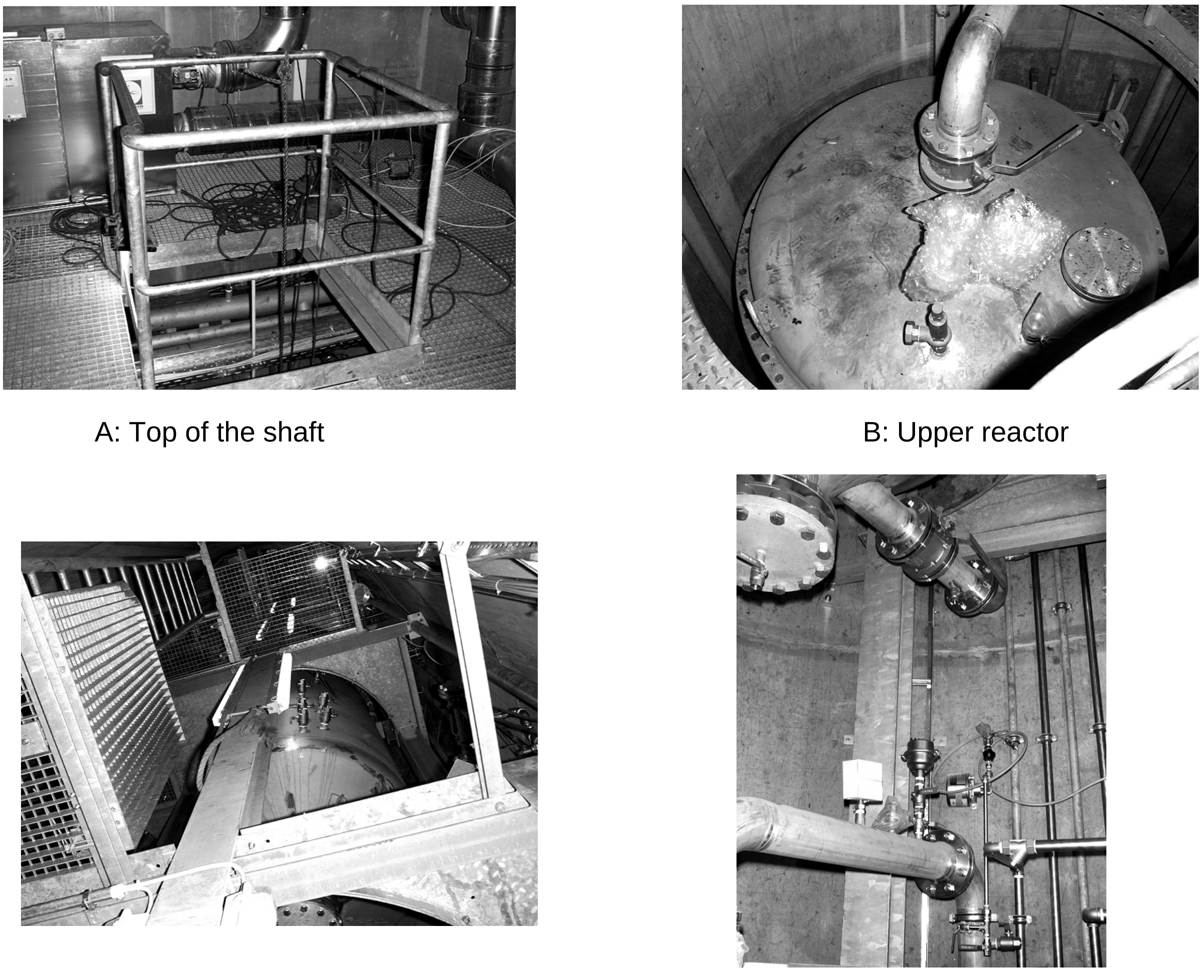


Fig. 4. General set-up of the on-site mobile test unit.

The second phase of the Bitterfeld project consisted of experiments with larger scale *in situ* reactors at the Bitterfeld location. Five 22 meter deep shafts (figure 5) were made available for the research groups within the SAFIRA project.

Fig. 5. The 22 meter deep shaft which contains the "NOBIS" in situ reactors.

The four reactors used in the NOBIS project (Chapter 3) 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 project, the groundwater is 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 is managed by UFZ.



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 shaft from bottom to top.

Fig. 7. The shelters covering the shafts at the Bitterfeld/Wolfen site.

CHAPTER 3

EVALUATION OF SUITABLE PROCESSES FOR THE BIODEGRADATION OF THE CONTAMINANTS AND CRITICAL PARAMETERS

3.1 Introduction

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

Given the high sulphate concentration (up to 1000 mg l^{-1}) (table A1, (Appendix A)), the transformations, when possible, 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 which will have to be bioremediated are trichloroethene (TCE), dichloroethene (DCE) and chlorobenzene (CB). The possibilities for anaerobic and aerobic conversion of the different compounds are evaluated below. Thereafter, a degradation system was selected.

3.2 Conversion of chlorinated ethenes under anaerobic and aerobic conditions

TCE and lower chlorinated ethenes are biodegradable under both aerobic and anaerobic conditions. Tetrachloroethene (PCE) is only (bio)degraded under anaerobic conditions. Several pure cultures of bacteria have been isolated which are able to use PCE as an energy source [3, 4, 5, 6]. However, the transformation in those cases is often limited to the removal of one or two chlorine atoms. Normally, *cis*-1,2-DCE (cDCE) is the main product formed. *Dehalococcoides ethenogenes* is the only bacterium able to transform PCE to vinyl chloride (VC) (and ethene) [5]. In this case, the last step in the transformation (VC to ethene) are believed to be cometabolic.

Complete reductive dechlorination of PCE and TCE (figure 8) is almost exclusively observed with mixed cultures e.g., [7, 8, 9]. In most cases, it is not clear whether sulphate reducers, fermentative or other bacteria are responsible for the complete reductive dechlorination of PCE and TCE [10, 11, 12]. Under methanogenic conditions, PCE was suggested to be transformed to CO_2 via the formation of VC [13]. The reductive dechlorination of TCE was observed both in soil and groundwater e.g., [14, 8]. Sulphate reducing enrichment cultures were found to transform PCE to TCE and cDCE [15].

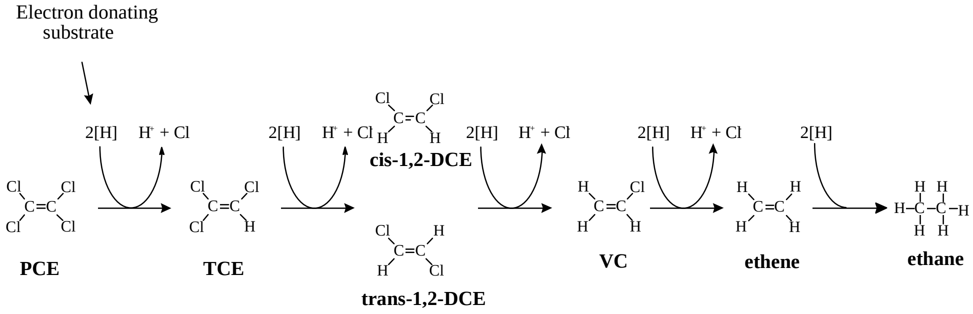


Fig. 8. Complete reductive dechlorination of PCE and TCE under anaerobic conditions.

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 e.g.[16]. 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) 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. I.e., at a low hydrogen concentration, dechlorinating bacteria have higher hydrogen conversion rates than other (methanogenic) bacteria, thus preventing the "spill" of electron equivalents for a use other than the dechlorination reaction [17, 18, 19]. Lactate, but also volatile fatty acids like propionate and butyrate seem to be suitable substrates. This, however, seems to be strongly dependent on the micro-organisms 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 [20-22].

Under aerobic conditions, TCE and lower chlorinated ethenes are degraded via cometabolic reactions [10, 23, 24, 25]. VC is the only compound that can serve as a carbon source for aerobic micro-organisms. Cometabolic conversion of chloroethenes usually occurs with micro-organisms which grow on methane, ethene, propane, ammonia, or propene and show mono- or dioxygenase activity [10]. The bacteria involved usually have a broad substrate range and gratuitously transform TCE leading to the formation of 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 cDCE, and other DCE isomers (figure 9), and VC has been reported [10].

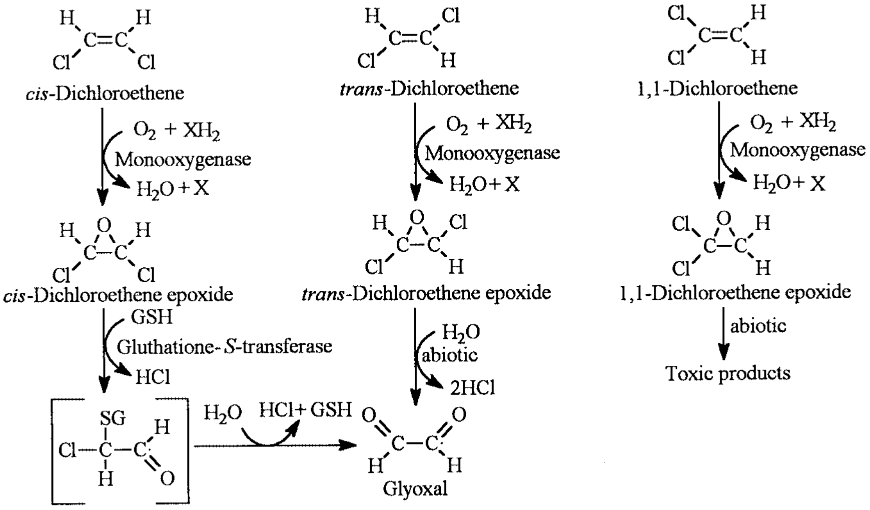


Fig. 9. Epoxide formation from the DCE isomers under aerobic conditions. (Figure taken (with kind permission of Kluwer Academic Publishers) from [10]).

3.3 Conversion of chlorinated benzenes under anaerobic and aerobic conditions

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 [26, 27]. However, the formation of benzene in those cases was not irrevocably shown, because in one case benzene was not measured and in the other, benzene concentrations were very low. Most researchers report on the accumulation of tri-, di- and monochlorinated benzenes with mixed cultures under anaerobic conditions, e.g., [28, 29, 30, 31]. Methanogenic conditions seem to be more favourable than sulphate reducing conditions and conditions with higher redox potentials [29]. Nevertheless, this may also be strongly dependent on the source of the micro-organisms.

Anaerobic dechlorination of lower (tri- and di-) chlorinated benzenes to monochlorinated benzene has been reported under anaerobic conditions by micro-organisms, which had been priorily adapted to higher chlorinated benzenes [32]. Mineralisation of benzene was observed under methanogenic, sulphate reducing and iron reducing conditions. So far, nothing is known about the pathways used by micro-organisms 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 [10]. 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 favourable environmental conditions [33].

Aerobically, 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. In that case, chlorinated benzenes are degraded via an initial oxygenation of the aromatic ring. These reactions are catalysed by a dioxygenase (figure 10).

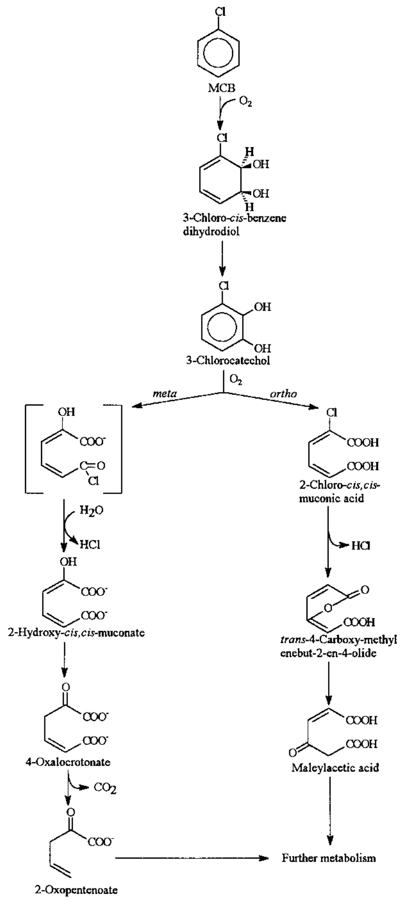


Fig. 10. Aerobic transformation of chlorobenzene.
(Figure taken (with kind permission of Kluwer Academic Publishers) from [10]).

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 [10].

3.4 The combined removal of chlorinated ethenes and chlorobenzene 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 more likely to be converted under aerobic conditions. Therefore, a sequential anaerobic-aerobic process should be implemented.

3.4.1 *The anaerobic reactor*

In the anaerobic step TCE should be completely dechlorinated to ethene (or ethane) (figure 8). In that way, the formation of toxic intermediate products in the aerobic part of the process may be avoided. Given the contaminants found in both the core soil 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, table A1 (Appendix A)) and the redox potential is relatively high. The main TCE dechlorination product found is cDCE. No VC and ethene are present (R. Trabitzsch, pers. comm). 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 chosen because of the broad spectrum applicability, which was thought to guarantee a successful dechlorination based on results of experiments described in literature (section 3.2). Also, this mixture resembles the composition of compost extract, which was originally planned to be used in the experiments. In case of complete dechlorination of the chloroethenes, the addition of electron donor will be minimised for practical (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 if all of the sulphate present would be reduced. 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 also, a microbial population may develop, which is able to dechlorinate the dichlorinated benzenes leading to the formation of chlorobenzene and benzene. It may, however, take some time to enrich for these micro-organisms.

3.4.2 *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 strength of the electron acceptor in time. As soon as transformation of chlorobenzene would be achieved under certain environmental conditions, the operating conditions in the reactor would be kept as such.

Firstly, the aim was to degrade the chlorobenzene present in the groundwater under denitrifying conditions (pathway I, figure 11), because results from other researcher within the SAFIRA project showed that chlorobenzene conversion under these conditions may be possible [34]. Also, the addition of nitrate to the groundwater is more practical than the supply of oxygen.

Secondly, trace amounts (up to 3 mg/l) will be added to the influent (preferably as oxygen saturated water) if transformation of chlorobenzene under denitrifying conditions is not possible (figure 11, pathway II). Results from experiments carried out in the framework of other projects have shown 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 [35, 33]. In those cases the amount of oxygen added was not enough to oxidise the aromatic compounds. However, it may have been the case that the oxygen added was able to oxidise 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 catechols which are formed may be mineralised to CO_2 via anaerobic routes. If anaerobic conditions are not favourable, complete mineralisation under aerobic conditions will be tested. Aerobic mineralisation should be easily achieved [10].

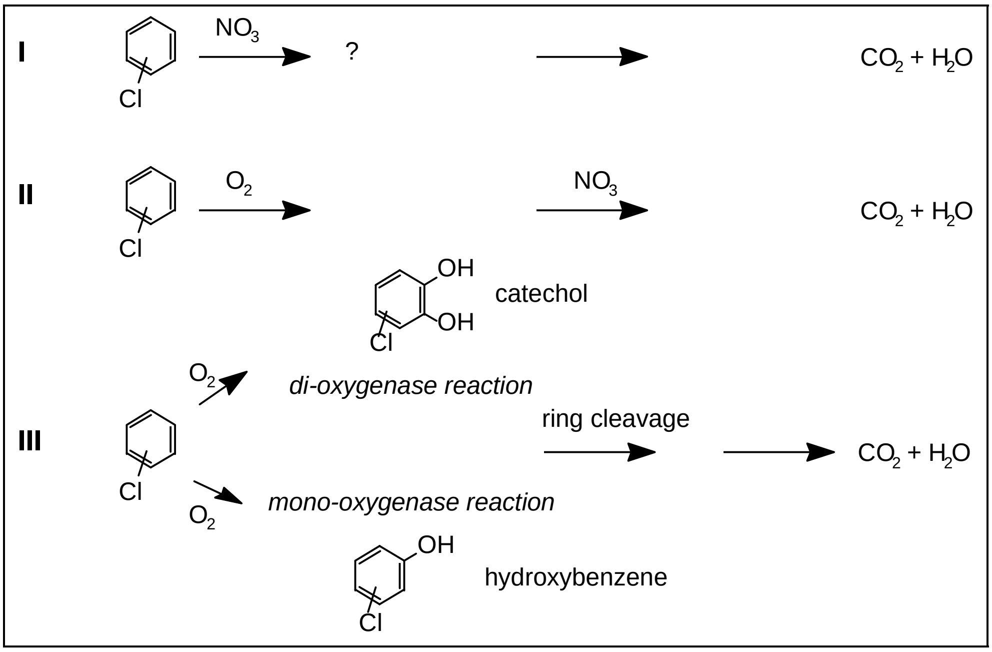


Fig. 11. Operation strategies of the microaerobic reactor.

3.4.3 *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 micro-organisms 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 and least preferred 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 (see Chapter 5 for additional information).