UFZ-Bericht

SAFIRA

**Abstracts of the Workshop
of November 17-18, 1999
at Bitterfeld / Germany**

Holger Weiß[1], Huub Rijnaarts[2], Sjef Staps[2],
Peter Merkel[3] (Editors)

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Applied Geology Group

UMWELTFORSCHUNGSZENTRUM LEIPZIG-HALLE GMBH

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Introduction

The SAFIRA project (SAnierungsForschung In Regional kontaminierten Aquiferen) focuses on the development of reactive walls for the treatment of regional contaminated aquifers. The project is managed by UFZ (UmweltForschungsZentrum Leipzig-Halle) and the University of Tübingen.

Within the SAFIRA project, different research groups are investigating a number of different technologies at an underground test site in Bitterfeld. Among them is a consortium from the Netherlands, lead by TNO (Netherlands Organisation for Applied Scientific Research), with Tebodin, HBG/HWZ and Shell as partners. The Dutch research project is supported by NOBIS (Netherlands Research Programme for Biological In Situ Remediation).

Fall 1999, the SAFIRA programme at Bitterfeld had come at an interesting point. The test site had been officially opened, most results of the on-site mobile test unit had been obtained and the in-situ reactors had been started up.

On November 17-18, 1999, UFZ and TNO jointly organised a workshop at the test site in Bitterfeld. The workshop was attended by about 50 representatives from the different research groups involved in SAFIRA, NOBIS representatives and members of the Knowledge Exchange Group related to the Dutch research project.

The workshop focused on:
– the methods applied
– the results obtained so far
– practical, large scale solutions for the regional groundwater problem.

This report presents the workshop programme, the abstracts of the presentations and a selection of the slides that were used within the brainstorm session.

We do hope that the workshop and this report will be followed-up by a further and fruitful knowledge exchange between all parties involved and that this may contribute to finding innovative, optimal solutions for the regional groundwater problems in Bitterfeld and other areas.

Programme UFZ / TNO Workshop on the SAFIRA project
Bitterfeld, November 17-18, 1999

Wednesday 17th November 1999

Introduction
> **Chairman: Peter Grathwohl (Universität Tübingen)**

14.00   Opening

14.15   Relation TNO – UFZ – SAFIRA
         Huub Rijnaarts, TNO

14.30   SAFIRA / Bitterfeld
         Holger Weiss, UFZ

14.45   The NOBIS program in the Netherlands,
         Harry Vermeulen, director NOBIS

15.00   Focal points of the ecological / economical reconfiguration in the "Neue Länder"
         Fred Walkow (Landratsamt Bitterfeld)
         Karl Enders, Peter Peklo (Bitterfelder Vermögensverwaltung)

Technical presentations I
> **Chairman: Holger Weiss (UFZ)**

15.30   Microbial colonization of the subsurface at the test site and degradation of chlorobenzenes by autochthonous bacteria of the quarternary aquifer
         Lothar Wünsche (UFZ)

16.00   Break

16.30   Biodegradation of chloroethenes and chlorobenzenes in a two-phase anaerobic/ microaerobic treatment zone system
         Sjef Staps, Miriam van Eekert, Huub Rijnaarts (TNO)

17.00   The influence of groundwater specific parameters on the performance of in–situ reactors instancing in-situ activated carbon filtration.
         Peter Grathwohl, Sybille Kleineidam, Siggi Krafft (Universität Tübingen)

17.30   Elimination of chlororganic compounds by adsorption and simultanous microbiological degradation on activated carbon
         Peter Werner, Stefan Döring (Universität Dresden)

18.00   Degradation of halogenated organic pollutants in ground water by ultrasound-assisted catalytic oxidation
         Jörg Hofmann (Universität Leipzig)

18.30   Closing remarks

Thursday 18th November 1999

Technical presentations II
Chairman: Huub Rijnaarts (TNO)

9.00   Zeolite based catalysts for the hydrodehalogenation of chlorinated com-
pounds in groundwater
Christoph Schüth, Sascha Kummer (Universität Tübingen)

9.30   Dechlorination of chlorohydrocarbons in groundwater by electrochemical and
catalytic reactions.
Frank-Dieter Kopinke (UFZ)

10.00   Development of coupled in situ reactors
Andreas Dahmke, Dirk Schäfer (Universität Kiel)

10.30   Break and excursion Bitterfeld test site

Brainstorm session
Chairman: Jürgen Wiesner (DECHEMA)
Discussion leader: Bert Satijn (NOBIS)

11.30   Integrated groundwater management in the Bitterfeld area: a vision for 2010

13.00-13.30   Lunch

Evaluation
Chairmen: Holger Weiss (UFZ), Huub Rijnaarts (TNO)

13.30-14.00   Evaluating remarks, summary and conclusions

Excursion

14.00-17.00   Excursion to the Bitterfeld / Wolfen region

List of attendees

Babel, W.	UFZ
Beuningen, M. van	De Telegraaf
Bonekamp, J.	HWZ
Döring, U	TU Dresden
Eekert, M. van	TNO-MEP
Feist, B.	UFZ
Grathwohl, P.	University of Tübingen
Häntzschel, D.	INC Leipzig
Hattem, W.	Port of Rotterdam
Heersche, J.	Edon
Hetterschijt, R.	NITG-TN
Hofmann, J.	INC Leipzig
Höfle, M	GBF Braunschweig
Janse, J.	Biosoil
Klein, J.	Hattingen
Kopinke, F.-D.	UFZ
Lazik, D.	UFZ
Logemann, F.	TNO-MEP
Lorbeer, H.	TU Dresden
Lörtzer, M.	TNO
Mackenzie, K.	UFZ
Merkel, P.	University of Tübingen
Müller, A.	TZW Karlsruhe
Müller, J	GSF München
Opdam, H.	Arcadis
Parkinson, C.	Shell
Popp, P	UFZ
Read, D.	University of Reading
Rijnaarts, H.	TNO-MEP
Satijn, B	NOBIS / SKB
Schäfer, D.	University of Kiel
Schelwald, L.	Port of Rotterdam
Schoonbeek, R.	Province of Groningen
Schulze, S.	TZW Karlsruhe
Schüth, C.	University of Tübingen
Slenders, J.	TNO-MEP
Sman, B.	Geodelft
Staps, S.	TNO-MEP
Subklew, G	FZ Jülich
Trabitzsch, R.	UFZ
Trommelen, J.	De Volkskrant
Visser, E.L.	Tebodin
Vogt, C.	UFZ
Weiß, H.	UFZ
Wennrich, R	UFZ

Wiesner, J.   DECHEMA
Wünsche, L.   UFZ

The pollution of soil and groundwater in Bitterfeld

F. Walkow[1], K. Enders[2], P. Peklo[2]

[1]   District Administration Bitterfeld

[2]   ChemPark Management Bitterfeld

In Germany it is not necessary to explain what Bitterfeld means. Bitterfeld has become a symbol for any kind of pollution and destruction of landscape in the New States. In January 1990 a report of the SPIEGEL-magazine focused a worldwide interest Bitterfeld as "the dirtiest town of Europe". Even a newspaper of the GDR titled "Bitterfeld - Cernobyl of GDR's chemistry" despite the fact that nuclear energy has never been produced in Bitterfeld. Many important and less important politicians as well as some international movie stars visited Bitterfeld. For example Jane Fonda cried bitterly tears when she saw the so called Silver lake, one of our largest dump sites.

Since this time Bitterfeld has been the outstanding example for the consequences of the economic and ecologic policy of the GDR. Ten years later Bitterfeld is the best ecologically investigated district of Germany and plays a pioneering role in the contaminated site remediation in East Germany. Now it is much easier to divide between the true and the imagined problems of our district. So let me give you a short review on the two ecologic main problems. At first some short information about geography, history and economy of the Bitterfeld district.

The Bitterfeld district belongs to the federal state Saxony-Anhalt. It is the northern edge of the so called Chemistry Triangle, a large industrial region in East Germany dominated by chemical industry during the last century. The other two edges are Halle an der Saale and the better known Leipzig, the starting point of the political turn in the GDR and the reunification.

The Bitterfeld district has a population of 110 thousand people on an area of 504 square kilometers. The biggest towns are Bitterfeld and Wolfen with 16.000 and 33.000 inhabitants respectively.

The river Mulde divides the district into two parts: the flat west, dominated by agriculture an the wooded, hilly east. Most of the people live in the centre around large plants of chemical industry.

The most important ecologic problems we are still concerned about, result from the surface mining and the chemical industry.

Lignite mining began in Bitterfeld in the mid-19th century. Bitterfeld's lignite was fueling the industrial growth of the country and was the primary fuel source for the chemical industry. The importance of lignite continued well into the 20th century as it

provides energy for the rapidly increasing industry in Mid Germany. In the GDR, lignite was the only source for electric power generation. In 1990 the active mining was finished for economic reasons.

At this time a mine reclamation program has been started financed by the Federal Government. An outstanding project of this program is the mine Goitzsche.

During its mining period from 1949 to 1991 about 320 million tons of lignite were extracted, necessitating the movement of 850 million cubic meters of overlay shelf. This resulted in the formation of an residual open-cast covering an area of 60 square kilometers. Mine reclamation measures are currently under way with the aim of creating a landscape containing a water surface of about 24 square kilometers.

The first chemical operations were established in Bitterfeld over 100 years ago, attracted by low cost lignite and clear water from the river Mulde.

Bitterfeld particularly gained in importance through the production of basic chemicals such as chlorine, sodium hydroxide, aluminium and magnesium. Over the years, new products and even whole product lines based on chlorine were developed, such as pesticides and a variety of dyestuffs. Manufacturing a range of over 4.000 different items, the Bitterfeld/Wolfen site was one of East Germany's most productive and innovative locations.

The invention of the modern color film process and the production of cellulose fibres were highlights in the history of the AGFA headquarters in Wolfen in the fourties. The Chemiekombinat Bitterfeld and the Filmfabrik Wolfen had been the biggest local companies employing about 30.000 people.

At a color infrared aerial photo from 1991 you can see the close mixture of chemical plants, former open pit mines used as dump sites and the residential area of Wolfen. This includes the 100 year old Farbenfabrik, part of the Chemiekombinat Bitterfed, there is the Filmfabrik Wolfen.

Both companies, especially the Chemiekombinat, were well known for air pollution. Most of their plants were built in the prewar period of the world war I and II and were in operation till 1990. For this reason the people called it "GDR's biggest open air industrial museum".

In the last decade of the GDR all environmental data were top secret by law of the communist government. So at this time no one was able to evaluate the real environmental risks.

Starting with the closure of the ecologically terrible cellulose fibre producing plant in Wolfen there has been a significant drop in the level of air and water pollution.

This is largely due to the fact that many environmentally harmful and economically unviable production facilities have been closed down. Until now the pollution of soil and groundwater are the main ecologic problems of Bitterfeld and the other sites of

chemical industry in East Germany. In 1994 the Federal Government and the New States signed the Contaminated Site Remediation Agreement providing the money for all measures that must be executed.

After the political turn no information about soil pollution was available because of the lacking interest of the political leaders in environmental protection. A considerable financial support of the Federal Government and the state Saxony-Anhalt enabled the new environmental protection agency of the Bitterfeld district and the chemical companies to carry out investigations of environmental pollution.

Soil Pollution

In 1990/91 two survey investigations were carried out concerning the top soil contamination with chlorinated hydrocarbons covering the former Chemiekombinat Bitterfeld and the centre of the Bitterfeld district on about 100 km^2, twenty percent of the whole area of the Bitterfeld district. The surveys included differently used areas reaching from chemical industry, residential areas, fields to an natural protection zone along the river Mulde. The investigated compounds were lindane derivatives, DDT, chlorinated benzenes, phenol, biphenyl, dioxin and furane.

Resulting from the one hundred years of industrial use the contamination in the centre of the Bitterfeld district is much higher than the German background level, but lower as expected.

For instance, the dioxin level outside the CKB is four times higher than the German back ground level. The dioxin level on the edges of the investigated area approaches the back ground level. The samples of highest contamination exceed the orientation values for agriculture use and these for residential as well as industrial areas. After the primary survey the most exposed places were objects of further investigations.

Nearly all chlorinated organic compounds producing plants were located in the Werk Nord of the CKB. Here the highest contamination has been found until now. The neighboured villages Greppin and Jeßnitz have the highest dioxin levels of all communities of the Bitterfeld district. Surprisingly, the dioxin level in the blood of Greppin's: inhabitants are lower than the German average. The dioxin level of the biggest towns Bitterfeld and Wolfen were about fifty percents of the district population lives is tolerable.

Further places of top contamination are the sediments, banks and flood plains of the creek Spittelwasser and the river Mulde.

The Mulde comes from Saxony, a part of Germany with a long tradition of metallurgy and chemistry. The samples upstream Bitterfeld represent the pollutant input into the Bitterfeld district. The level of chlorinated hydrocarbons of the Mulde sediments in this zone is ten times lower than downstream Bitterfeld. The pollution with organic pollutants increases considerably in the Bitterfeld district showing its maximum near a former mouth of a wastewater channel of the Chemiekombinat. Downstream Bit-

terfeld, the pollution level of the Mulde sediments nowhere decrease to the input or back ground level.

The creek Spittelwasser is the most important feeder river of the Mulde in the Bitterfeld district. It has been used as a channel for effluent of households and industry for decades. Since the beginning of the chemical industry at the end of the nineteenth century industrial process water never had been treated until 1994, when the first sewage treatment plant has been put in operation. The low gradient of the Spittelwasser favours sedimendation. On some places the sediment layer has a thickness up to 2 meters. Today the Spittelwasser contains about 20.000 tons of contaminated sludge. In the sludge of the Spittelwasser banks we found the highest dioxin concentration outside the Chemiekombinat: about 200 thousand ng TE. By the way, the Spittelwasser is part of a natural protection zone in a forest like a jungle.

An further indication of the contamination via water is the distribution of dioxin in the flood plains of the Mulde. The Mulde has two or more floods every year. They carry the sediments downstream and into the flood plains. Inside the dikes the pollution level tends to increase corresponding to increasing flood frequencies. The highest pollution occurs in hollows, where the water stays for a long time after a flood, providing good conditions for sedimentation. Outside the Mulde dikes, the pollution level fits in with the German back ground level.

The carry of sediments into the flood plains leads to a very large contamination of the soil. Statistical methods have been performed in order to find out the differences and similarities in dioxin profiles between samples of different origin along the rivers Mulde and Elbe down to the estuary into the North Sea near Hamburg. Now it is evident, that the Bitterfeld chemistry polluted the Mulde and Elbe sediments down to the Hamburg harbour, a distance of about 350 kilometres!

Most of the land in the flood plains of the Mulde has been used agriculturally for a long time. There are pasture land, fields and gardens. The soils of these areas show a critical pollution level with respect to the orientation values of the Federal Bureau of Health. To avoid a harmful intake of pollutants by man the carry over of dioxin as well as lindane derivatives and DDT must be controlled officially. With respect to the use of pasture land the main problem is lindane. The grass contains lindane above the legal limits for animal food. On about 5 square kilometers the use of pasture land is forbidden by order due to lindane. The remediation of large, diffuse contaminated areas is one of the unsolved problems until now.

Groundwater pollution

In former times, when all available coal was extracted from a mine site, the operators moved to another and left the original mine abandoned. The chemical enterprises found theses mines to be useful and cheap deposits for any kind of waste. All of these dump sites do not have a barrier against migration of pollutants into the ground water. Unfortunately, the underground is formed by sandy material, the so called Bitterfelder Glimmer. The first natural barrier is a clay layer forty metres below the surface. The biggest dump site is the mine Antonie, containing 70.000 tons of

lindane derivatives. The lindane was put into the open pit as a hot reaction mixture diluted in chlorobenzene.

Knowing the former practice, the district administration established a groundwater monitoring around the big enterprises and dump sites covering an area of about 150 square kilometres. This is a map designed after our first monitoring campaign 1991.

We have investigated a set of special compounds related to product lines of the local industry: for instance, chlorinated paraffines, chlorinated benzenes and phenols as well as some unspecific pollutants.

Another map shows the different zones of equal concentration represented by different colours. With respect to the so called negligibility level, defined by an expert group of the states, the concentrations of all chemistry specific compounds are above this level in the whole monitoring area.

Another more detailed map shows that the yellow and the red zones nearly outline the areas of the industrial plants and dump sites. Beside the dump sites leaking plants and process water pipelines mainly contributed to the pollution. So, there is no doubt, that the contamination has been caused by the chemical enterprises. A very important realization, concerning the financing of the remediation costs!

The monitoring give us information about the actual state of the groundwater. But we know, the groundwater table and flow have been strongly changed by the chemical industry and the open pit mining until now. We also know that a permanent state will be established when the reclamation of the mine Goitzsche will be completed in the year 2004. The strongest actual influence on the ground water flow comes from three open pit mines: the Goitzsche, Köckern and the Freiheit III, still operating as dump site.

In order to plan future groundwater remediation measures a groundwaterflow simulation has been elaborated. After the flooding of the open pit mines, the future groundwater flow direction wilt be similar to that of the pre-industrial period. Then pollutants will migrate to north east, passing the town Bitterfeld and the village Greppin, finally reaching the river Mulde.

Last year, we got an impression, what this means to the residential areas. Constant rain for weeks and a flood of the Mulde led to a very high ground water table in Greppin. Highly contaminated ground water reached the basements of some houses. The concentrations of evaporated pollutants in the air were so high, that the school had to be closed. Some other houses got a ventilation system to take out the gaseous pollutants.

An actual survey shows that there are no technologies available on the market for cleaning up the water of the red zones. The now existing plans for future groundwater management aim for the conservation of the present state. This means, to avoid the migration of the pollutants by permanent pump and treat. But no one knows how to treat with tolerable cost.

Despite a successful remediation of many contaminated sites of the chemical industry and mine reclamation, the top soil contamination in the Mulde flood plains and the ground water pollution are still unsolved environmental problems. But we are hopeful, that the scientists of the Environmental Research Centre Leipzig and their cooperators will succeed in developing useful technologies for these big challenges.

Microbial colonization of the subsurface at the test site and degradation of chlorobenzenes by autochthonous bacteria of the quarternary aquifer

L. Wünsche[1,3], H. Lorbeer[1], C. Vogt[1], K. Seifert[2], S. Jorks[1], B.C. Hard[1] W. Babel[1]

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[3] Leader of the subproject

Introduction

The groundwater in the region of Bitterfeld has been contaminated to a high degree with industrial chemicals - intermediates, final- and by-products - of very different chemical structure, properties and risk potentials due to activities of the chemical industry in this region for more than hundred years.

Considering the huge dimension of the groundwater pollution (about 200 million m^3 distributed over an area of more than 25 km^2) only the development of special passive remediation techniques using in situ- reactors ("reactive barriers") for plume treatment according to the "funnel and gate" principle might offer suitable solutions for such an environmental problem. Bioremediation processes using the degradative potential of the autochthonous microbial community of the contaminated aquifer can be regarded as promising variants of this procedure.

The hydrogeological situation at the selected test site is characterized by the presence of two aquifers separated by a lignite seam (in a depth between about 22 and 28 m) which acts as a local aquitard. The upper, quarternary aquifer is polluted predominantly by chlorobenzenes, mainly monochlorobenzene (MCB). Chloroaliphatics were found only in traces (range of some µg/l), unsubstituted benzene was detected in relatively low concentrations (Table 1). The lower, tertiary aquifer ranging from about 28 m down to the regionally distributed clay aquitard which marks the border of groundwater bearing strata in about 50 m depth is contaminated only with small concentrations (some µg/l) of di- and trichloroethenes and traces of different chloroaromatics at the test site.

Based on the different degree of contamination by chloro-organics and the technical-economic feasibility of an in situ-remediation process according to the "funnel and gate"-principle the investigations were focused on the quarternary aquifer.

Table 1   Pollutants of the groundwater from the quarternary aquifer at the Bitterfeld test area (data from Popp, P. and Möder, M., 1997 and 1998, internal UFZ reports).

Substance	Concentration (µg/l)
Monochlorobenzene	3,130 – 33,000
	(18,000 - 32,000)[1]
1,4- Dichlorobenzene	90 – 1,000
	(200 - 400)[1]
1,2- Dichlorobenzene	20 – 180
	(30 - 80)[1]
Benzene	20 – 180
Trichloroethene	< 10 – 460
1,2- cis- Dichloroethene	10 – 280
1,2- trans- Dichloroethene	10 – 60
Chloromethylphenols	43.5
Trichlorophenols	9.2
2,4- Dichlorophenol	3.3
Dimethylphenols	1.4
Detected mass- spectrometrically after enrichment:	
1,1,2- Trichloroethane	
1,1,2,2- Tetrachloroethane	
Bromobenzene	
1- Chloro- 2- methylbenzene	
1,3- Dichlorobenzene	
Vinyl chloride	
Tetrachloroethene	
Tetrachlorobenzene	
Toluene	
m/p- Xylene	

1 = average values of the investigation period in the mobile test unit.

Characterization of the quarternary aquifer as microbial habitat

Apart from the high pollution with MCB, the quarternary aquifer is characterized by a special combination of environmental factors (Table 2) which should allow the de-velopment of a specialized bacterial community. Temperature and pH values are in relatively favourable ranges and almost constant, inorganic nutrients (S, N, P) are available in sufficient amounts. The deficit of available electron acceptors must be regarded as a limiting factor for bacterial growth. Molecular oxygen and nitrate are

practically not detectable. Sulfate is certainly present in a high concentration but it is seemingly not (or only in a very low extent) used by sulfate-reducing bacteria in this environment due most probably to the redox potential suboptimal for this ecophysiological group: in spite of the presence of sulfate-reducing bacteria and practically unlimited amounts of sulfates no formation of metal sulfides in the aquifer was observed; only traces of H_2S were found sporadically. Furthermore, the groundwater contains only very small amounts of potential organic carbon sources others than chloroorganics: The total content of organically bound carbon, based on non-volatile substances, amounts to 6 - 8 mg/l; only a small (unknown) part of it might serve as potential carbon substrates for the groundwater bacteria.

It should be mentioned that the actually measured concentrations of electron acceptors, potential carbon sources, macro- and micronutrients in the groundwater and also the bacterial colonization density of the aquifer must be regarded as steady state concentrations within an open dynamic system.

Table 2   *Ecologically relevant abiotic factors characterizing the groundwater of the quarternary aquifer at the test site.*

TOC (mgl^{-1})	20 – 30
TOC_{nv} (based on non-volatile substances $\cong$ non- chloroaromatics) (mgl^{-1})	6 – 8
NO_3^- (mgl^{-1})	≈ 0
SO_4^{2-} (mgl^{-1})	700 – 800
Cl^- (mgl^{-1})	390 – 470
PO_4^{3-} (mgl^{-1})	6.5 - 16.5
NH_4^+ (mgl^{-1})	4.2 - 6.6
Dissolved O_2 (% saturation)	≈ 0
E_H (mV)	85 – 215
PH	6.7
T (°C)	14

Microbial colonization density of the quartenary aquifer

The subsurface at the test site is inhabited by bacteria down to the maximum drilling depth (50.5 m below the surface). The content of viable cells of the solid phases (sediments) varied with the depth and reached maximal 10^6 cfu/g sediment dry matter in the quarternary aquifer; the colonization density of the tertiary aquifer was sig-

nificantly lower (Figure 1). The total bacterial density in the groundwater of the quarternary aquifer amounted to approximately 10^5 cells/ml. Yeasts and filamentous fungi were not found in the most samples, a tiny abundance ($< 5 \times 10^2$ cfu/g) was only detected in the lignite- bearing strata and in the topsoil (drilling depth 6 m).
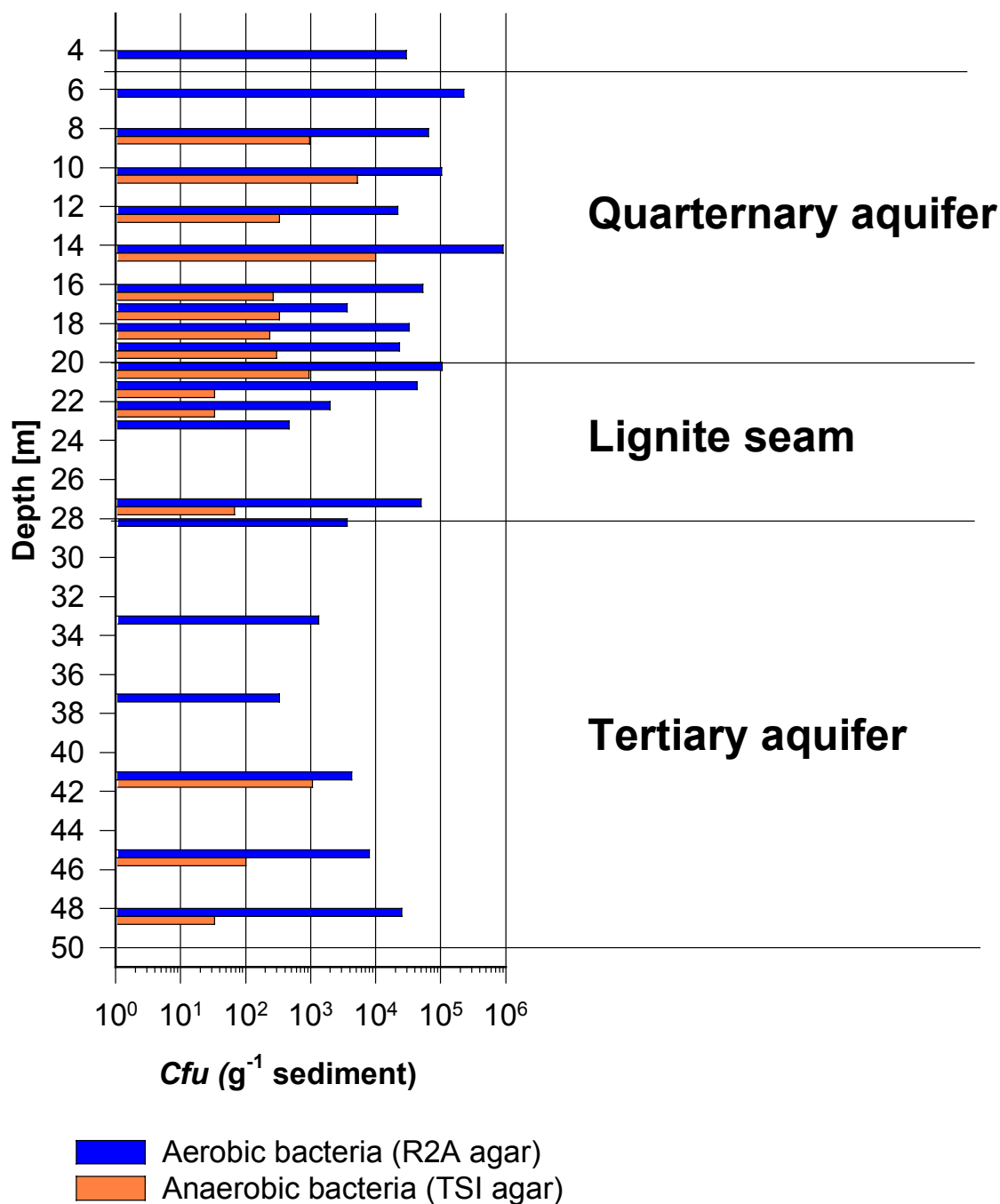

Figure 1   *Bacterial colonization of the subsurface at the test site (SAFBIT 1/97 and 2/97).*

Although the quarternary aquifer is practically free of molecular oxygen, aerobic bacteria represented, with about 7×10^5 cells /ml groundwater and more than 10^6 cfu/g sediment dry matter, the quantitatively predominant ecophysiological group of the autochthonous bacteriocenosis (Table 3). Due to methodological reasons, this group included also facultatively anaerobic bacteria. It could be demonstrated by the replica technique that the aerobic bacteriocenosis consisted at least partially of denitrifying bacteria. Using the MPN method, however, relatively low colonization densities of denitrifying bacteria were found in sediments and groundwater, in the same magnitude than sulfate- reducing bacteria (Table 3). Iron-reducing bacteria were present in significantly higher concentrations than these groups (Table 3), reaching approximately 35 to 65% of the abundance of the aerobic/facultatively anaerobic bacteria. The colonization density of the different ecophysiological groups reflects the influences of the abiotic environment, especially of redox potential and availability of electron acceptors.

Table 3   Colonization of groundwater and sediments of the quarternary aquifer by different ecophysiological groups of bacteria.

Sample	Total cell counts (DAPI staining)	Aerobic bacteria (colony forming units on R2A/100, agar)	Nitrate-reducing bacteria (MPN)	Sulfate-reducing bacteria (MPN)	Iron-reducing bacteria (MPN)
Groundwater SAFBIT 7/97	6.9×10^5 ml^{-1}	1.2×10^5 ml^{-1}	2.0×10^4 ml^{-1}	8.0×10^3 ml^{-1}	not determined
Sediment 18-19 m SAFBIT 30/98	8.8×10^5 g^{-1}	7.1×10^4 g^{-1}	1.2×10^3 g^{-1}	1.6×10^3 g^{-1}	2.4×10^4 g^{-1}
Sediment 20-21 m SAFBIT 30/98	1.1×10^6 g^{-1}	1.0×10^5 g^{-1}	6.3×10^2 g^{-1}	1.1×10^3 g^{-1}	6.7×10^4 g^{-1}

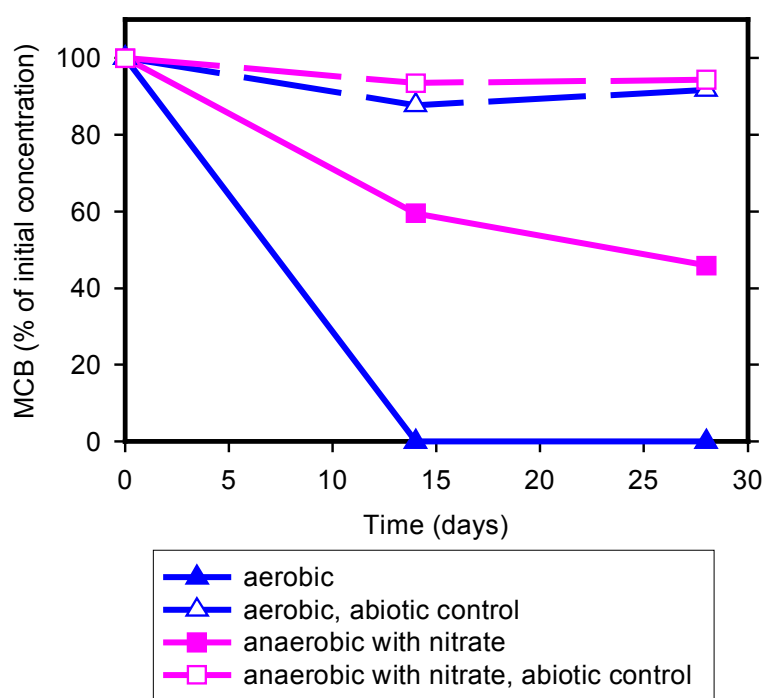**Potential of the autochthonous bacteriocenosis for the degradation of chlorobenzenes**

The biodegradation of chlorobenzenes has been intensively studied in the last decades. Under anaerobic conditions high chlorinated benzenes were reductively dechlorinated to MCB and the three isomers of dichlorobenzene (DCB) which are regarded as indegradable and, therefore, persisting substances under anaerobic conditions.

There are only some indications in the literature that benzenes with one or two Cl-atoms might be degraded anaerobically, but the mechanisms are completely unknown. The aerobic pathways of the degradation/mineralization of low chlorinated benzenes, however, are elucidated in detail and well understood (Figure 2).
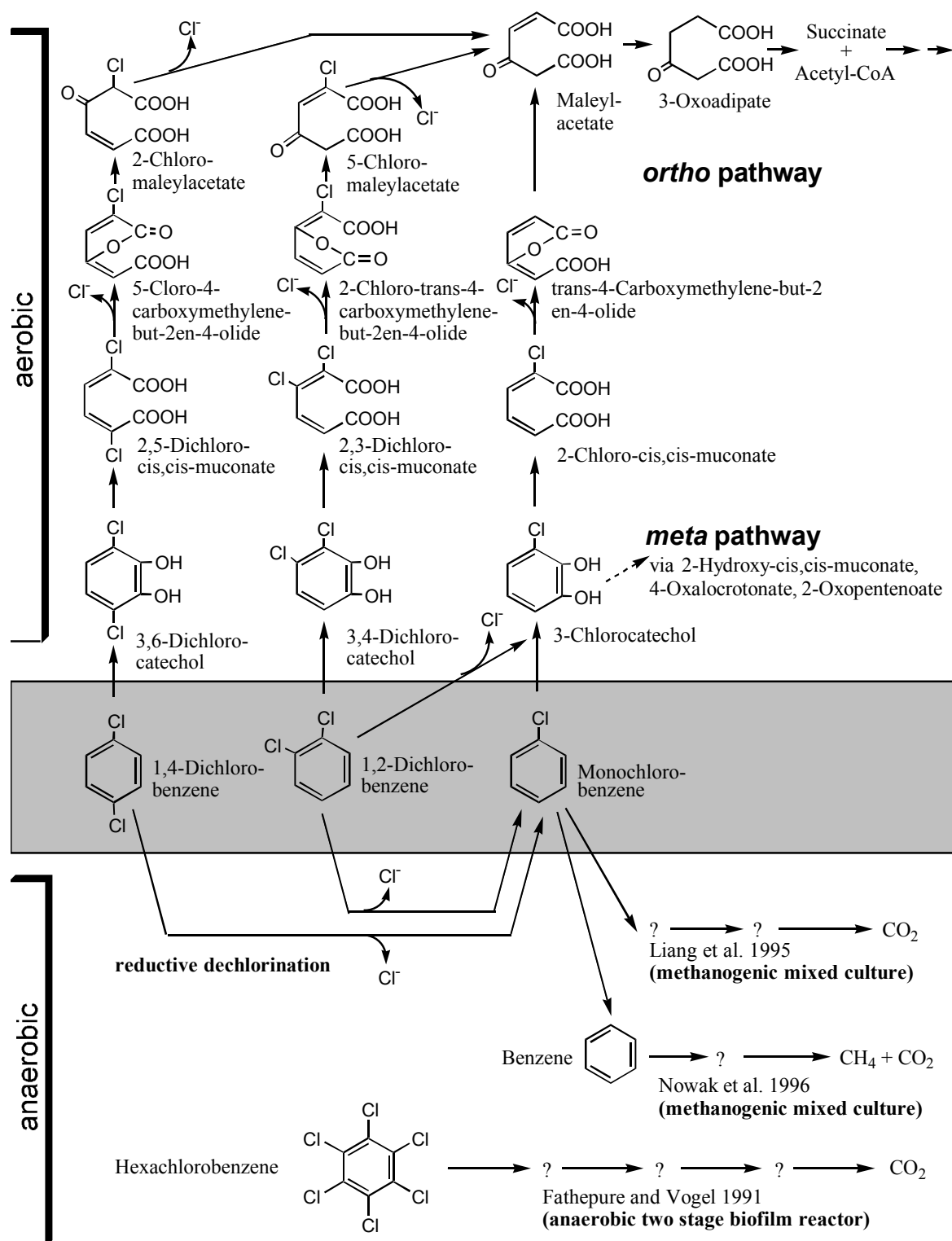
Figure 2   Pathways for the degradation of the main chloroaromatic contaminants (MCB,1,4- and 1,2-DCB) of the quaternary aquifer.

An extended screening programme at the beginning of our investigations showed that the autochthonous bacteriocenosis of the quarternary aquifer of the Bitterfeld test site is capable of degrading the main pollutants MCB and 1,4- DCB both under aerobic and anaerobic conditions. Basically, the anaerobic degradation processes proceeded significantly slower than the aerobic mineralization, the degradation of MCB under aerobic and denitrifying conditions (Figure 3) is quoted as an illustration of this general statement.

*Figure 3   Degradation of MCB by the autochthonous bactericenosis of the Bitterfeld aqui-
fer under aerobic and anaerobic (denitrifying) conditions. Initial MCB-
concentration: 18 mg/l (n=3).*

Aerobic degradation of MCB

More than 10 strains could be isolated from the quarternary aquifer which were capable of growing aerobically on MCB as sole source of carbon and energy. Strains with the best degradation properties (Figure 4) utilized 80 – 100 mg/l MCB within 48 h at 14°C (corresponding to the in situ-temperature of the aquifer). Members of the genus *Rhodococcus* predominated among the active MCB-degrading strains, but also Gram- negative bacteria with high degradation potential were isolated.

By feeding [14]C- labeled MCB it was shown that the autochthonous bacteriocenosis of the quarternary aquifer mineralized MCB: After 5 days of incubation about 7% of the fed radioactivity were found in the biomass, approximately 47% in the formed CO_2 (Figure 5).
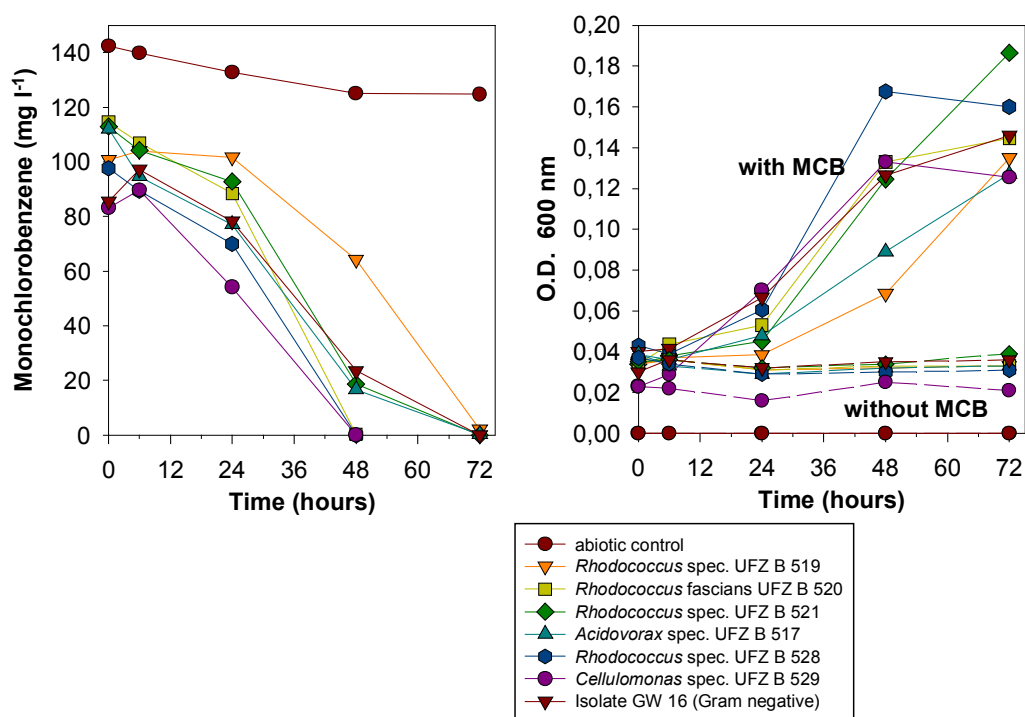
Figure 4   *Degradation of MCB under aerobic conditions at 14 °C - isolates from the autochthonous bacteriocenoses.*
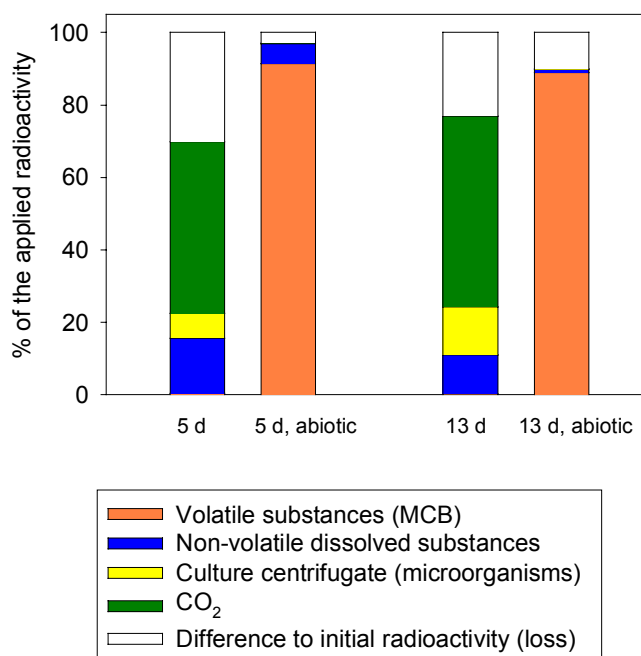

Figure 5   *Complete mineralization of monochlorobenzene by the autochthonous bacteria of the Bitterfeld bacteriocenosis under aerobic conditions - Application of ^{14}C-labelled monochlorobenzene.*

Anaerobic degradation of MCB

Using nitrate and sulfate as alternative electron acceptors a significant reduction of the MCB concentrations in the culture suspensions was measured under different laboratory conditions. In all experiments the chlorobenzenes (MCB, in some cases also 1,4- DCB) were the sole growth substrate. In contrast to processes with molecular oxygen as electron acceptor, the degradation processes were much slower even under optimized conditions. For example, in fed batch cultivation under denitrifying conditions the fed MCB (between 14 and 18 mg/l) was no more detectable in the culture suspension after 10-32 days of incubation (Figure 6).
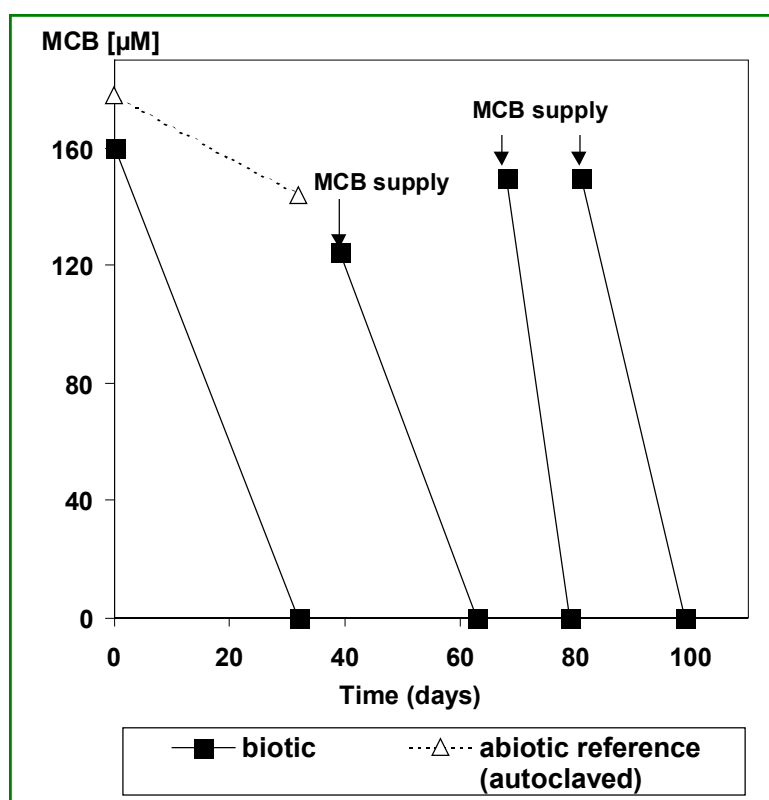

Figure 6   Degradation of monochlorobenzene by an enrichment culture in fed-batch cultivation under denitrifying conditions.

Anaerobic degradation processes were only observed when mixed cultures (enrichment cultures from the quarternary aquifer) were used as inoculum. Although denitrifying and sulfate-reducing taxa could be detected within these mixed cultures by analyzing their 16S rDNA (Table 4), pure cultures capable of degradation of MCB could be isolated not yet.

The mechanisms of the anaerobic conversion of MCB are still unknown and under intensive investigation in our laboratories. Both denitrifying and sulfate- reducing enrichment cultures grew with nitrate and sulfate, respectively, as electron acceptors on MCB as sole growth substrate. The expected metabolites CO_2, nitrite (in denitrifying cultures) and sulfide (in sulfate-reducing bacteria) could be detected during the

cultivation processes, but up to now it was impossible to establish complete, reliable mass balances. Although these experiments were performed with the common laboratory equipment for anaerobic work, it can not be excluded absolutely that traces of oxygen got admitted to the culture suspensions (e.g. by diffusion through tubes and plugs, as contaminant of the gas phases and solutions, etc.). These traces of O_2 might be necessary to initiate the degradation process. After that the further degradation might take place via the typical pathways of denitrification and sulfate reduction.

Table 4   Enrichment cultures from the quarternary aquifer capable of metabolizing chlorobenzenes anaerobically.

Denitrifying mixed culture
- growth on monochlorobenzene as sole source of carbon and energy under denitrifying (anaerobic) conditions
- consists of least 5 components which are most probably (according to analyses of their 16S rRNA) strains of
  - Hydrogenophaga palleroni
  - Pseudomonas stutzeri
  - Lactosphaera pasteurii
  - Agrobacterium tumefaciens
  - an iron- oxidizing denitrifying bacterium

Sulfate- reducing mixed culture
- grows on mono-, 1,2- and 1,4- dichlorobenzene as sole source of carbon and energy under sulfate- reducing (anaerobic) conditions
- consists of some Gram- negative and Gram positive sulfate- reducing strains which belong most probably to the genera
  - Desulfotomaculum and
  - Desulfovibrio

Degradation of chlorobenzenes in semi- technical scale

The results of the investigations in bench scale were confirmed successfully in semi-technical scale in the on site- plant (mobile test unit) in Bitterfeld. The microbiological experiments were performed in a column reactor of steel, which was filled by original sediment material from the quarternary aquifer (Figure 7). The column was continuously fed with original groundwater at the in situ- temperature of 14°C. After establishing steady state conditions, concentrated nitrate solution (16 mM KNO_3) was dosed resulting in a final concentration of approximately 1 mM nitrate in the groundwater inflow. The relation KNO_3 solution to groundwater as well as the retention time of this mixture in the column could be varied within a wide range. To avoid an access of air (oxygen) the sytem was completely closed, the gas phases in the sampling bottles and over the nitrate solution in the storage tank consisted of nitrogen. As a consequence of the nitrate feeding the concentration of MCB in the outlet of the column decreased considerably. The nitrogen content in the outlet was also significantly lower than the initial concentration due to formation of nitrite (and, possibly but not analyzed, molecular nitrogen). The degradation rate depended on the

retention time (Figure 8 and 9). At the highest retention time which was investigated (12 days) about 95% of the MCB and 91% of 1,4- DCB were degraded. These values correspond to absolute concentrations of about 1 mg/l MCB and 0.01 mg/l 1,4- DCB in the bioremediated groundwater.
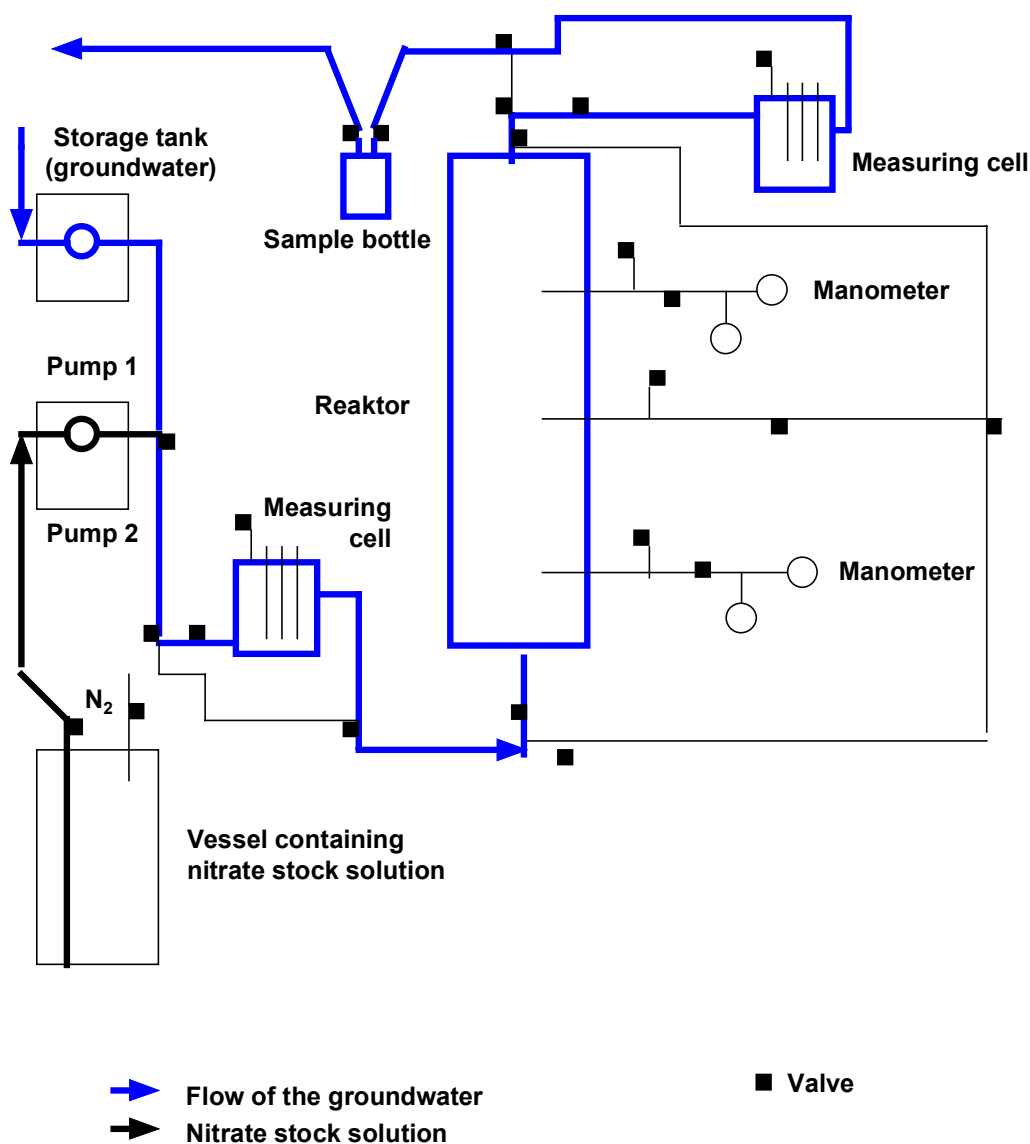

Figure 7   *Flow diagram of the on site- plant (mobile test unit), column 3.*

The results of our investigations in the mobile test unit in semi- technical scale demonstrate that the in situ- bioremediation of the chlorobenzene contaminated groundwater is possible by supporting the denitrifying autochthonous bacteriocenosis by feeding nitrate solution. The efficiency and long- term stability of the "nitrate procedure" will be investigated in the SAFIRA pilot plant under large- scale conditions.
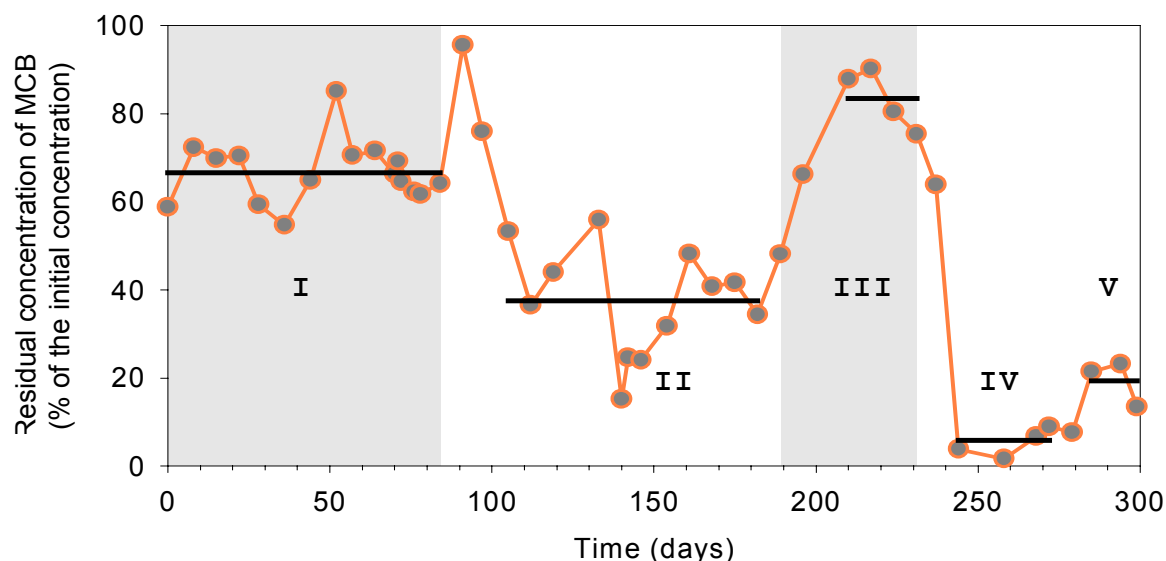
Figure 8   *Degradation of monochlorobenzene in the on-site-reactor (horizontal lines characterize the average value in the test phase during a stable steady state).*
Test phases:

> *I   Reference phase (without addition of nitrate), retention time 4 days*
>
> *II   Dosage of nitrate solution, retention time 4 days*
>
> *III Control phase (by-pass)*
>
> *IV   Dosage of nitrate solution, retention time 12 days*
>
> *V   Dosage of nitrate solution, retention time 6 days.*
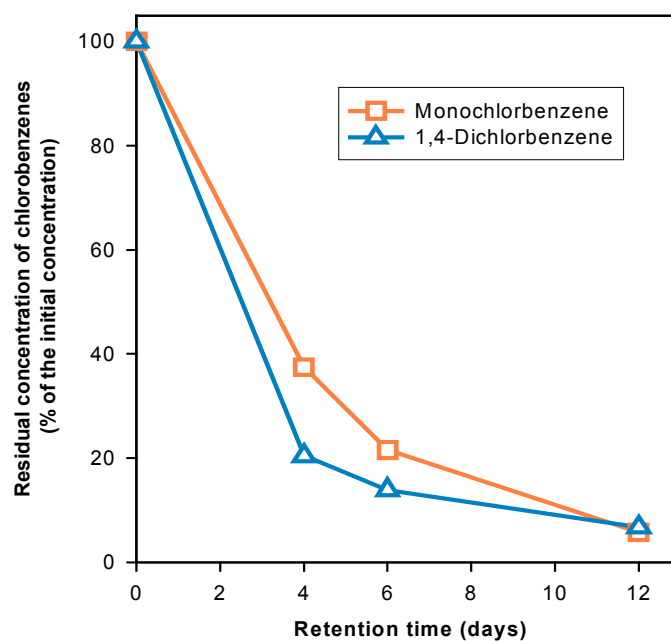
Figure 9   *Degradation of chlorobenzenes in the on-site reactor under denitrifying conditions as function of the retention time.*

Summary

1. The colonization density of the groundwater of the quarternary aquifer amounted to about 10^6 cells/ml. The quantitatively predominating ecophysiological groups are aerobic/facultatively anaerobic and iron- reducing bacteria, the abundance of denitrifying and sulfate-reducing bacteria is significantly lower.

2. The autochthonous bacteriocenosis is capable of degrading mono- and dichlorobenzenes when site-related limitations are removed, e.g. by addition of electron acceptors:
   - Under *aerobic conditions* monochlorobenzene is completely mineralized both by the bacteriocenosis and pure cultures isolated from aquifer material
   - Under *anaerobic conditions* and by application of nitrate and sulfate, respectively, as alternative electron acceptors the degradation processes occurred slower compared to aerobic degradation. The mechanisms of the anaerobic degradation are still unknown. It is possible that a primary ring modification requires traces of oxygen and the following degradation occurs under denitrifying /sulfatereducing conditions.

3. In the mobile test unit at Bitterfeld the almost complete elimination of the chlorobenzenes was demonstrated under in situ- related conditions at semi- technical scale. Continuous supply of nitrate solution to the original groundwater resulted in the degradation of 94% (corresponding to residual concentrations of $\approx$ 1 mg/l) of the original concentration of monochlorobenzene at sufficient retention times (12 days)

Biodegradation of chloroethenes and chlorobenzenes
in a two-phase anaerobic/microaerobic treatment zone system

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H. Rijnaarts[1], R. Hetterschijt[1], J. Mol[2], E. Visser[2],
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[1]   TNO
[2]   Tebodin
[3]   HBG-HWZ
[4]   Shell

Abstract

The remediation of groundwater contaminated with chloroethenes and chloroben-zene via stimulated natural attenuation (NA^+ process) is tested in a sequential anaerobic microaerobic sys tem. In this process, the chloroethenes are degraded in the first anaerobic stage, whereas chlorobenzene is degraded under microaerobic conditions. First results obtained with small scale column systems show that complete reduction of TCE takes place under anaerobic conditions, provided that sufficient electron donor (lactate, acetate, propionate and butyrate) is present. High sulphate concentrations are present in the Bitterfeld groundwater. The presence of sulphate may cause problems because it remains unclear from the experiments whether the reduction of sulphate is necessary before transformation of TCE can occur. The amount of electron donor needed for the reduction of sulphate is around 500 to 1000 times higher than the amount needed for the degradation ofthe chlorinated ethenes. The addition of electron donor and nitrogen is essential for complete dechlorination of TCE to ethene. Supply of a nitrogen source especially facilitates the reduction of cDCE and VC to ethene.

The degradation of chlorobenzene in the second phase of the NA^+ process was only possible with the addition of H_2O_2 to the groundwater. No degradation of chlorobenzene occurred under nitrate reducing conditions. Nitrate was only partially reduced.

Introduction

The Bitterfeld area is contaminated with a mixture of chlorinated aliphatic and aromatic compounds due to industrial activities of mainly the chemical industry. Because of lignite mining the groundwater level was kept low in the past, but the artificial lowering will be ceased in the very near future. This will lead to a migration of contaminated groundwater towards river plains and the village of Bitterfeld. The contamination levels vary among the upper and lower aquifers. The lower aquifer was mainly contaminated with chlorinated aliphatics (trichloroethene (TCE) and lower chlorinated ethenes) and benzene; whereas the upper aquifer contains primarily chlorinated benzenes [13]. Sulphate is found in very high concentrations in the Bitterfeld groundwater (up to 750 mg/l).

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 main research aim of the NOBIS project is 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.

The NOBIS part of the project consists of a stimulated bioremediation alternative (Natural Attenuation (NA)[+]) to remove both chlorinated ethenes and chlorobenzene.

Biological conversion of chloroethenes and (di)chlorobenzene and benzene

Chlorinated ethenes
Chlorinated ethenes, except PCE, are degraded both under aerobic and anaerobic conditions. PCE is only degraded under anaerobic conditions. Complete reductive dechlorination of TCE (Figure 1) is only observed with mixed cultures e.g., [6, 9, 11, 12]. 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.
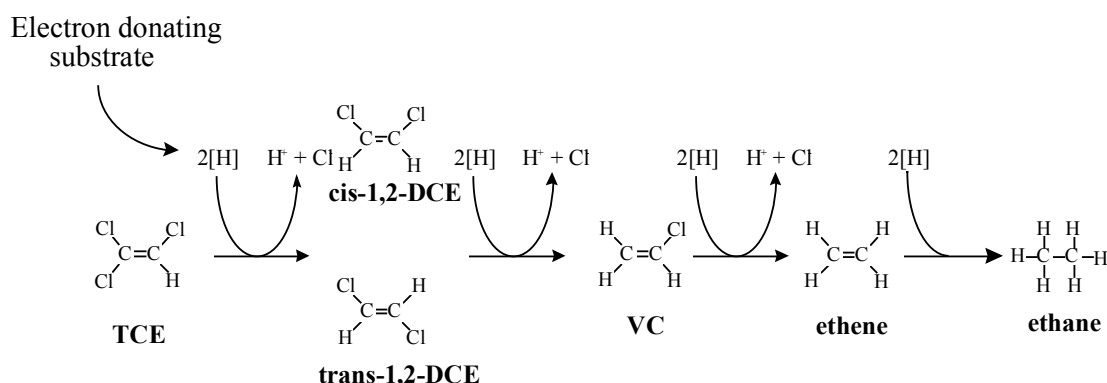

Figure 1 Reductive dechlorination of TCE.

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. Lactate, but also volatile fatty acids like propionate and butyrate seem to be suitable substrates [5, 7, 10]. 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, iron and manganese reducing conditions in microcosm studies [3, 4].

Under aerobic conditions, TCE and lower chlorinated ethenes are degraded via cometabolic reactions. VC is the only compound that can serve as a carbon source for aerobic microorganisms. The aerobic conversion of TCE, cis-1,2-DCE, and other DCE isomers, and VC may lead to the formation of toxic oxidised intermediates (ep-

oxides) which lead to a deterioration of the degradation, via inactivation of the enzymes responsible for their formation [1].

(Di)chlorobenzene and benzene

Anaerobic dechlorination of lower (tri- and di-) chlorinated benzenes to monochlorinated benzene has been reported under anaerobic conditions by microorganisms, which had been adapted to higher chlorinated benzenes [2]. Mineralisation of benzene was found under methanogenic, sulphate reducing and iron reducing conditions. So far, nothing is known about the pathways used by microorganisms to degrade benzene. Information about benzene transformation under denitrifying conditions is diverse. 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 microcosms studies. Apparently, under these conditions, the aromatic ring is activated via hydroxylation and after ring cleavage, the products are mineralised under anaerobic conditions. However, the presence of oxygen may also lead to more favourable environmental conditions [8, 14].

Tri-, di- and monochlorinated benzenes can be used as sole source of carbon and energy under aerobic conditions. Chlorinated benzenes are aerobically degraded via an initial oxygenation of the aromatic ring. These reactions are catalysed by a dioxygenase. 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).

Set-up of the experiments

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 chlorinated benzenes are more likely to be converted under aerobic conditions. Therefore, a sequential anaerobic-aerobic process should be implemented. In the anaerobic step, if feasible, TCE should be completely dechlorinated to ethene. 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) and the redox potential is relatively high. The addition of an electron donor will be necessary to lower the redox potential and serve as a supply of electrons for dechlorination. In the anaerobic reactor, a mi-

crobial population may develop, which is able to dechlorinate the dichlorinated ben-zenes leading to the formation of chlorobenzene and benzene.

In the second microaerobic reactor the chlorinated benzenes will be degraded. Ini-tially, the reactor will be operated under denitrifying conditions (Pathway I in Figure 2). If transformation of chlorobenzene under these conditions does not occur, the oxygen concentration will be increased to around 3 mg/l, which may lead to initial oxidation followed by further conversion under denitrifying conditions (pathway II). If necessary, the oxygen concentration will be further increased to levels sustaining the initial hydroxylation of the aromatic ring and even complete mineralisation (path-way III).

Aquifer material from the contaminated site will be used in the experiments with both the anaerobic and the microaerobic reactor. In this way the environmental conditions will resemble the situation *in situ*.
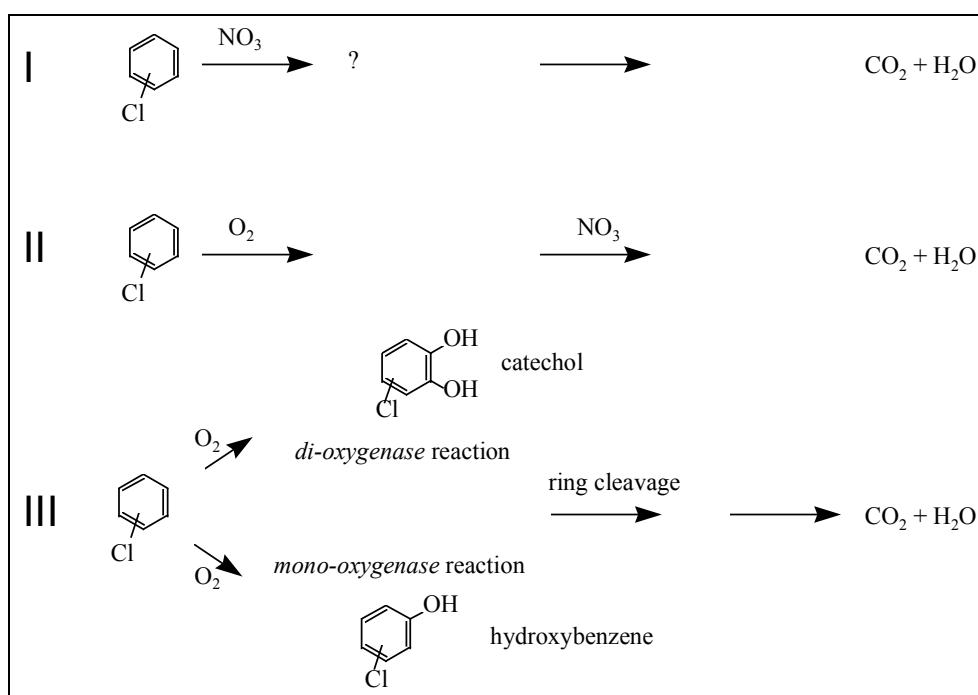

Figure 2   *Operation schedule of the microaerobic reactor.*

Aim of the experiments

The anaerobic column experiments should provide information on:

− whether or not complete reductive dechlorination of TCE and DCE in the Bitter-feld groundwater occurs under anaerobic conditions.

− the amount of electron donor needed for complete dechlorination of the chlorin-ated ethenes. This is especially of interest because of the high amounts of sul-phate (around 750 mg l^{-1}) present in the groundwater. It is currently unknown, whether sulphate reduction and dechlorination of the ethenes can occur simulta-neously or if all the sulphate must be removed before complete dechlorination

can take place. If all the sulphate must be removed, the amount of electron donor needed for the reduction of sulphate will be around 5000 to 1000 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 microaerobic column experiment should provide information on:

− whether transformation of chlorobenzene is possible under the conditions tested.

− the amount of nitrate and/or oxygen needed for the removal of chlorobenzene. Initially, the column will be run with nitrate as the sole electron acceptor. If chlorobenzene removal is not observed, an additional amount of oxygen will be supplied to the influent together with the nitrate to improve or enhance the degradation of chlorobenzene.

Material and Methods
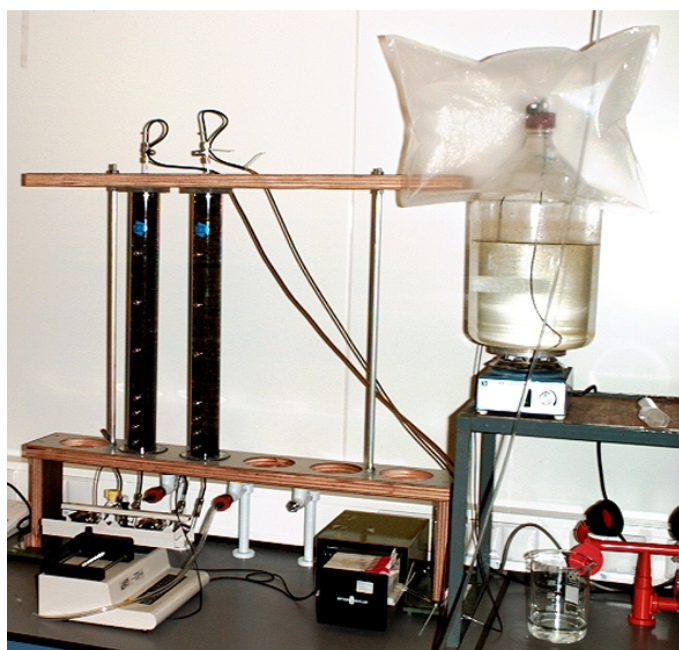
Figure 3   Anaerobic column systems.

The transformation of chloroethenes was investigated in duplicate column systems operated under anaerobic conditions (Figure 3). The groundwater for the anaerobic columns was taken from the Safbit 2 sampling well from 28 meters depth, because this groundwater contains TCE. The groundwater was sampled with a procedure to prevent contact with oxygen. Aquifer material from the Bitterfeld location was used. The degradation of TCE in the groundwater is tested in multiport columns, which are made of airtight PVC. The columns have a volume of 880 ml. Assuming a sediment porosity of 40% this leads to a working volume of 350 ml. The columns have 7 sampling points which are placed along the height of the columns. The columns were filled under anaerobic conditions with the soil, while continuously saturating with

groundwater to assert the degassing of the soil and uniform packaging of the column.

The columns are upwardly flown through with anaerobic groundwater amended with electron donor. A mixture of lactate, acetate, propionate and butyrate is currently dosed at equal electron equivalent base, which leads 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). At a later stage during the experiments nitrogen was added to the groundwater as NH_4Cl.

The groundwater containment vessel is closed airtight and connected to a gas bag filled with N_2 to prevent the influx of oxygen. The influent groundwater is pumped into the columns. All connecting lines and tubes in the system are made of Viton® or stainless steel to prevent the adsorption of the chlorinated compounds. The column is operated with an initial hydraulic retention time of 2 days (groundwater flow around 178-200 ml d^{-1}). The columns are run in the dark in a temperature controlled room at 20°C.

The experiment was divided into four phases (Table 1) to test different methods to enhance the reductive dechlorination of the chloroethenes in the groundwater.

Table 1   Operating conditions of the two anaerobic columns.

Phase	Period (days)	Column 1	Column 2
I	0 – 33	1 * ED	1 * ED
II	34 – 78	2 * ED	2 * ED
III	79 – 120	3 * ED	2 * ED + 50 mg/l NH_4^+
IV	121 - 149	4,5 *ED	3 * ED + 75 mg/l NH_4^+

The microaerobic column (Figure 4) is run with chlorobenzene (CB) containing groundwater from the location. The degradation of CB and other chlorinated aromatic compounds in the groundwater is tested in a stainless steel column, which has a volume of 7.85 l. Assuming a porosity of 40%, this leaves a working volume of 3.1 l. 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 is upwardly flown through with groundwater.

The influent of the column consists of groundwater amended with nitrate at a concentration of 2.4 mM (KNO_3). This concentration is twice the concentration needed for complete oxidation of 20 mg l^{-1} chlorobenzene in the groundwater. The nitrate was added in a 10 times concentrated solution to the groundwater to minimise dilution of the groundwater.

Figure 4   Microaerobic column system.

At a later stage during the experiment small amounts of oxygen (around 3 mg/l) were added to the groundwater. This was achieved via saturation of the nitrate solution with pure oxygen. During the period when transformation under completely aerobic conditions was investigated, the oxygen concentration in the groundwater was further increased and oxygen was dosed as H_2O_2.

The column is operated with an initial hydraulic retention time of 2 days (groundwater flow around 65-70 ml h^{-1}).

The column is run in the mobile on-site test unit. In this unit the temperature is controlled at 20°C.

Results and discussion

Anaerobic conversion of chlorinated ethenes

Phase I

The addition of electron donor at a dosage, which would have been enough for the complete reduction of both the sulphate and the chlorinated ethenes present (1 * ED) in the groundwater, did not lead to the transformation of the chlorinated ethenes present. Small amounts of PCE and TCE were converted to presumably cDCE, but the higher chlorinated ethenes are not completely transformed to lower chlorinated ethenes under these conditions. More than 90% of the VFA and lactate were con-

verted to unknown products. During this period sulphate reduction started, but was also not complete.

The lack of dechlorination could have been caused by:

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

These options were tested in following phases of the laboratory experiments

Phase 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 5). The dechlorination of TCE to *cis*-1,2-dichloroethene (cDCE) was complete in both columns (Figure 6). Also PCE was slightly converted to lower chlorinated ethenes. The reason for the incomplete dechlorination is not clear. PCE is expected to be dechlorinated at least as easily as TCE. During this phase cDCE, tDCE and VC were not converted to (lower chlorinated) ethene(s).
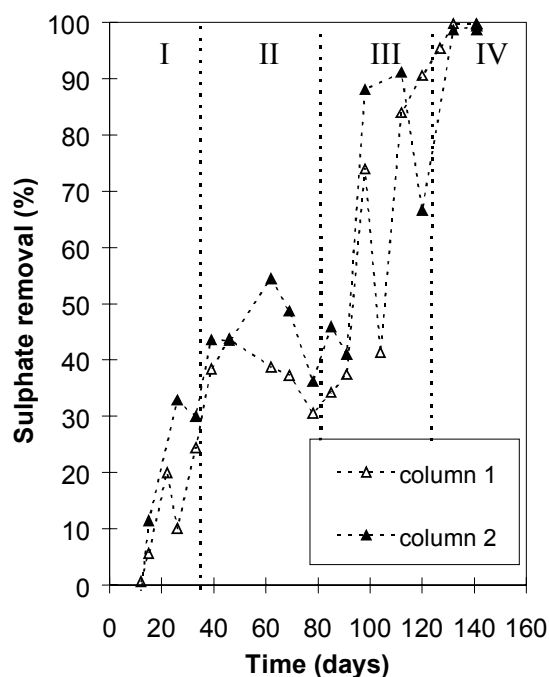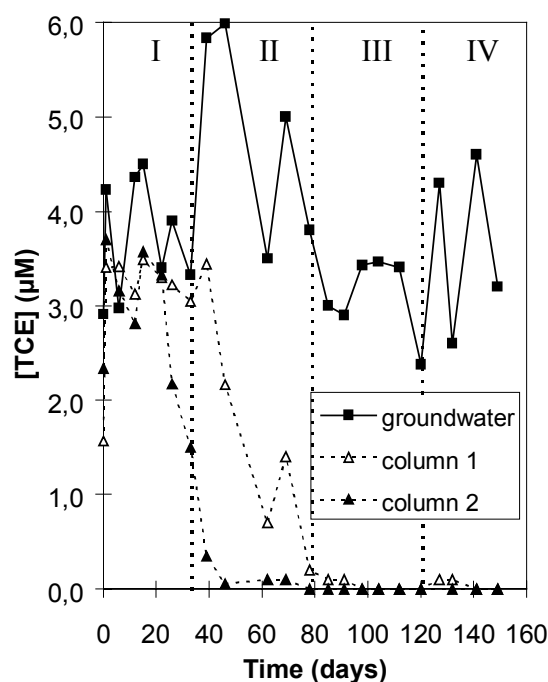

| Figure 5 | Sulphate removal in the anaerobic columns. | Figure 6 | Removal of TCE in the anaerobic columns. |

Phase III

The increase of the electron donor concentration in column 1 to 3*ED did not lead to further extensive dechlorination of the cDCE to VC and ethene (Figure 7). PCE was

almost completely converted in both columns. Only a small amount of VC was formed under these conditions from cDCE, because tDCE was hardly degraded.

The addition of 50 mg NH_4^+/l in column 2 also caused only little effect (Figure 8). 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.

Phase IV

A further increase of the electron donor concentration to 4.5 * ED in column 1 did not significantly enhance the 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 8). 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 cDCE (in Phase III: 2*ED + 50 mg/l 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 phase. Because the increase of the electron donor concentration (from 2*ED to 3*ED) alone did not lead to the desired transformation of cDCE (Figure 2.7), 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 cDCE to ethene will grow.
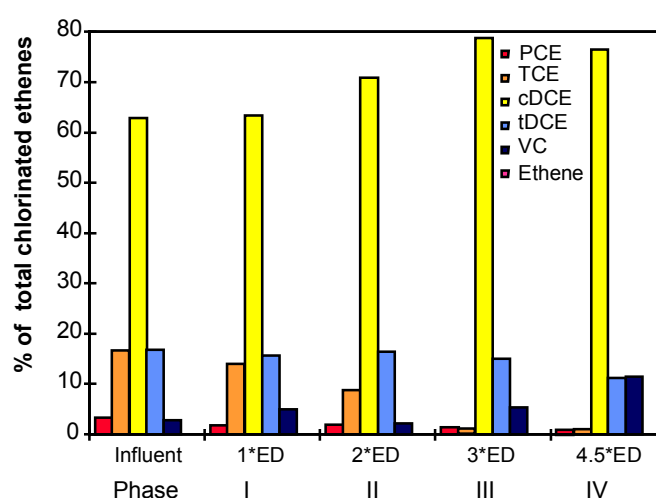

Figure 7   *The effect of increased electron donor concentration on the TCE transformation in the Bitterfeld groundwater.*
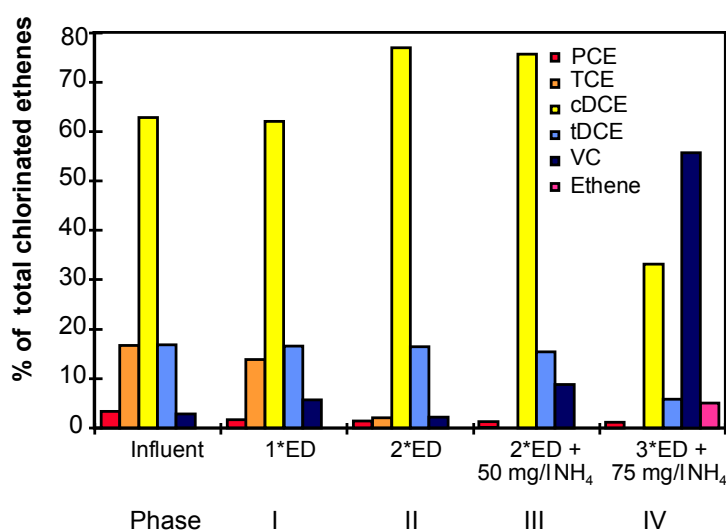
Figure 8   *The effect of increased electron donor concentration and nutrient addition on the TCE transformation in the Bitterfeld groundwater.*

For the anaerobic reaction step it is not yet clear whether complete removal of sulphate is necessary for the dechlorination. Obviously, if this is the case, it is very unfavourable for the economics of the process as a whole. The reduction of the sulphate requires around one thousand times the amount of electron equivalents compared to the complete reductive dechlorination of TCE.

It has been reported that reductive dechlorination and sulphate reduction can occur simultaneously. In some cases sulphate inhibits dechlorination. However, sometimes chlorinated ethenes are the preferred electron acceptor compared to sulphate or the other way around. From our laboratory experiments the conclusions can still go both ways. The role of sulphate is under further investigation.

It is expected that with a follow-up experiment with addition of nitrogen to the groundwater directly from the start, the amount of ED necessary to sustain dechlorination will be lower than the 3 * ED that was added in this experiment. Another possibility for long term experiments may be to quickly reduce the aquifer material with a large dosage of electron donor (shock load), followed by the supply of smaller amounts of (another) electron donor to sustain dechlorination and sulphate reduction (the latter, if necessary).

Microaerobic conversion of chlorobenzene

Initially, the transformation of chlorobenzene in the Bitterfeld groundwater was investigated under denitrifying conditions. However, the addition of nitrate alone, did not lead to the transformation of substantial amounts of chlorobenzene (Figure 9). The addition of small amounts of oxygen did also not result in an increase in the removal of chlorobenzene. Up to this period, nitrate was supplied at a concentration of 2.4 mM (around 150 mg/l NO_3^-). The nitrate concentration in the effluent of the column varied from 67 to 94 mg/l in the effluent. Nitrate conversion was not complete.

The reason for this incomplete conversion is not known. Nitrite concentrations were always below detection limit. Therefore, it is highly unlikely that the incomplete denitrification is caused by nitrite toxicity. A shortage of TOC in the groundwater combined with the inability of the denitrifying bacteria present to use chlorobenzene as the carbon source, could be the explanation.

Chlorobenzene reduction under denitrifying condition so far was seldom observed. We found no removal of chlorobenzene, which also could have been caused by other non-biological processes, like adsorption.

Oxidation of chlorobenzene under denitrifying conditions occurs according to the following reaction:

$$C_6H_5Cl + 5.6NO_3^- + 4.6H^+ \longrightarrow 6CO_2 + 4.8H_2O + Cl^- + 2.8N_2$$
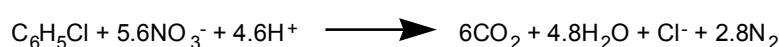
The amount of NO_3^- needed for chlorobenzene conversion is 2.8 g per g chlorobenzene. Twice the amount of nitrate needed was added to the groundwater.

Earlier, research carried out in our laboratory and by others had also shown that addition of small amounts of oxygen (25% of the total reducing capacity of the aquifer) stimulated the degradation of benzene in a strongly reduced aquifer [8, 14]. In that case benzene was assumed to be initially oxidised followed by further degradation under anaerobic conditions. In contrast with these results, the addition of a small amount of oxygen to the groundwater hardly lead to a any increase of the chlorobenzene removal in our column system. A reason for the difference in results may be found in the nature of the sediment used in the experiments. The oxygen may have been used to oxidise sediment components and not for microbiological activation of the aromatic ring.
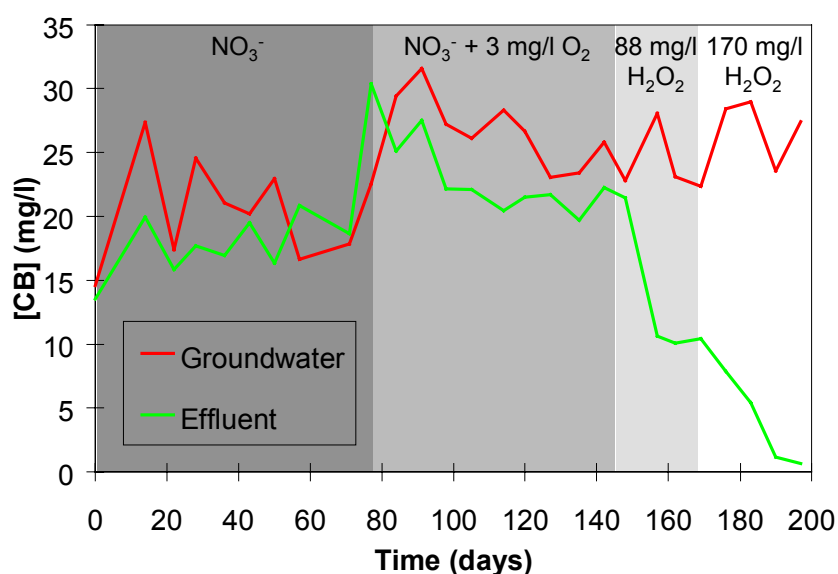

Figure 9   Transformation of chlorobenzene in the microaerobic column.

After the oxygen concentration in the groundwater was increased to the amount (in theory) sufficient for complete mineralisation of chlorobenzene via the addition of hydrogen peroxide (88 mg/l H_2O_2), chlorobenzene removal increased. With the increase of oxygen concentrations in the groundwater the addition of nitrate to the groundwater was ceased, because the mineralisation of chlorobenzene with oxygen as the electron acceptor was now the only process likely to occur. A further increase of the amount of hydrogen peroxide led to an improved chlorobenzene transformation (Figure 9).

Mineralisation of chlorobenzene under aerobic conditions requires a substantial amount of oxygen:

$$C_6H_5Cl + 7O_2 \longrightarrow 6CO_2 + 2H_2O + Cl^- + H^+$$

$$2H_2O_2 \longrightarrow O_2 + 2H_2O$$
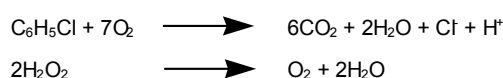
The amount of H_2O_2 needed for chlorobenzene mineralisation is 4.2 g per g chlorobenzene.

Our experiments showed that the addition of twice the amount of oxygen needed for complete mineralisation (added in the form of 170 mg/l H_2O_2) is necessary to obtain the transformation of substantial amounts of chlorobenzene. Only half of the chlorobenzene is converted when the oxidant : chlorobenzene ratio is 1:1 (88 mg/l H_2O_2). This much higher than what was originally calculated. This could be due to an insufficient degree of oxidation of the aquifer material, but this can not be founded by evidence.

At the moment chemical degradation of chlorobenzene in the column can not be excluded. The importance of chemical degradation processes may be found out by lowering the oxygen concentration again after complete degradation of the chlorobenzene is obtained. If the degradation of chlorobenzene continues to proceed at the same level, this is evidence for biological transformation of the chlorobenzene. Also the products formed during degradation are unknown. This remains to be investigated.

General discussion

Under the applied conditions too much electron donor and oxygen have to be administered to the anaerobic and microaerobic column, respectively, to sustain sufficient degradation of the target compounds. This makes the process less economically and technologically feasible.

In general it can be stated that for the process of in situ biotransformation of the compounds to become feasible the amount of compounds which are used to stimulate the biological processes will have to be decreased. It is also expected that lower amounts of electron donor and oxygen will be able to stimulate the desired transformation processes. For the anaerobic step, this assumption is based on the fact that complete dechlorination started only after the addition of nitrogen to the groundwater. This improvement in process performance was not linked to the increase of the

amount of electron donor. If the nitrogen is added to the groundwater at an earlier stage during the start-up, it is likely to have a beneficial effect on the process as a whole. This will result in a lower demand for electron donor.

In the microaerobic step, the possibility of the transformation of chlorobenzene with small amounts of oxygen is still believed to be feasible given the positive results described in literature.

Conclusions

Chlorinated ethenes under anaerobic conditions:

− Complete reduction of TCE takes place under anaerobic conditions, provided that sufficient electron donor is present.

− It is still unclear, whether sulphate has to be reduced before dechlorination can take place or whether simultaneous transformation takes place.

− Supply of a nitrogen source facilitates the reduction of cDCE and VC to ethene.

Chlorinated benzenes under microaerobic conditions

− No degradation of chlorobenzene occurred under nitrate reducing conditions. Nitrate was only partially reduced.

− The addition of higher levels of oxygen facilitates the removal of chlorobenzene.

Future research

Future research will focus on the possibilities of lowering the electron donor concentration in the anaerobic column. Also, the use of other electron donors that are equally effective, but lower in costs will be evaluated. The application of the mixture of lactate and volatile fatty acids that is applied at the moment is not suitable for long term economical stimulation of biological remediation. Other electron donors, either commercial products or mixtures like compost extract or pure products like methanol (which is relatively cheap) will be considered.

Also, the fate of sulphate in relation to the dechlorination processes will be investigated. When it turns out that the sulphate will not have to be completely reduced prior to dechlorination, this will lead to a decrease in the amount of electron donor needed and a decrease in the amount of sulphide formed. This would make the process economically and technologically more feasible.

The TOC of the groundwater and the effluent of the system will be followed more closely.

For the microaerobic step the future research will deal with the application of low amounts of oxygen in combination with nitrate as the electron acceptors for chlorobenzene degradation.
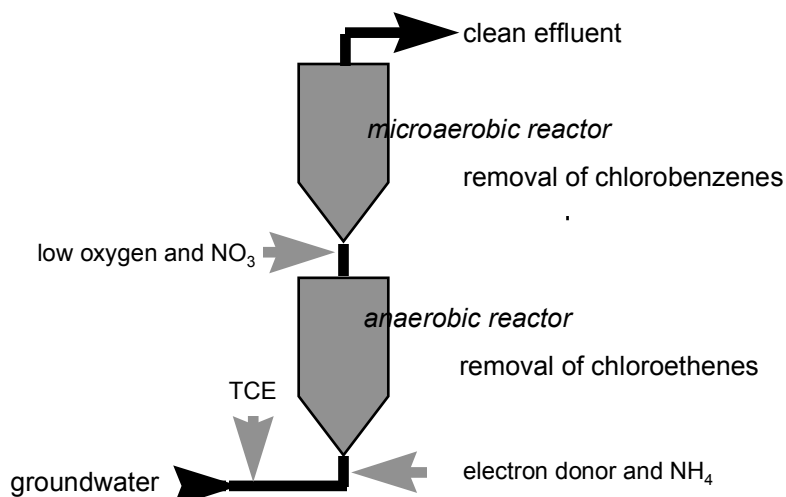
Figure 10 The set-up of the in situ reactor systems.

For both reaction steps, research will focus on the background demand of electron donor and oxygen needed to create the appropriate conditions for transformation of the chloroethenes and chlorobenzene, respectively. Future research will also include the combination of a sequential anaerobic/aerobic system to evaluate the fate of sulphide formed in the anaerobic reactor system in the microaerobic reactor.

The NA+ process will be further tested at a larger scale in the in situ reactors at the Bitterfeld location (Figure 10). The reactors (two anaerobic-microaerobic systems) will be started up with electron donor and nitrogen for the anaerobic phase and nitrate with a low oxygen concentration for the microaerobic phase.

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The influence of groundwater specific parameters on the performance of in-situ reactors based on the example of in-situ activated-carbon-filtration

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Main focus of this SAFIRA-project is the development and implementation of in-situ techniques for the remediation of groundwater contaminations. However, all in-situ reactors are affected by groundwater-specific processes like plugging and chemo- or biofouling due to precipitations or the growth of biomass which can reduce the removal efficiency of the systems. Also the transport of contaminants sorbed to small particles may lead to a low but constant flux of contaminants in the effluents of the reactors.

In this project the influence of these processes on the performance of the SAFIRA reactors will be investigated based on the example of activated carbon filtration. Although activated carbon filtration is a standard method in drinking water treatment, little is known about the long-term performance of this technology for contaminant removal under in-situ conditions in groundwater. The long-term stability of the contaminant removal mechanisms is crucial for the economically successful application of any technology.

The basic principle of the activated carbon filtration is the adsorption of dissolved contaminants onto the activated carbon. The adsorption of the contaminants occurs onto the internal surface of the activated carbon particles. One gram of activated carbon can have a surface area as high as 1000 m². Packed into columns which are operated in a flow-through mode, the activated carbon can effectively remove contaminants from water. Figure1 shows the results of an experiment were 10 mg/l TCE (trichloroethylene) were pumped through a column packed with 56 g of activated-carbon. After displacing the pore-volume about 1200 times TCE was finally detected in the effluent and concentrations increased thereafter. Under ideal conditions, this breakthrough of contaminants is observed when the sorption capacity of the activated carbon is reached. Assuming equilibrium conditions and deionized water, the sorption capacity depends only on the contaminants concentrations. However, under in-situ conditions the sorption capacity is strongly influenced by the hydrochemistry of the groundwater. Especially the precipitation of mineral phases, the growth of biomass or blocking of pores due to particles can reduce the performance of activated carbon filtration ("chemo-, biofouling"). As electron microscope images show, the surface of the activated carbon used for extended periods of time gets coated with various materials. The thickness of the coating can be in the range of 2 µm. This surface coverage may lead to a reduced sorption capacity as well as to slower sorption kinetics resulting in an earlier breakthrough of contaminants through the filter.
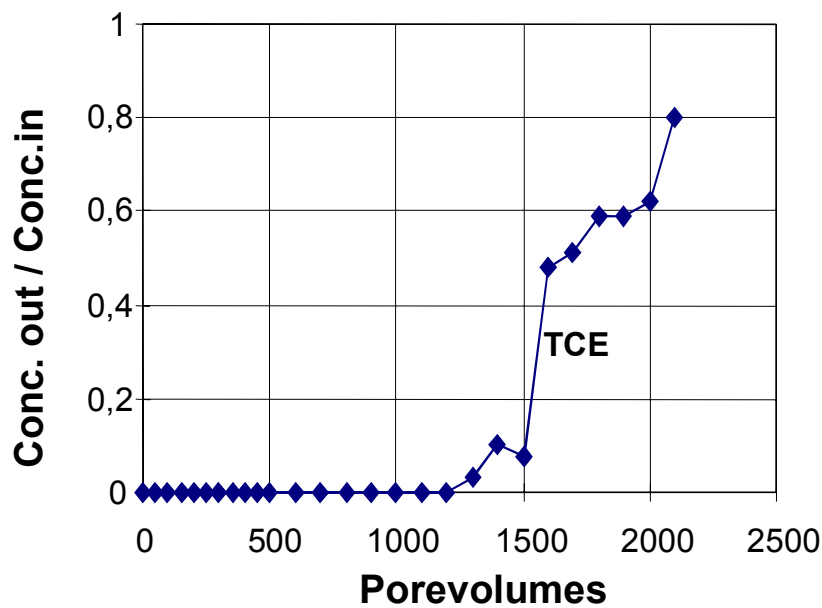
Figure 1   Breakthrough of TCE in a column experiment with activated carbon.

The goals of this SAFIRA project include:

1. The determination of the long-term release of contaminants from the softcoal seam present in the aquifer at the site.

2. The investigation of the mechanisms leading to particle enhanced contaminant transport.

3. The evaluation of the long-term performance of in-situ activated carbon filtration.

A seven months column experiment in the mobile test unit at the SAFIRA site in Bitterfeld was already performed to study the performance of the activated carbon filtration with groundwater. The activated carbon (Adako AGK 303) was packed in a column (100 cm x 28 cm) and operated in a flow-through mode. The mean residence time of the groundwater in the carbon bed was approx. 30 hours. Within the seven months of the experiment, approx. 180 pore-volumes were exchanged. At the end of the experiment samples of the carbon were taken and analyzed for contaminant concentrations.

Within the seven months of the column experiment, the chlorobenzene as the major contaminant in the groundwater was removed effectively by the activated carbon (inflow concentrations ~ 20mg/l) (Figure 2). The extraction of the activated carbon with hot methanol at the end of the experiment revealed sorbed chlorobenzene only at the first 10 cm oft he carbon pack. However, in the first four months very low and decreasing chlorobenzene concentrations were detected in the effluent. It is assumed, that this is due to particle-facilitated transport of chlorobenzene through the activated carbon bed.
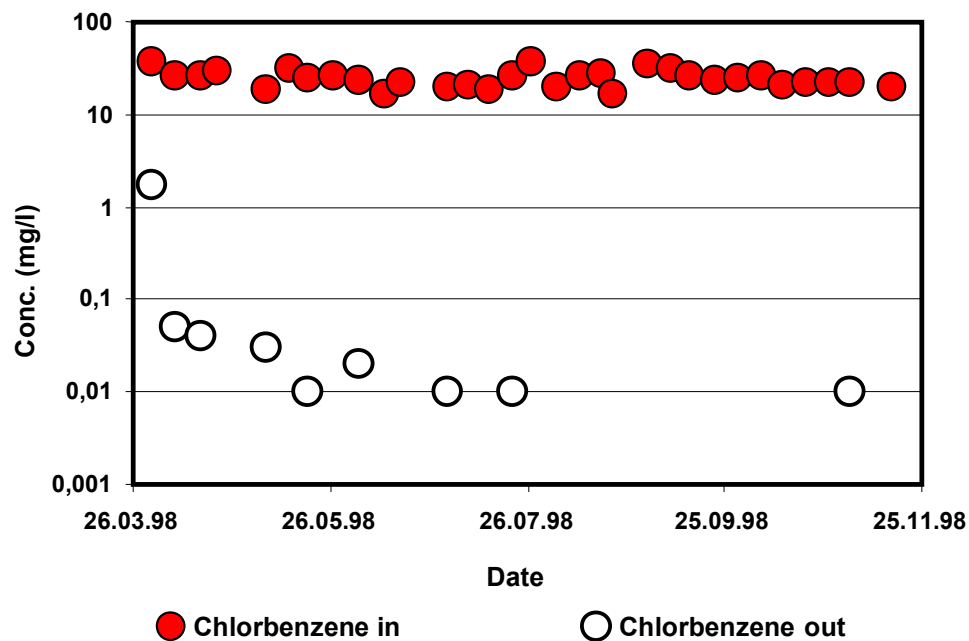
Figure 2   Results of the seven months column experiment in the mobile test unit.

In conclusion, it was shown, that activated carbon filtration is a very effective method to remove chlorobenzene from the Bitterfeld groundwater. Within the seven month of the experiment, the sorption capacity of the activated carbon was not reached and no breakthrough of contaminants was observed. However, the low contaminant concentrations in the column effluent in the beginning of the experiment need further investigations.

Elimination of volatile organic compounds by adsorption and simultaneous microbiological degradation on activated carbon

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Abstract

The efficiency of classical remediation technologies for contaminated soils and groundwater is limited. At many sites, remediation of aquifers using active methods, i. e. pump-and-treat technologies, is expected to require continuous pumping measures for decades or even longer. As a consequence emerging technologies like passive in-situ systems for plume treatment are promising. The application of passive systems is very interesting from the economical point of view since it seems to be a relatively cheap and reliable long-term remediation technology.

Passive remediation systems like porous and permeable reactive walls or "Funnel-and-Gate" systems intersect the path of the contaminant plume. By the natural groundwater flow the contaminants are transported into the reactive zones where decomposition takes place. Downstream water will be deliberated from the contaminants. Various biological and abiotic methods for the treatment of ground- and wastewater contaminated with volatile organic hydrocarbons (VOCs) are suggested in literature.

A very promising way for the treatment of VOC-contaminated aquifers in passive systems seems to be the stimulation of microorganisms capable to mineralize the pollutants. The system used in the SAFIRA project combines microbial degradation with adsorption of the VOCs on granular activated carbon. The microorganisms covering the activated carbon as a biofilm degrade the adsorbed pollutants resulting in a continuous biological regeneration of the adsorbent.

Preliminary results are promising. The current laboratory investigations focus on the bioavailability of the contaminants adsorbed on activated carbon. In first experiments Monochlorobenzene was chosen as a model compound, because it is the main contaminant at the Bitterfeld site. In the frame of the SAFIRA project the experiences obtained in the laboratory will be transferred to the large scale subsurface treatment facilities.

Some remarks on the degradability of volatile organic compounds present in the Bitterfeld aquifer

At the Bitterfeld site halogenated compounds represent the predominant contaminations, which are relatively resistant to microbial attack under the natural in-situ con-

ditions. Bioremediation techniques, that completely transform halogenated compounds into innocuous metabolites without any toxic end products, may be best suited for the treatment of contaminated soil and/or groundwater. A comprehensive knowledge of the factors limiting microbial degradation of the site-specific contaminants is a prerequisite for the successful implementation of large scale bioremediation.

Aliphatic halogenated compounds

Because of the high electronegativity of the halogenated substituents especially higher halogenated aliphatic compounds are poorly accessible for oxidative attack. The majority of investigations address the reductive dehalogenation of VOCs under anaerobic conditions. Due to lower energy production with decreasing number of halogen substituents reductive dehalogenation often stops on the level of Vinylchloride (VC). Under anaerobic conditions, this dead end product often causes environmental problems because of its high toxicity [17, 10, 1]. Nevertheless a complete reductive dechlorination of TCE - even by a pure culture, *Dehalococcoides ethenogenes* – has been demonstrated recently [6].

Aromatic chlorinated compounds

The predominant hazardous compound present in the Bitterfeld testaquifer is Monochlorobenzene with a concentration >10 mg/l. Dichlorobenzenes and Trichlorobenzenes have also been detected in low concentrations (350 µg/l 1,4-Dichlorobenzene; 60 µg/l 1,2-Dichlorobenzene; 40 µg/l Trichlorobenzenes). The lower chlorinated benzenes are well biodegradable under aerobic conditions [2, 15]. The reductive dechlorination of the higher chlorinated benzenes seems to stop on the stage of Monochlorobenzene [13]. Besides the chlorinated compounds some aromatic hydrocarbons like benzene are present in low concentrations (40 µg/l).

The composition of the contaminants at the Bitterfeld site indicates a considerable anaerobic biotransformation of the initially present highly chlorinated aliphatic and aromatic compounds to less chlorinated ones which are not further degraded without additional measures.

Biological regeneration of activated carbon

In the 70th first investigations on the bioregeneration of activated carbon were published [5, 3]. The process takes advantage from the microbial colonisation on the surface of the granular activated carbon resulting in simultanous regeneration of the loaded adsorbent. The biological activated carbon (BAC) process has been studied by several authors [16, 7, 11, 4].

The kinetics of activated carbon bioregeneration is a function of the pollutant desorption rate. The type of activated carbon, the physicochemical properties of the pollutants, and the contact time between the contaminant and the activated carbon

significantly affect the bioavailability [4, 14]. A stimulation of the degradation rates of microorganisms is possible by establishing suitable growth conditions [8, 12].

First results from the laboratory tests and progress in the research programme

The TU Dresden and DVGW-TZW research programme in the frame of SAFIRA is based on data obtained by [1] concerning the microbial reductive dechlorination of volatile aliphatic chlorinated hydrocarbons (chlorinated ethenes). A mixed culture isolated from soil showed the capacity to degrade Tetrachloroethene (PCE), Trichloroethene (TCE), Dichloroethene and VC to Ethene in batch experiments. Rates up to 90 µmol/(l×d) PCE degradation were determined. The rate of dechlorination in small scale activated carbon columns was fairly high, too. Up to 65 µmol/l PCE were transferred during 30 minutes empty bed contact time per kg activated carbon by simultaneous adsorption and decomposition. In contrast to the control experiment based only on adsorption no breakthrough was observed during these long term experiments.

Since Monochlorobenzene is the predominant contaminant in the Bitterfeld testfield aquifer, the effect of activated carbon on its bioavailability has to be studied in the beginning. In first experiments, biodegradation by the autochthonous microorganisms was examined under aerobic conditions. Respirometric batch experiments revealed a considerable oxygen consumption even in the presence of activated carbon. Next experiments will focus on the biodegradation rates obtained at different ratios of Monochlorobenzene to activated carbon.

During the research programme the chlorinated aliphatic hydrocarbons will be studied, too, although the concentration of those compounds in the Bitterfeld testaquifer is low. However there are other areas in the industrial area of Bitterfeld where chlorinated aliphatic hydrocarbons can be found in much higher concentrations.

Simultaneous adsorption and biodegradation of pollutants present in the Bitterfeld aquifer in the pilot plant of SAFIRA

The objective of the research proposal is the adsorption of the contaminants on activated carbon and their induced degradation by adapted microorganisms attached to the carbon surface. The pilot plant for the intended investigations consists in 2 lines of 2 reactors. The reactors of the first line are filled with granular activated carbon and the reactors in the second line are containing nonadsorbing material in order to distinguish between biological and adsorbing processes. The groundwater is pumped through an anaerobic zone prior to an aerobic zone. During the first step the higher chlorinated hydrocarbons (e. g. PCE, TCE) will be dechlorinated to a certain extend. In the aerobic zone the metabolites from the first step and monochlorobenzene are expected to be mineralized. If the co-contaminants do not serve as co-substrates for the dehalogenation, other co-substrates will be added. The operation of the pilot plant will be based on the results obtained from the laboratory scale experiments.

Perspective

The main objective of the research programme is to extend the operation time of activated carbon filter systems by biodegradation of the contaminants adsorbed. Similar to the biological activated carbon (BAC) already used in drinking water treatment facilities, it is planned to develop a long lasting reactive system for subsurface reactors. The SAFIRA programme provides both the possibility for basic research in the laboratory and its application in pilot scale under real aquifer conditions.

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Degradation of halogenated organic pollutants by ultrasound-assisted catalytic oxidation
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The contribution of the "Institut für Nichtklassische Chemie" to the SAFIRA project is the degradation of halogenated organic pollutants by ultrasound-assisted catalytic oxidation, involved with the project B.3.3.

Contaminated ground water treated by funnel and gate systems contains mainly aliphatic or olefinic halogenated hydrocarbons, which are dehalogenated by iron zero reactive walls. In the ground water at the Bitterfeld area there are mainly halogenated aromatic hydrocarbons, like chlorobenzene as a major representative, as pollutants. They cannot be degraded with this technique.

The catalytic oxidation is one of the so called advanced oxidation processes (AOP) which makes it possible to degrade aromatic compounds in waste water.
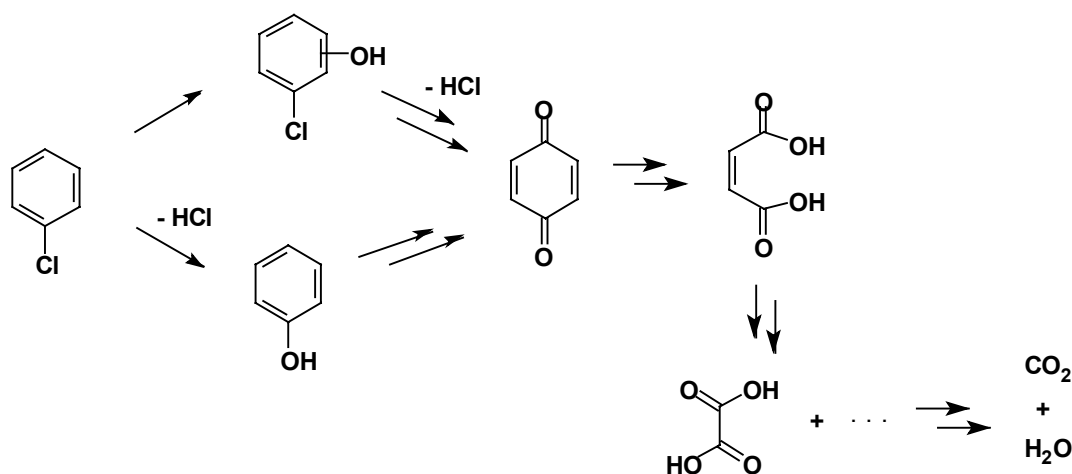

Figure 1   Mechanism of the catalytic oxidation.

The identified degradation products suggest a process based on hydroxyl radical chain reactions (Figure 1).

Starting with the generation of the hydroxyl radicals at the catalyst surface the chlorobenzene molecule undergoes a hydroxylation or a hydroxylation with a loss of the organic chlorine.

As an intermediate the benzoquinon undergoes a ring opening to aliphatic hydrocarbon acids with further oxidation. Out of the possible further reaction products the maleic acid and the oxalic acid were identified by ion chromatography.

At least at the total oxidation carbon dioxide and water are formed. But to have a positive environmental effect it is sufficient to change the organic chlorine into chloride or to convert the chlorobenzene to halogen-free organic compounds. Further degradation steps can be done cheaper by aerobic or anaerobic biological processes.

Figure 2 shows the concentrations of chlorobenzene, chlorophenol, chloride and the sum of chlorine containing compounds in the catalytic oxidation process with MOLoxW 2101 and hydrogen peroxide at 20 °C. Without the oxidation catalyst no change of the chlorobenzene concentration was detected within two days. There isn't any degradation of chlorobenzene.


Degradation of chlorobenzene with catalytical oxidation
(MOLoxW 2101, 20 °C, 20 mg/l chlorobenzene,
1.5-times excess of hydrogen peroxide)
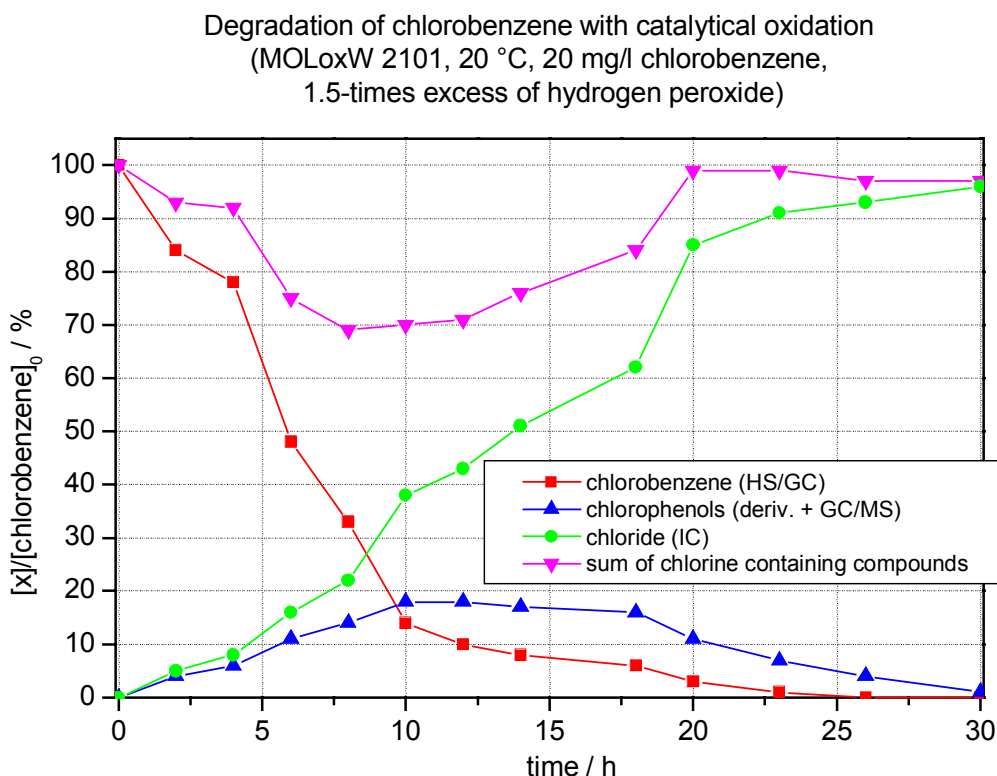
Figure 2   Degradation of chlorobenzene: concentration of chlorobenzene, chlorophenols, chloride and the sum of chlorine containing products. Concentrations were detected by Headspace / Gas-Chromatography (HS/GC), Gas-Chromatography / Mass-Spectrometry (GC/MS) and Ion-Chromatography (IC).

It is cognizable that a decrease of chlorobenzene concentration goes along with a temporary increase of the intermediate chlorophenol. The increase of the inorganic chlorine concentration points at the conversion from the organic chlorine of the water pollutants to the chloride as a mineralization product. There is a chemical degradation of the groundwater pollutants, not affected by biological processes.

Additionally ultrasound is used to clean the surface of the full-metal catalyst from precipitated oxidation products or solid particles suspended in the ground water and to activate the catalytic surface of the catalyst periodically. In order to reach this effect the ultrasound has to be strong enough to clean the surface of the full-metal catalyst, but weak enough not to destroy the catalytic effective coating of the metal.

The three main characteristics of ultrasound transducers are their field of sound, the power and their frequency of irradiation. Figure 3a shows three different kinds of ultrasound transducers with their ultrasound field, all working at a frequency of 25 kHz.
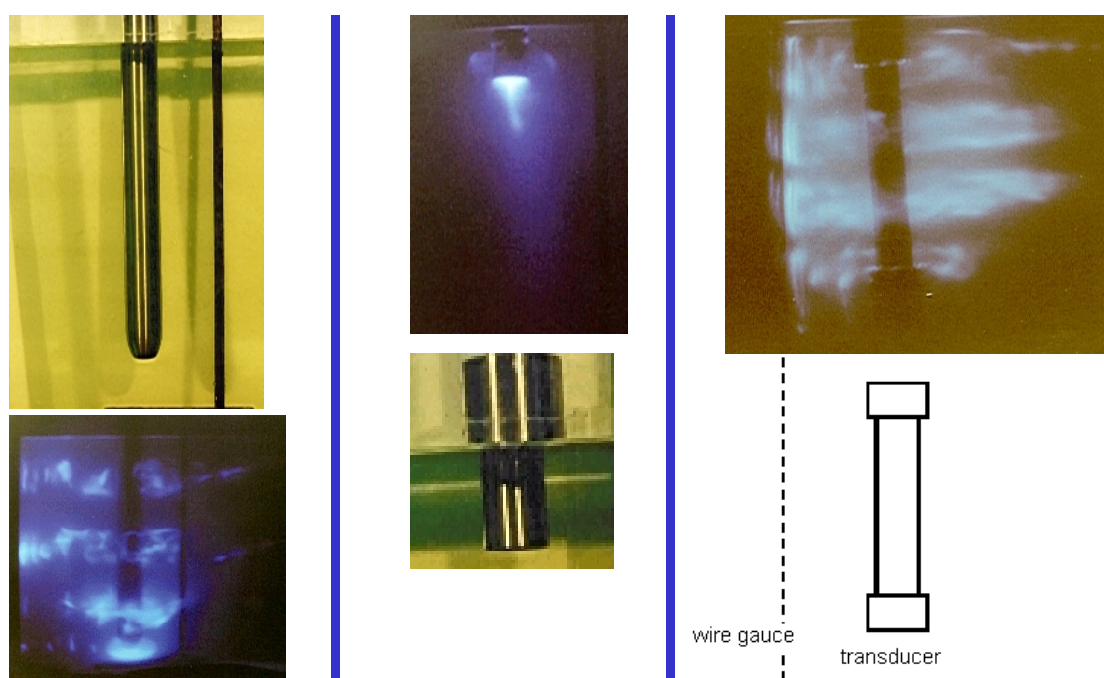
Figure 3a   Ultrasound field of a rod-like, a short rod-like and a push-pull transducer with a working frequency of 25 kHz.

On the left hand of the Figure 3 a common rod like Sonotrode with the belonging sound-field detected by the chemoluminescense of Luminol in water can be seen. Bright areas mark cavitation going along with high density of ultrasonic irradiation.

This transducer produces inhomogeneous areas of high ultrasonic intensity unable to clean a large area without moving the transducer. The transducer type in the middle of the chart has a small area of very high ultrasonic intensity, so strong, that the catalytic coating of the full metal catalyst is destroyed.

At last the right picture shows a rod like transducer working at the push-pull principle. On the left side of this picture a wire mesh of the full metal catalyst parallel to the transducer can be seen. The transducer generates a strong, homogeneous ultrasonic field, but this is not sufficient for the penetration of the wire gauze used as the full metal catalyst.

A solution for the technical problems described before is the right combination of transducer type and it's working frequency. The planar transducer shown in the Figure 3b has a working frequency of 850 kHz and forms an extended ultrasonic field with a medium-strong intensity.
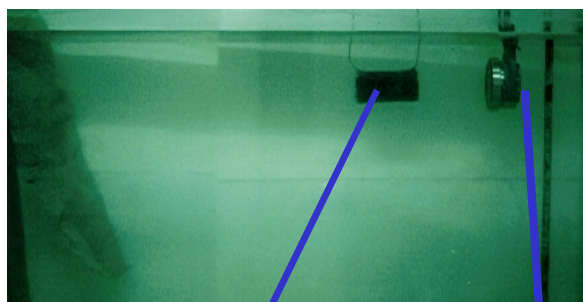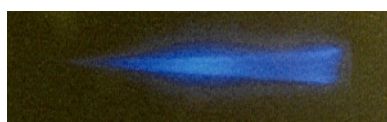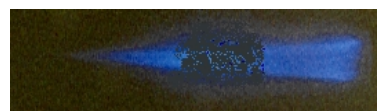

Photo with catalyst and transducer

Ultrasound field without catalyst   with catalyst

Figure 3b   Ultrasound field of a planar transducer with a working frequency of 850 kHz.

The ultrasound of this transducer is able to penetrate the wire mesh completely without destroying of the catalytic coating on it. The wire mesh in this experiment is exactly the same like in the oxidation reactor in the pilot plant.

Different kinds of catalysts were tested in order to optimize the consumption of hydrogen peroxide and the degradation rate of chlorobenzene at given temperature.

On the one hand a full metal catalyst made of a wire mesh formed as a hose or formed by metal splinters were tested. The catalyst is a coated or special treated wire mesh. The advantage is his high mechanical stability, the disadvantage the limited surface of the catalyst.

Another type of catalysts are the so called fixed bed catalysts with an aluminum oxide or silicon dioxide substrate. These catalysts are produced in several forms.

They are modified with compounds like iron, nickel or copper oxides. A special kind of fixed bed catalyst are the precious metal catalysts. The catalysts are spherical or formed rod-shaped. An advantage of the fixed bed catalysts is their exact definable composition, the disadvantage is their limited stability against mechanical treatment.

After the improvement of the technical equipment like the kind of catalyst, hydrogen peroxide concentration, kind of ultrasound transducer and it's frequency the method of catalytic oxidation of pollutants with hydrogen peroxide has to be adapted up to the pilot plant in Bitterfeld. This adaptation of the ultrasound assisted catalytic oxidation follows in four consecutive steps.

First: In order to choose the optimized catalyst lab scale experiments in head space vessels were performed at different temperatures, hydrogen peroxide concentrations and amounts of catalyst. In Figure 4a the temperature dependence of the catalytic oxidation of chlorobenzene in deionized water is shown. This diagram describes the relative concentration of chlorobenzene versus time in a temperature range from 30 °C – 80 °C. As expected the reaction rate of chlorobenzene degradation increases dramatically with increasing temperature.
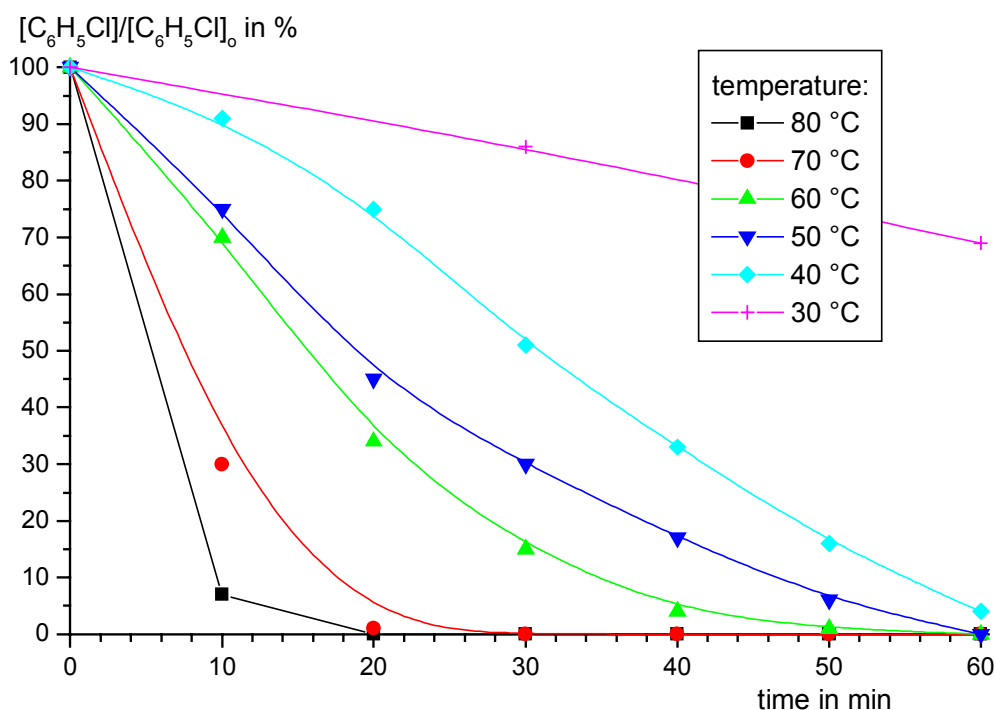

Figure 4a   Temperature dependence of the catalytic oxidation of chlorobenzene in deionized water; catalyst LoxW 2101, ml/l H_2O_2, $[C_6H_5Cl]_0$ = 20 mg/l.

Although the temperature of the quick lab scale experiment is higher than the reaction temperature in the reactor at the pilot plant in Bitterfeld, the results of the lab scale experiment give a first hint of the suitability of the tested catalyst for catalytic oxidation with the advantage of fast feasibility.

The Figure 4b describes the relative concentration of chlorobenzene versus the time in a concentration range from 0.1 up to 4 ml per liter reaction solution. The degradation rate of chlorobenzene increases with increasing concentration of hydrogen peroxide.

The reduplication of the hydrogen peroxide concentration means not a doubling of the reaction rate. One has to choose the optimum concentration of oxidation agent which is for this experiment about 0.5 up to 1.0 ml per liter water solution for economical and technical reasons.

Second: Bench scale tests were carried out in glass made continuous reactor with a volume of two liters. Experiments were made at different temperatures and concentration of the oxidation agent.
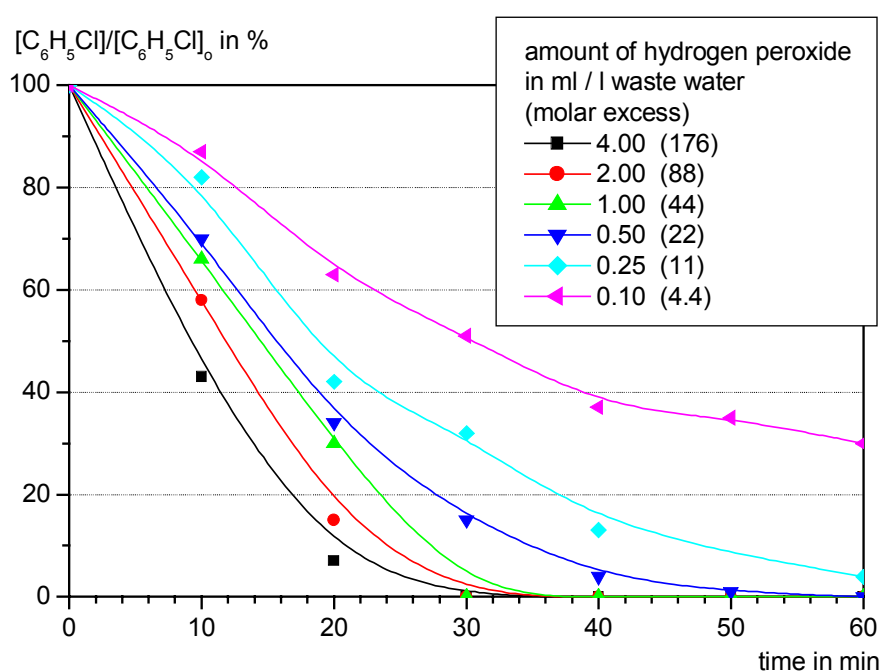

Figure 4b Catalytic oxidation of chlorobenzene in deionized water – dependence of the degradation rate on the amount of oxidation agent; catalyst MOLoxW 2101, temperature 60°C, chlorobenzene 25 mg/l

Third: In a mobile test unit made of stainless steel with ten liters capacity, the method was tested under nearly aquifer conditions at the test site in Bitterfeld.

This step of the adaptation was finished, now we concentrate our activities on the fourth part at the pilot plant in Bitterfeld.

A variation of the test method is the concentration dependence of the catalytic oxidation of chlorobenzene in ground water in dependence on the concentration of oxidation agent hydrogen peroxide.

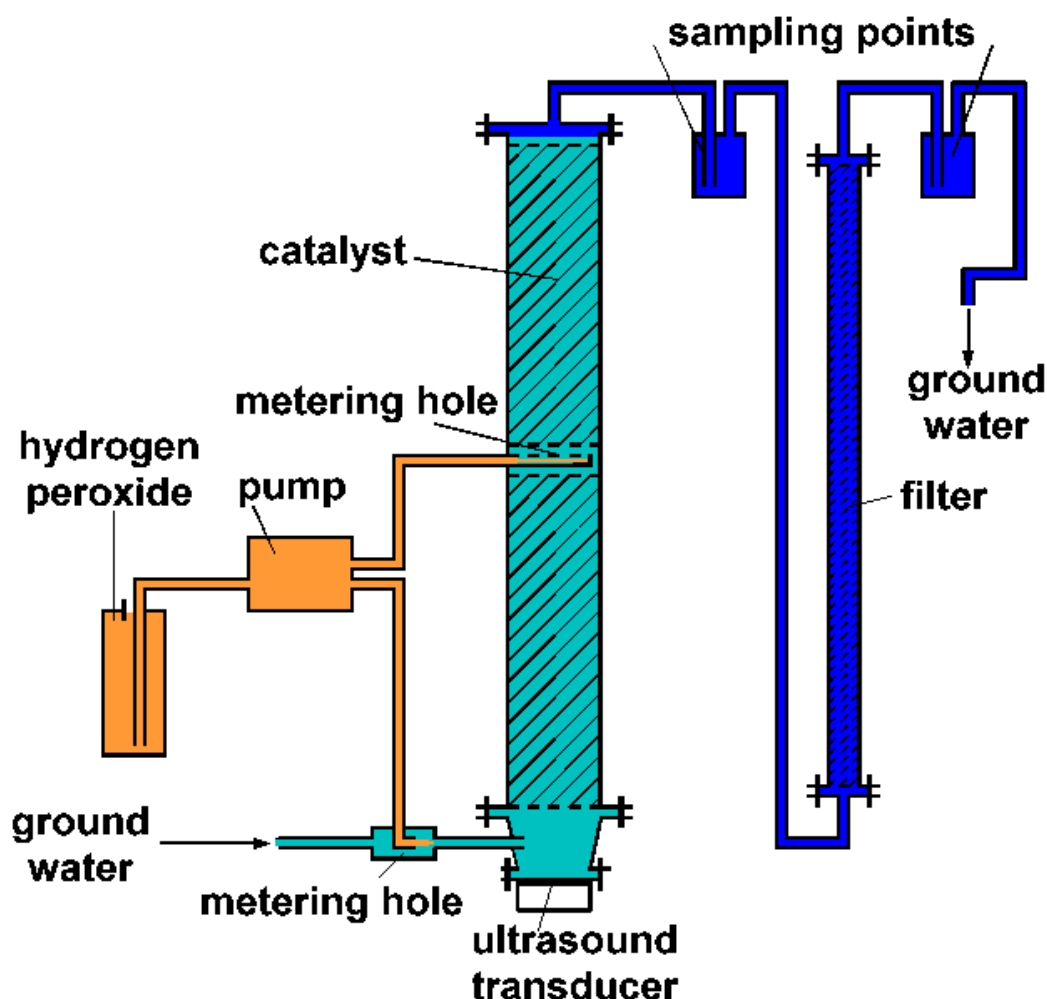A schematic diagram of reactor used in the mobile test unit is presented at the Figure 5.

Figure 5 *The schematic diagram of ultrasound assisted catalytic oxidation process in the mobile test unit.*

The mobile test unit permits the testing of the experimental method under aquifer conditions. It consists of a tube of stainless steel containing the catalyst, the ultrasound transducer at the bottom of the cylindrical reactor, two metering holes for an uniform distribution of the oxidation agent in the catalyst layer, an adsorber column (filter for heavy metals) with a sampling point before and after. The reactor in the mobile test unit was examined over a duration of 21 days. Working conditions of this equipment are 17 °C, similar to the temperature of the ground water, a flow rate of 200 ml per hour and a concentration of chlorobenzene of approximately 20 mg/l. The volume of the reactor is about ten liters, the catalyst again MOLoxW 2101 with the oxidation agent hydrogen peroxide.

Ultrasound was applied to clean the surface of the full metal catalyst, had a frequency of 850 kHz and was used in interval mode (on/off ratio = 1:1) one minute per day.

The results of the experiments in the mobile test unit are shown in the Figure 6.

The chlorobenzene concentration is plotted against the time. The line with circles marks the chlorobenzene concentration in the inflow pipe whereas the line with squares marks the chlorobenzene concentration in the outflow pipe.
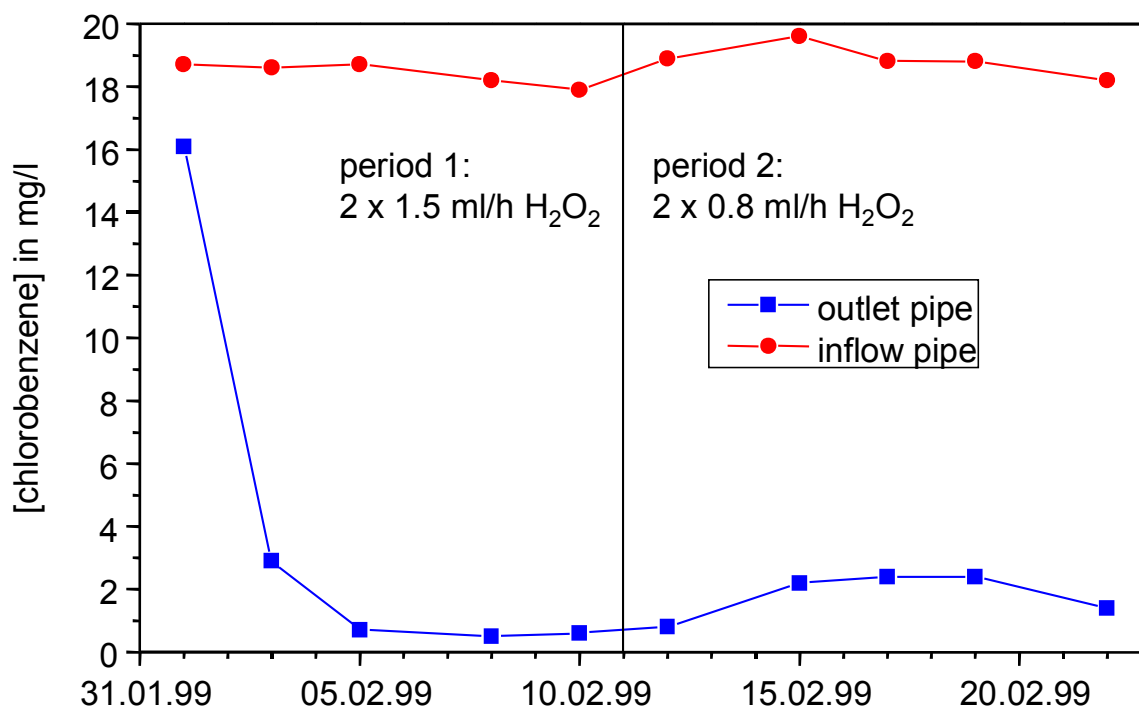

Figure 6   Results of the out-door experiments in the mobile test unit. Chlorobenzene concentration at the inflow and outflow pope of the mibile test unit. Catalyst MOLoxW 2101, 17 °C

Tests were made at two stages with different hydrogen peroxide concentrations first 1.5 ml per hour at each metering hole and second 0.8 ml per hour at each metering hole.

At the beginning of the experiment an induction period of nearly five days is necessary to start the oxidation reaction and to get constant low chlorobenzene concentration at the outflow. In a second period the concentration of the oxidation agent is divided once in order to save hydrogen peroxide to an optimized, economically concentration.

As a result the concentration in the outflow pipe increases slightly as a response to the decreased hydrogen peroxide concentration.

At this chart the importance of an optimized hydrogen peroxide dosage is shown. With the half amount of oxidation agent it is possible to obtain nearly the same degradation rate of chlorobenzene.

Fourth: In the pilot plant under in situ conditions the adopted method of catalytic oxidation is performed in two 35 liter reactors made of stainless steel and equipped with oxidation catalyst as one example for a possible oxidation catalyst. They are in

shaft number three below the ground water spring axis at the ground of the concrete tube in a depth of 23 meters. After the contaminated ground water passes the oxidation reactors and the adsorber column (heavy metal selective adsorber) the purified water is directed into the aquifer reactor. In the aquifer reactor the effect of the ground water treatment with oxidation catalyst and hydrogen peroxide on the aquifer is monitored.

One has to take into account that the catalytic oxidation of ground water with hydrogen peroxide means a change from reducing to oxidizing conditions in the aquifer. To examine, weather and which effects are present, will be the aim of our investigations.

Summary

With heterogeneous catalytic oxidation using hydrogen peroxide as oxidation agent halogenated aromatic hydrocarbons can be degraded in ground water. The most important problem at the process of catalytic oxidation is the adaptation of the process parameters. The following problems had to be solved in the adaption of the Ultrasound-assisted catalytic oxidation.

- At fixed ground water temperature an optimized hydrogen peroxide dosage has to be determined by tests in order to dehalogenate the ground water pollutants completely and use a minimum amount of oxidation agent at the same time.

- Different types of oxidation catalysts, like full metal catalysts or fixed bed catalysts have to be tested.

- The catalyst must not decompose hydrogen peroxide without degradation of halgonated hydrocarbons.

- And should have a high degradation rate for chlorinated hydrocarbons at low reaction temperatures.

- The catalytic surface must be stable against mechanical and ultrasound treatment.

Zeolite based catalysts for the hydrodehalogenation of chlorinated compounds in groundwater

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[1] University of Tübingen, Geological Institute, Applied Geology Group

Catalytic hydrogenation of organic compounds with noble metals is widely used in chemical synthesis and is typically run at high concentrations, high hydrogen pressures and temperatures and in the gas-phase or organic liquids. Catalytic hydrogenation is potentially applicable for the removal of contaminants present in water or air. Recent studies have focused on hydrodechlorination of halogenated hydrocarbon compounds (HHC) in water. These studies indicate that catalytic hydrogenation converts many environmental contaminants into harmless products [1,2]. For instance, the hydrodehalogenation of perchloroethene (PCE) and trichloroethene (TCE) with hydrogen gas and a Pd-on-γ-alumina catalyst occurs nearly at mass-transfer-limited rates, even at ambient temperatures and in water [3]. Other contaminants that are amenable to catalytic hydrode-chlorination include chlorinated benzenes and biphenyls, and γ-hexachlorocyclohexane (Lindane) [4]. For unsaturated HHCs hydrodechlorination can be followed or accompanied by hydrogenation yielding the fully hydrogenated product. For example, chlorinated ethylenes yield ethane and polycyclic aromatic hydrocarbons yield partially or fully hydrogenated products.

The lack of catalysts that are optimized for water treatment and data that demonstrate the longevity of these catalysts under treatment conditions hindered the implementation of this technology. This paper describes the development of a Pd catalyst that is resistant against deactivation by ionic poisons and reports data that demonstrate its effectiveness for the treatment of HHCs in groundwater. Optimal catalyst properties were achieved by embedding the palladium in a microporous and hydrophobic zeolite support with narrow hydrophobic pores to selectively exclude ionic species but large enough for rapid diffusive transport of hydrophobic HHC molecules to the internal sites [5]. Exclusion of ionic species is important because nitrate ions, for instance, can lower catalyst activity by competing with the HHCs for reducing power, and reduced sulfur species can poison the catalyst. The catalyst's ability to selectively react with HHCs while excluding ionic poisons was evaluated in kinetic batch experiments using 1,2-dichlorobenzene (1,2-DCB) and sulfite anions dissolved in deionized (DI) water as a model system. Sodium sulfite was used because it deactivates Pd at a moderate rate and 1,2-DCB was used because its dehalogenation rate was slow enough to be measurable in batch tests.

Zeolites can be prepared with varying pore sizes and constant hydrophobicity, or vice versa. The hydrophobicity increases with increasing Si/Al ratio. At a Si/Al ratio of 7-10, the surface hydrophobicity is intermediate and the purely siliceous form (Si/Al= ∞) is strongly hydrophobic. The Si/Al ratios and pore sizes of the zeolites that were used for this study are summarized in Table 1 The pores of ZSM-5 are oval (0.53nm x 0.56nm) and slightly smaller than 1,2-DCB, which has a kinetic diameter of 0.6nm.

By contrast, the pores of zeolite Y are slightly larger than that of 1,2-DCB (0.74nm) and the mesoporous MCM-41 used here has pore diameters of about 2.7nm, 4.5 times larger than the diameter of 1,2-DCB. Zeolite Y and MCM-41 were available in three different Si/Al ratios ranging from 6 for the moderately hydrophilic Y(6) to indefinite fo the hydrophobic MCM-41(∞). The Y and ZSM-5 zeolites were obtained from Degussa AG (Hanau, Germany). The mesoporous MCM-41 were synthesized using the method of Kresge et al. Palladium was applied by wet-impregnation to obtain a 1% w/w Pd loading.

Table 1 *Zeolites used in the batch experiments. All wet impregnated with 1% wt/wt palladium*

Support	Pore diameter	Si/Al-Ratio
ZSM-5 (16)	0.53 x 0.56 nm	16
Y (6)	0.74 nm	6
Y (15)	0.74 nm	15
Y (200)	0.74 nm	200
MCM-41 (8)	2.7 nm	7.8 ± 0.3
MCM-41 (24)	2.5 nm	23.9 ± 0.3
MCM-41 (∞)	2.7 nm	∞

The data shown in Figure 1 left were obtained in DI water without added sulfite. They indicate that for the dehalogenation of the hydrophobic 1,2-DCB, the pore size is the rate-controlling factor whereas the hydrophobicity is insignificant. As expected, the transformation rate of 1,2-DCB increases with increasing pore size indicating decreasing mass transfer resistance. The slowest rate (0.0021 min^{-1}) was observed for zeolite ZSM-5, the catalyst that excludes 1,2-DCB from intra particle sites. The slow observed rate is attributed to the small fraction of external sites. The transformation rates of the Y(6), Y(15), and Y(200) catalysts, which have pores slightly larger than that of 1,2-DCB, were 0.20 min^{-1}, 0.19 min^{-1}, 0.31 min^{-1}, respectively, suggesting that internal sites significantly contribute to the observed reaction. The Si/Al ratio, however, appears to be of secondary importance. The rates of the mesoporous MCM-41 (8), MCM-41 (24) and MCM-41 (∞) catalysts were much faster (3.8 min^{-1}, 5.1 min^{-1}, and 1.1 min^{-1}, respectively), consistent with less mass transfer resistance by the larger pores. MCM-41 dehalogenation rates are more variable than the Y catalysts and a consistent relationship between the Si/Al ratio and the dehalogenation rate cannot be discerned.

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dehalogenation rates are more variable than the Y catalysts and a consistent relationship between the Si/Al ratio and the dehalogenation rate cannot be discerned.

Figure 1   *Hydrodehalogenation of 1,2-dichlorobenzene with 1 % wt/wt palladium on six different support materials. Batch experiments with 0.5 g/l catalyst at room-temperature and ambient pressure.*
Left: Experiments performed in deionized, hydrogen saturated water.
Right: Experiments performed in deionized water with 30 mg/l Na_2SO_3. Stable degradation rates were found only for the hydrophobic zeolite Y (200).

In water containing sulfite, all catalysts were deactivated with the exception of zeolite Y (200), which was only partially deactivated (Figure 1 right). ZSM-5, the catalyst that reacts only at external sites, and the mesoporous MCM-41 catalysts were deactivated within minutes, indicating sulfite and 1,2-DCB had access to the same reactive sites. By contrast, deactivation of the microporous Y catalysts depended on the Si/Al ratio. The moderately hydrophilic Y catalysts with Si/Al ratios of 6 and 15 were completely deactivated within minutes. The dehalogenation rate on the hydrophobic Y(200) catalyst decreased only for the first few minutes but then remained stable at approximately 40% of the rate observed in DI water. Apparently, this catalyst selectively excluded sulfite from internal Pd sites while being accessible for 1,2-DCB. In all experiments, mass balances based on the benzene production were better than 80%, indicating that dechlorination and not sorption was the removal mechanism.

A catalyst based on the palladium impregnated zeolite Y-200 was operated in the SAFIRA mobile test for about 4 month. The ground water was pumped directly out of a well through a stainless steel column with a H_2 pressurized silicon tube (1 bar) embedded in a quartz gravel pack to introduce hydrogen diffusively, followed by a bed of 250 g of the pelletized zeolite Y (200) catalyst. The ground water quality at this site is characterized by high concentrations of inorganic constituents. The major contaminant is chlorobenzene at concentrations of approximately 20 mg/l. In preliminary experiments, the reactor on site failed within 20 days. Catalyst failure was attributed to catalyst poisoning by biologically produced hydrogen sulfide. To control biological sulfide formation, the reactor was flushed once a week for 2 hours with an aqueous solution of 10g/l H_2O_2. The data shown in Figure 2 were collected after

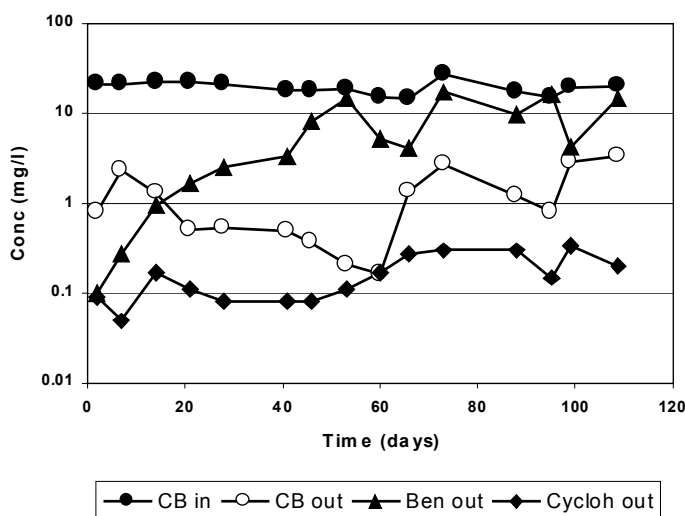adopting this procedure. They show sustained high catalyst activity during the four-months study period.

Figure 2   Results of the experiment in the mobile test unit in Bitterfeld. Chlorbenzene (CB), Benzene (Ben) und Cyclohexane (Cycloh).

Benzene and cyclohexane were the observed products with benzene breaking through after approximately 50 days. The delayed appearance of benzene is attributed to sorption by the hydrophobic support. The effluent concentration of chlorobenzene remained low and relatively constant. The data scatter is unexplained but could stem from intermittently formed CO_2 and H_2 bubbles that may have lowered the residence time. The small concentrations of cyclohexane detected in the outflow indicate that benzene is slowly hydrogenated. Although benzene is not a desirable product, it is readily biodegradable under aerobic conditions.

In conclusion we could show, that Pd impregnated zeolites can be engineered to be resistant against deactivation by ionic poisons and that these catalysts maintain activity in groundwater for several months. The high efficiency of the catalyst may make it possible to treat groundwater with small reactors in treatment wells [6].

[1]   C. Schlimm, E. Heitz, *Environ. Prog.* 15, 1 (1996) p. 38.

[2]   S. Kovenklioglu, Z. Cao, D. Shah, R. J. Farrauto, E. N. Balko, *J.AIChE,* 38, 7 (1992) p. 1003.

[3]   G. Lowry, M. Reinhard, *Environ. Sci. Technol.*, 33 (1999) p. 1905.

[4]   C. Schüth, M. Reinhard, *Appl. Cat. B: Environ.*, 18, 3-4 (1998) p. 215.

[5]   C. Schüth, S. Disser, F. Schüth, M. Reinhard, *Appl. Cat. B: Environ.*, in press.

[6]   W.W. McNab Jr., R. Ruiz, M. Reinhard, *Environ. Sci. Technol.*, 34 (2000) p. 149.

Dechlorination of chlorohydrocarbons in groundwater by electrochemical and catalytic reactions

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The high concentration of chloroorganic compounds (COCs) at the Bitterfeld test site requires a fast and complete method suitable for dechlorination of a wide range of dif-ferent COC classes. We chose the reductive dechlorination pathway in order to avoid unpredictable toxic intermediate products, which would have to be considered if an oxidative dechlorination method had been chosen.

In recent years, the traditional pump & treat technology received a strong competitor with the new concept of *in situ* groundwater remediation using reactive iron barriers. The so-called 'rusty walls', which were first developed by GILLHAM and co-workers in 1989 [1] for clean-up of chlorohydrocarbon-contaminated sites, have proved to be a suitable technique.

Metallic iron is able to reduce most aliphatic chlorohydrocarbons to the chlorine-free substances (Equation 1), although with different dechlorination rates.
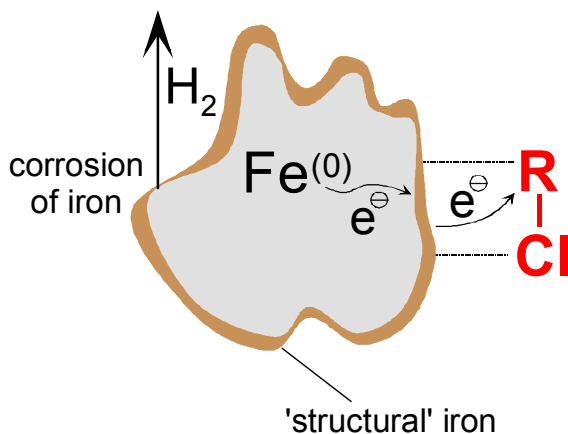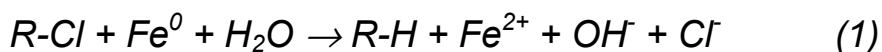
$$R\text{-}Cl + Fe^0 + H_2O \rightarrow R\text{-}H + Fe^{2+} + OH^- + Cl^- \qquad (1)$$

Figure 1   Direct electron transfer as reduction mechanism.

For example, the half-lives for the dechlorination of PCE and TCE are markedly be-low 1 hour. For other compounds, such as cis-dichloroethylene or vinylchloride, a much longer time period is needed for reduction. Unfortunately, iron fails completely as a reducing agent for compounds such as methylenechloride and the whole class of chlorinated aromatics [1]. Looking at the reduction mechanism using iron barriers,

that is the direct electron transfer from the iron or the so-called structural iron(II)-cation on the iron surface (Figure 1), then it is not immediately apparent why chloroaromatics are not reduced. The reduction potentials for the two-electron-transfer, resulting in chlorine-free hydrocarbons and chloride, are about + 500 mV. The standard redox potential of the iron electrode is about - 440 mV [5]. This means that the free reaction enthalpy for the hydrodechlorination with iron is in the range of about 200 kJ/mol for each dechlorination step. This is actually a very high thermodynamic driving force, whereby the aromatic compounds are no exception. If one assumes that the reduction is a sequence of two single-electron-transfers forming the radical anion in the first step, then the unexpected behavior of the aromatic hydrocarbons can be explained, especially that of monochlorobenzene. The first step of the reduction during a direct electron transfer (e.g. from metallic iron) is therefore kinetically hindered, even though all thermodynamic prerequisites for a successful reduction are fulfilled. Since the thermodynamical conditions for the reduction of chlorobenzene are favourable in principle, a change of the reaction mechanism should lead to success.

We are now using hydrogen as the reducing agent, which is for example always produced by iron-corrosion as shown in the illustration (Figure 2).
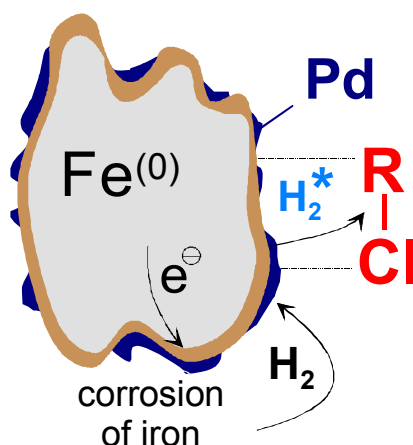

Figure 2   *Catalytic hydrodechlorination as reduction mechanism.*

Hydrogen is collected and activated by a noble metal catalyst (preferentially Pd), and therefore usable for splitting-off the C-Cl bonds. The reaction is a hydrogenolysis resulting in a fast and complete dechlorination of a broad spectrum of COCs (Equation 2). In contrast to iron, which is stoichiometrically consumed during reduction, the noble metal catalyst is not released into the aquifer.

$$R\text{-}Cl + H_2 \xrightarrow{\text{Pd catalyst}} R\text{-}H + HCl \qquad\qquad (2)$$
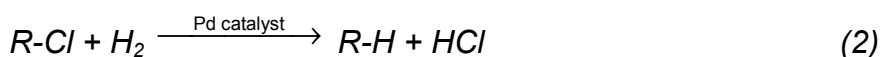
In water, Pd and Rh catalysts have the highest dechlorination activity. However, Pd causes a pure hydrodechlorination, whereas Rh effects a subsequent hydrogenation to the corresponding naphthenes.

Because the end products of the reaction (the dechlorinated hydrocarbons) are left to be dealt with by the microbiology of the aquifer, their biological degradability is naturally of considerable importance. In the case of the dechlorination products of chlorobenzenes, benzene the more human-toxic, but it is much better biodegradable than cyclohexane. Because of the latter and the lower costs compared with Rh, Pd has been chosen as the preferred catalyst. The Pd catalyst is not dependent upon iron as a carrier: it only requires the availability of hydrogen. Hydrogen can in principle be made available by three methods: from an external source, from iron corrosion (as shown), or electrochemically.

Exactly this principle (in-situ generation of hydrogen and use of a Pd catalyst) was recently described by an American research group [4]. The authors used an electrolytic cell with graphite electrodes to generate hydrogen. The TCE-contaminated water is enriched with hydrogen and the dechlorination occurred at a commercially available Pd/Al_2O_3 catalyst. The system permits relatively high flow rates. The results of MCNAB & RUIZ show that catalytic dechlorination on a large scale is successful in principle, but they also show that the system has a severely limited life. The catalytic activity is halved after only about 50 hours of operation. Although the catalyst may be regenerated by washing, nevertheless this makes the system unsuitable for *in situ* application. The potential of the catalytic dechlorination technique for in situ groundwater treatment depends mainly on the long-term stability of the catalytic system.

While preparing our field tests evaluating the suitability of the Pd-catalyzed hydrodechlorination for the Bitterfeld groundwater contamination, we carried out extensive laboratory experiments and found commercially available Pd systems (Pd on various oxidic carriers and activated carbon) to be very active hydrodechlorination catalysts. We have also evaluated the lifetime of Pd systems adding various potential catalyst poisons and came to the expected conclusions: when applying active but sensitive catalytic systems, one must always reckon with the problem of deactivation. After adding traces of sulfide ions to the test solution, the Pd-system completely loses its catalytic activity within seconds.

Under aquifer conditions, deactivation occurs mainly due to mechanisms such as poisoning by heavy metal or sulphur compounds. However, suspended matter or biofilms clog the catalytic surface.

Nonetheless, in the SAFIRA pre-study in Bitterfeld we wanted to use a very similar reactor concept: a commercially available Pd catalyst and electrochemical generation of hydrogen by in-situ water electrolysis.

We wanted to learn a bit more about the catalytic dechlorination under groundwater condition and we wanted to overcome the problems, which McNab and Ruiz reported about.

In contrast to [4], we used a separated electrolytic cell, where the anode and cathode compartments are passed subsequently. Because of the high chloride content in the Bitterfeld groundwater, hypochlorite (chlorine) is produced at the anode, which acts as an disinfectant, until it is completely reduced along the cathode. Figure 3 shows the construction scheme of the electro-catalytic reactor (a combined electrolytic cell / fixed-bed catalytic dechlorination reactor).
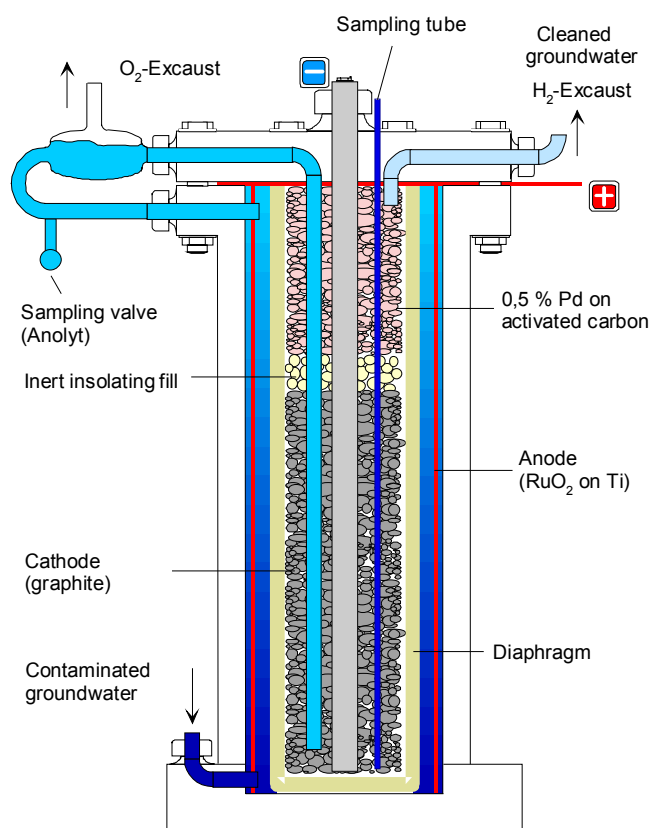

Figure 3 Scheme of the electro-catalytic reactor.

The reactor (described in detail by [2]) has been designed as a 20-liter flow-through type electrolytic cell, where the groundwater passes anode and cathode compartments in succession. The compartments are divided by a porous polyethylene diaphragm. The groundwater flows first through the anode compartment vertically from the bottom to the top of the reactor. The cathode is designed as a three-dimensional graphite electrode to which iron filings were mixed in order to ensure binding of sulfide ions which may possibly be carried in the groundwater or produced in anaerobic zones. The water electrolysis occurring after applying the voltage releases oxygen (and small concentrations of hypochlorite) into the anode compartment. The anolyte is then spontaneously degassed just before entering the cathode compartment, where dissolved oxidation products from the anodic process are reduced at the three-dimensional cathode. At the cathode, hydrogen is produced and dechlorination of aliphatic COCs may already occur. The groundwater enriched with hydrogen then passes the catalyst bed, where all remaining COCs can be reduced. Catalyst bed

and cathode are separated by a fill of inert and electrically insulating glass spheres. The operation of the reactor under field conditions is divided into different periods. Only the first three operation periods (180 days) will be discussed here: The electro-catalytic reactor was put into operation with a groundwater flow of 1.28 L/h and a current of 1 A (cell voltage 5 V). This corresponds to a mean residence time in the catalyst bed of about 75 min. ($\rho_{catalyst}$ = 330 g/L, $\varepsilon \approx 0.75$) or a catalyst load of 0.6 v/vh. Figure 4 shows the concentrations of benzene and chlorobenzene at the reactor outlet and the input of chlorobenzene as a function of time. Up to the operation day 50, only insignificant amounts of chlorobenzene and benzene are detected in the water leaving the reactor (removal > 99.5%). This alone is no proof of chemical reactions, because both compounds can be sorbed by the catalyst carrier.
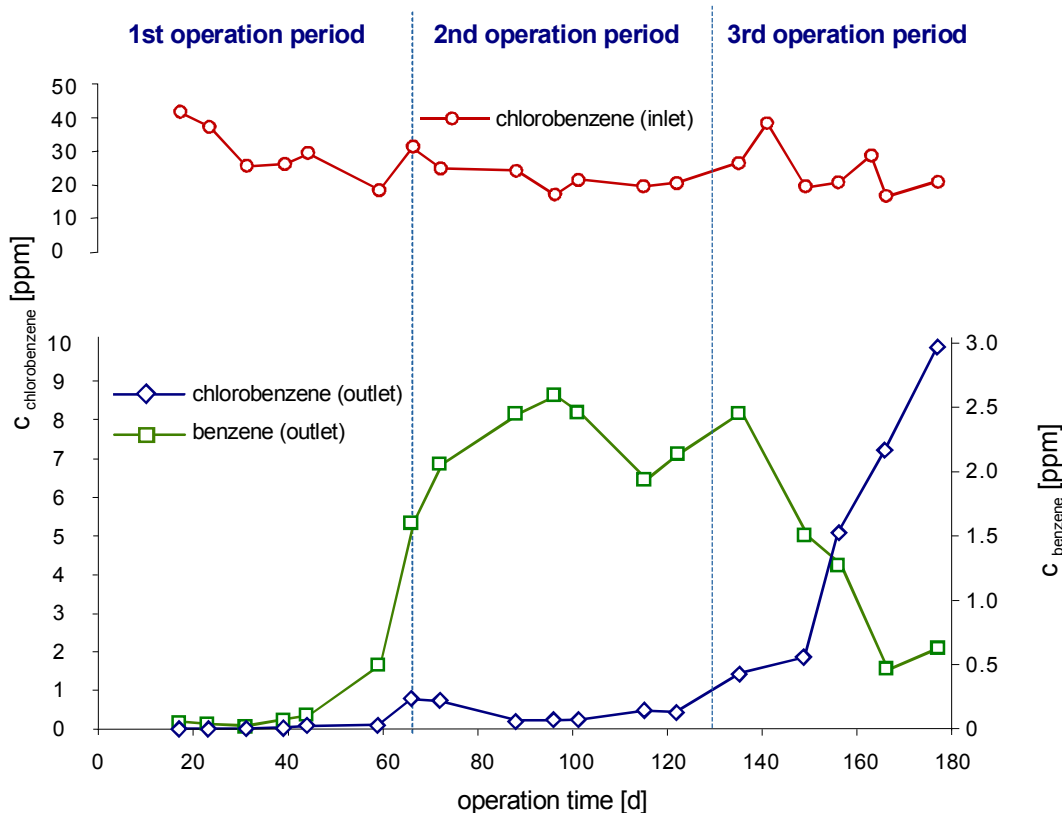
Figure 4   Chlorobenzene and benzene concentrations at the reactor in- and outlet.

Starting from operation day 59, benzene was analyzed in the outlet water as clear evidence of the reduction pathway. An activity test of the catalyst (sampled from various layers of the catalyst bed) at day 64 in the laboratory showed that the catalytic activity was undiminished.

After 6 months of operation the reactor was disassembled, because chlorobenzene started to break through. Activity tests of the catalyst showed the almost total loss of catalytical activity. Inspection of the reactor internals showed that the catalyst was covered with a brownish coating - washing the catalyst with diluted HCl evolved H_2S. The reason for the catalyst poisoning is depicted in Figure 5 and can be found from the analysis of inorganic groundwater constituents:
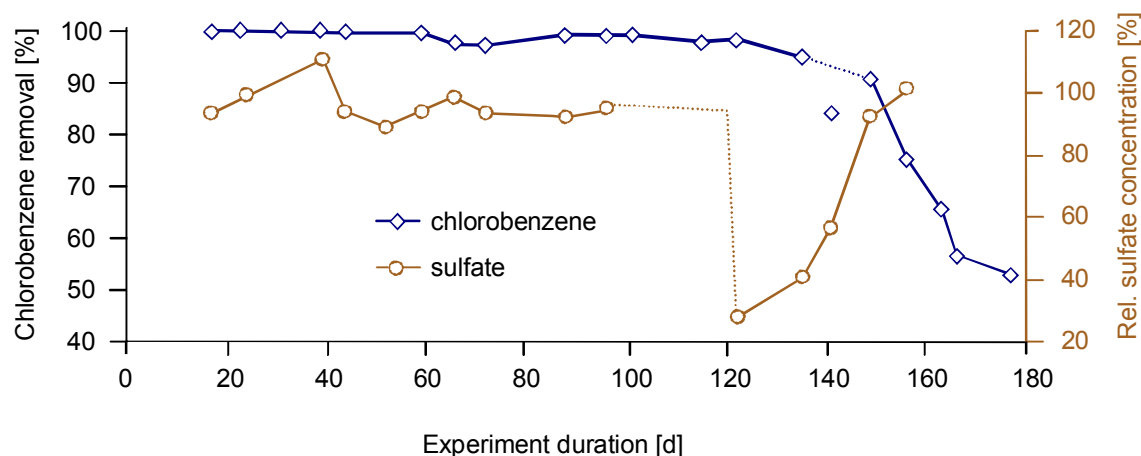
Figure 5   *Removal rate for chlorobenzene compared to the relative sulfate concentration in the reactor efflux.*

At day 121 a drastic decrease in the sulfate concentration from 800 mg/L to 220 mg/L was analyzed, whereas the concentrations of sulfate are equal under normal conditions at reactor in- and outlet. sulfides are known as very effective catalyst poisons produced presumably by microbial sulfate reduction. The reason for the spontaneous sulfate reduction is unclear. It may have been due to the break down of groundwater flow after outlet plugging. Because the water electrolysis (and therefore the gas production) continued during this operational disturbance, this led to an enrichment of the reducing agent hydrogen in the cathode compartment (formation of anaerobic conditions and total withdrawal of inhibiting agents).

The field experiment showed that the electro-catalytic reactor was able to almost completely remove chlorobenzene from groundwater over a time period of several months. The experiment also showed that the catalyst can be dramatically influenced by catalyst poisons and microbiological interference. *Therefore, a way to protect the catalytic system is required!*

Our approach favours membrane-supported Pd catalysts. The basic hypothesis is simple and plausible: the catalyst is embedded in a hydrophobic polymer membrane, which protects it from deactivation (Figure 6). The membrane acts simultaneously as a shield against hydrophilic, ionic catalyst poisons and as an absorber ('concentrator') of hydrophobic chlorohydrocarbons. The membrane enriches the pollutants to be treated and thereby supports the reaction kinetics.

The membrane materials preferred are silicon polymers (e.g. poly(dimethylsiloxane) = PDMS), because of their high diffusion coefficients. For example, the diffusion coefficient of benzene in PDMS is only 3 times lower than that in water. This is important in order to keep the transport resistance through the membrane as low as possible. Using a silicon matrix, one is not dependent upon additional catalyst carriers. Pd may as well be embedded in a highly dispersed form within the PDMS matrix. In

order to keep the transport hindrance of the silicone bulk phase as low as possible, we aimed to use thin polymer coatings. The membrane catalysts were designed (partially in co-operation with Dr. Fritzsch, GKSS Geesthacht) as silicone-coated commercially available supported catalysts, as foil (about 750 µm wall thickness), as 7 µm-coating on polyacrylonitrile fleece and as hollow fibre (wall thickness between 200 µm and 1 mm).
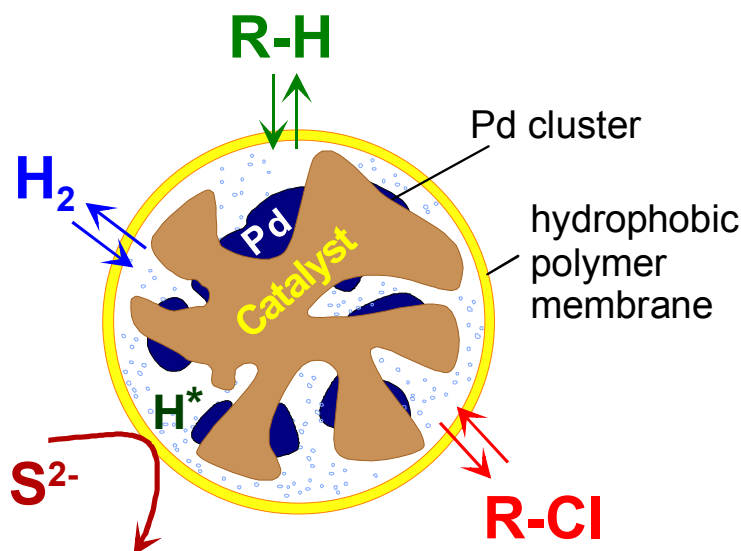

Figure 6   Scheme of the operating mode of a supported-catalyst particle coated by a hydrophobic polymer membrane.

The transport of the reaction product HCl out of the system is also important for the long life of the catalyst. We found in all our membrane investigations that HCl left the membrane completely, so that deactivation of Pd due to an excess of chloride did not occur.

We have achieved some very promising results on the laboratory scale with the systems outlined. The Pd/PDMS membranes (foil type) showed no reduction of the catalytic activity in the presence of sulfite ions, where conventional Pd catalysts were completely deactivated. In presence of sulfide ions, a reduction of catalytic activity was eventually observed. However, no complete destruction of the catalyst function occurred. The application of unprotected catalysts under these conditions would be unthinkable. We found that the unprotected Pd/Al_2O_3 catalysts loses its catalytic activity after addition of sulfite ions within seconds. In our experiments, the tube-like form proved to be an even more elegant method of applying membrane-supported Pd catalysts. The preparation of tube-like hollow silicone fibres containing 0.7 to 1.1% Pd led to catalysts which were very suitable for dechlorination applications even in presence of sulfur compounds, as can be seen in Figure 7. Even the addition of sodium sulfide and sulfite in stoichiometrical amounts does not result in deactivation of the Pd catalyst.
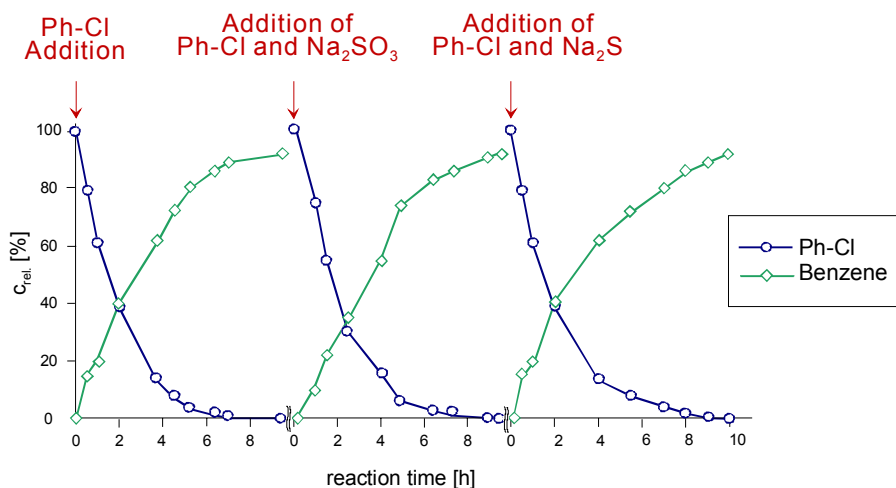
Figure 7   Chlorobenzene reduction using Pd/silicone catalysts of the hollow-fibre type with and without the addition of catalyst poisons (fibre: 4.2mm x 1.0mm x 500 mm, 0.7% Pd; Pd : S = 1 : 1).

We have successfully tested this system in the laboratory on various scales, where it proved to be more efficient and robust than all other catalytic systems investigated.

Figure 8 shows the scheme of a membrane reactor based upon which we built our membrane module in Bitterfeld. The tubular form of the catalytic system has the advantage of bringing hydrogen directly to its reaction partner, so that both reactants are present in high concentrations at the reaction site.
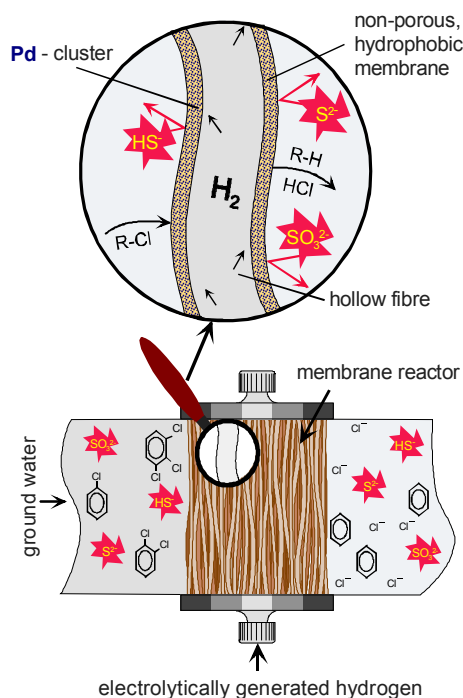

Figure 8   Scheme of a membrane reactor.

Our catalytic reactor (Figure 9) is installed at a depth of 19 m as part of a modular construction. The reactor module contains a 60m-Pd/fibre catalyst. The groundwater flows vertically from below through the reactor; pressure and temperature are analogous to the groundwater aquifer. The fibre catalyst is fed with externally-generated hydrogen from the inside of the tube.

Groundwater will be sampled frequently to inspect the performance of this new type of remediation method, where it must prove its worth and long-term stability under real groundwater conditions in the Bitterfeld region.
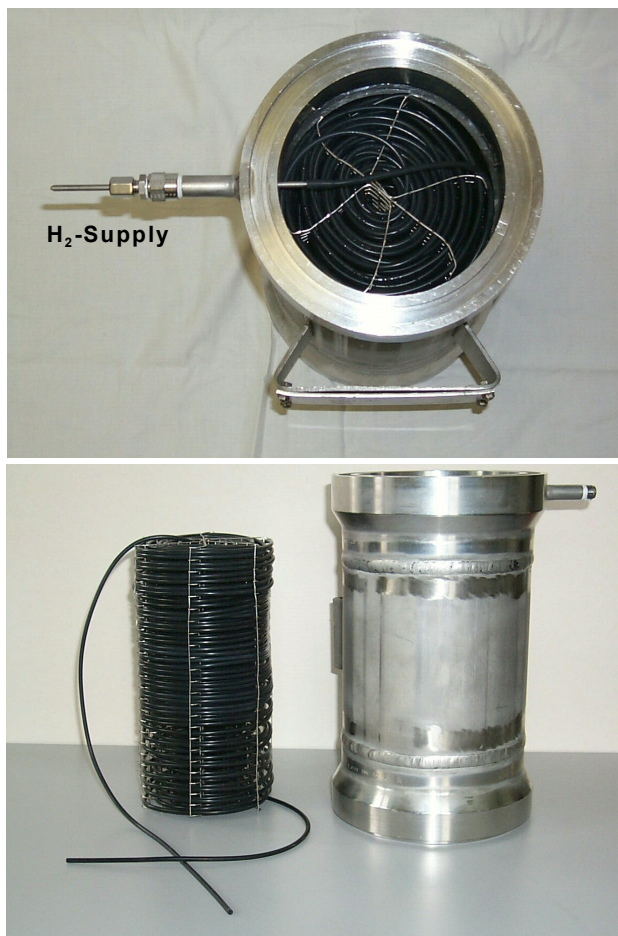
Figure 9   Membrane module installed in Bitterfeld in the pilot plant.

Parallel to the field experiments, studies at the laboratory scale were carried out.

It is important to determine how active a new catalyst is compared to conventional catalysts and whether it is economical enough to work with such a system. We determined specific activities for the palladium in different catalysts, which we tested for the reduction of chlorobenzene.

Because the Pd dispersity is not known for all catalyst samples, we calculated the specific activities as reaction volume divided by the Pd-mass and the reaction half time.

The commercially available catalyst Pd on γ-alumina shows the highest activity of the samples compared (more than double the activity of the membrane catalysts). At first sight, the hydrophobically protected systems, such as the zeolite-pellets or our membranes, show a much lower specific activity. It seems we have to pay for a hydrophobic protection from catalyst poisoning with a considerable amount of activity. However, the activity data alone can not sufficiently predict the performance of the catalytic system as a whole. In the last figure, an example of other important factors will be given: Figure 10 shows an example for the influence of the catalyst matrix on the selectivity of the catalytic system. We used the hydrodechlorination of carbontetrachloride as model reaction. In principle, carbontetrachloride can react on two pathways: directly in one step without the release of intermediates, and over a sequential channel, where we can observe intermediates. And indeed, we find both reaction channels simultaneously. Besides, chloroform does not use both reaction pathways, there is no sequential reduction. This can easily be proved by the absence of methylenechloride, which would be stable under the reaction conditions. Unfortunately, the hydrodechlorination of chloroform is slower by one order of magnitude than the direct reduction of carbontetrachloride. Therefore, the formation and reaction of chloroform dictate the reaction rate of the whole process.
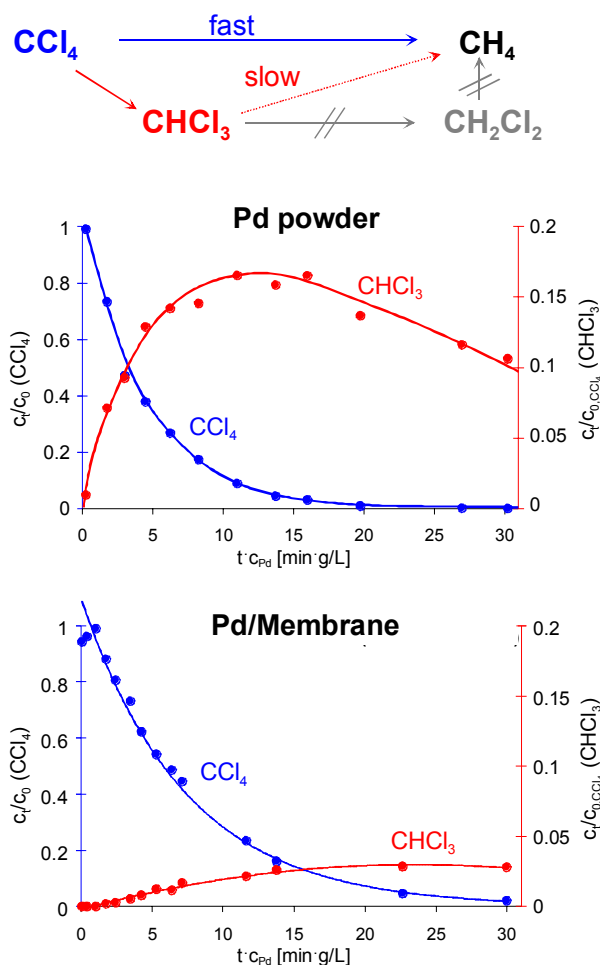

Figure 10   Influence of the catalyst matrix on the dechlorination selectivity

In figure 10 the concentrations of carbontetrachloride (in blue) and chloroform (in red) during the reaction are depicted for two catalyst systems. In the upper part using Pd powder and in the lower part using our Pd/Membrane. The specific activities of both catalysts are very similar for this reaction. However, the selectivity for the unwanted intermediate chloroform is very different. About 20% of carbontetrachloride is transformed to chloroform using Pd without the hydrophobic matrix and only 2% are converted using our new catalytic system. This is a very welcome experimental result, but there is no plausible explanation for it yet.

The comparison of simple activity data can smudge the whole picture of the performance of a catalytic system. Under field condition, we think only the resistance against biofouling will decide over the practical suitability of this new catalyst.

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Development of coupled in situ - reactors and optimisation of the geochemical processes downstream of different in situ - reactor systems

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The project is organised in 2 objectives:

Coupled in situ - reactors

Our concept is the remediation of the Bitterfeld aquifer by reactive walls, because reactive walls have shown to be a favourable and reliable method.

The Bitterfeld aquifer is contaminated with a mixture of different substances, e.g. MCB, DCB, benzene, TCE, DCE ..., which cannot be treated by a wall with one single filling. Hence, we use specialised fillings for several reactive walls in sequence to remove groups of contaminants with different chemical / physical properties from the groundwater.

Zero valent iron
It is well known, that zero valent iron is able to degrade reducible contaminants like TCE, DCE, VC, ... Other contaminants, like MCB, do not react with iron and will not be affected by a wall filled with iron. A secondary effect will be the stabilisation of pH and Eh due to the reaction of iron with water. The same reaction will cause the production of hydrogen, which can be consumed by microbial anaerobic degradation processes.

Activated carbon
Activated carbon is able to remove the contaminants found in the Bitterfeld aquifer from the water by sorption. The contaminants are not degraded, but accumulated in the carbon, hence, the carbon has to be replaced, if its sorption capacity is exceeded. Due to the large surface a microbial colonisation and degradation is expected in the activated carbon.

ORC™
ORC´s are oxygen releasing compounds, manufactured by REGENESIS. This material reacts with water and releases oxygen. Due to a special stabilisation process the oxygen release is slow and constant. We expect a microbial aerobic degradation of contaminants, but it is also possible, that a precipitation of minerals occurs, when ORC´s are combined with zero valent iron.

The main question, which has to be investigated in this project is: In which sequence should the reactive walls be arranged, in order to cause positive interactions? Pos-

sible interactions could be the production of hydrogen due to the reaction of iron with water and anaerobic, hydrogen consuming microbial degradation in the activated carbon. Another interaction could be the release of oxygen from ORC´s followed by aerobic microbial degradation on activated carbon. Several sequences of wall fillings will be tested in the laboratory and in the Bitterfeld pilot plant to investigate positive and negative interactions.

Optimisation of the geochemical processes

The direct flux out of the reactors is of minor relevance for the environment, much more important is the composition of the groundwater after flowing through a short distance of aquifer material. Due to the buffering capacity of the aquifer material we expect a stabilisation of the pH at a neutral value, a stabilisation of the Eh and a consumption of electron acceptors like oxygen in a usually anaerobic milieu.

Within the project we will investigate, which effects have different types of reactors on the composition of groundwater and aquifer matrix and which sequence of reactors is most favourable for the groundwater composition downstream of the reactive walls.

Preliminary results

First studies have been performed concerning the hydrogen production of different types of iron and the behaviour of Bitterfeld groundwater in a column filled with zero valent iron.

Hydrogen production
Figure 1 shows our experimental set-up for the measurement of hydrogen production. Deionised water is pumped by a peristaltic pump through a column (r = 10cm, L = 1m) filled with different types of iron. The hydrogen gas, produced by the reaction of water with iron, is sampled in a flask and its volume is measured over time. The hydrogen production rate of the three types of iron differs about two orders of magnitude, we found several mechanisms causing these differences:

Surface of the iron
A larger surface increases the reactivity of the iron and forces the H_2-production.

Chemical composition of the iron
A less pure iron seems to show an increased reactivity.

pH
A lower pH increases the H_2-production.

Flow velocity
A high flow velocity in the column increases the H_2-production.

TCE-concentration
The presence of TCE in the inflow of the column does not seem to influence the H_2-production.
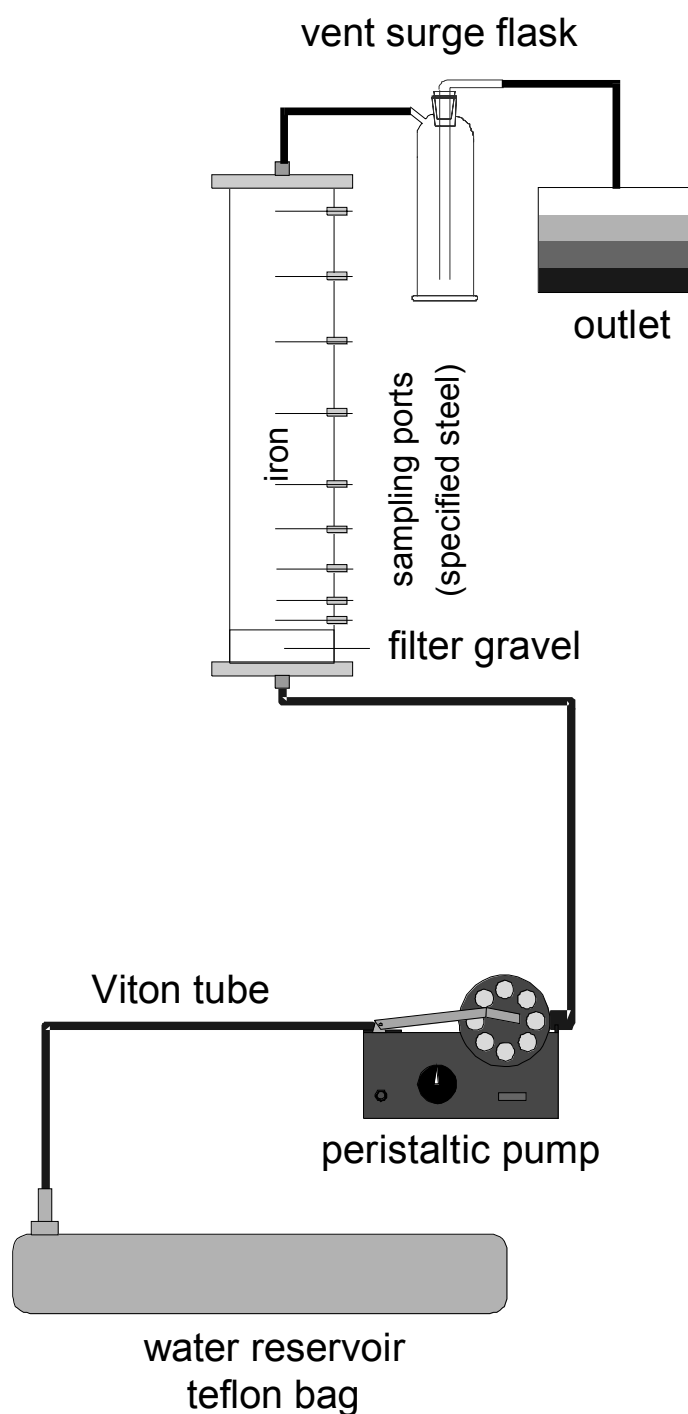
Figure 1   *Column experiment for investigation of hydrogen production.*

Behaviour of Bitterfeld-groundwater in a column filled with zero valent iron

A column, r = 10 cm, L = 1 m, filled with zero valent iron, was placed in the mobile test-unit (so called "Pollux") and has been charged with Bitterfeld-groundwater. We expected a fast degradation of all substances, which are reducible by zero valent iron, while all non-degradable substances should break through the column like a conservative tracer.
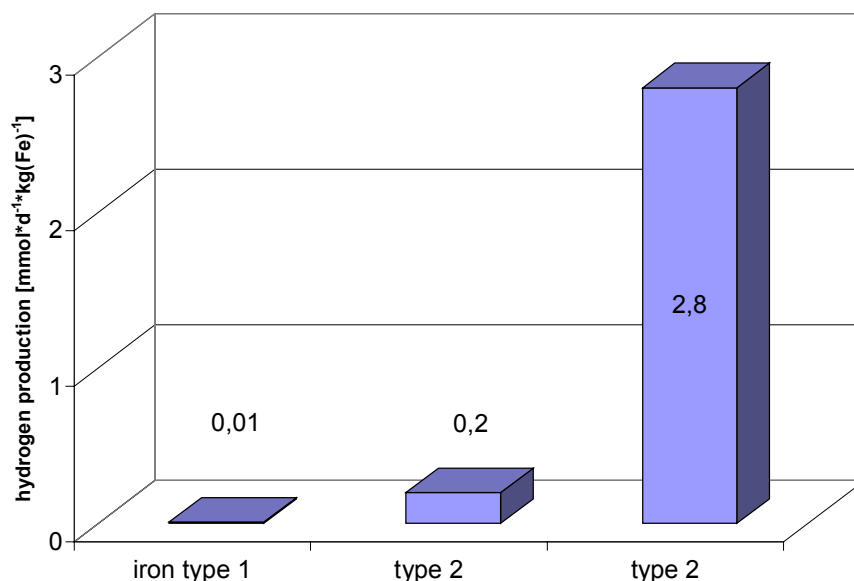
Figure 2   Hydrogen production rate of three different types of iron.

The behaviour of the degradable 1,1,2,2-tetrachlorethane (Figure 3) confirmed our first expectation. While we observe a concentration of about 0.04 mg/l at the inflow, the concentration at the outflow of the column is near zero due to the reduction of tetrachlorethane on the zero valent iron.
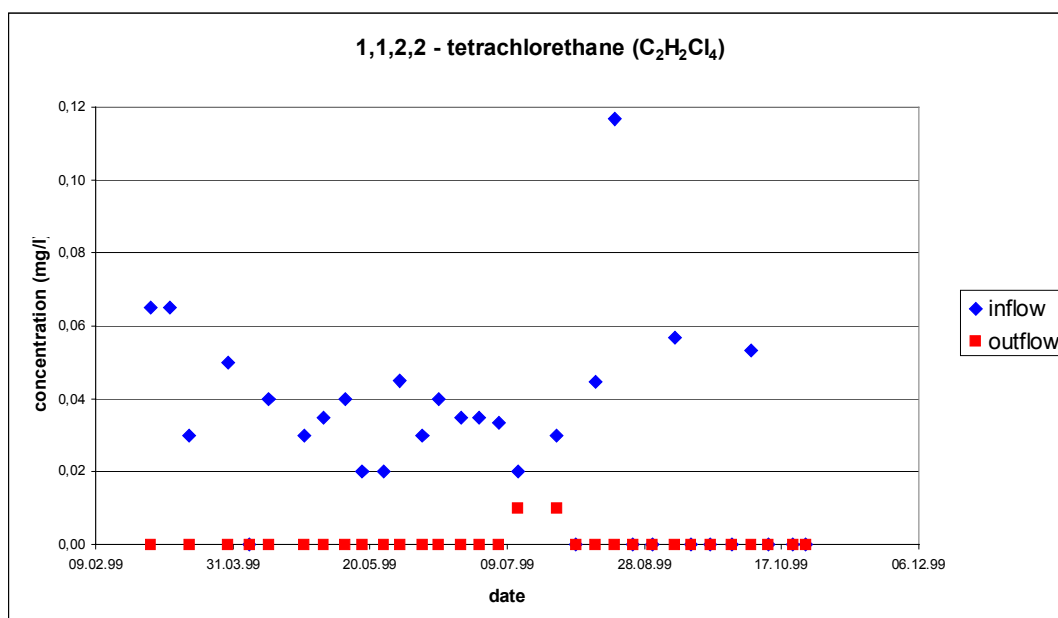

Figure 3   Concentration of 1,1,2,2-tetrachlorethane in the inflow and outflow of the column over time.

Benzene is not degradable by zero valent iron, hence we observe a fast break through of the inflow concentration after a lack phase, where we had some experimental set up problems (Figure 4).
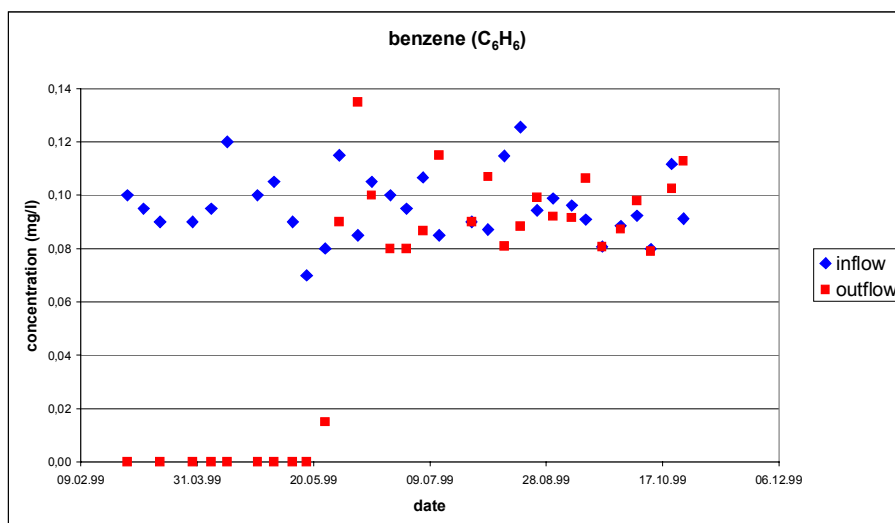
Figure 4   Concentration of benzene in the inflow and outflow of the column over time.

Monochlorbenzene is also not degradable by zero valent iron, we expected a break through of the inflow concentration comparable to the concentrations of benzene, but the measurements show a different behaviour (Figure 5). The first break through of MCB is much later than the break through of benzene and the increase of the concentration is much slower. Until October we did not observe a complete break through of the inflow concentration, there seems to be a permanent gap of about 8 mg/l. A reduction of MCB by zero valent iron cannot cause this gap, because this is thermodynamically impossible under the conditions prevailing in the mobile test unit. It is possible, that an aerobic microbial degradation occurs, because there may be a low diffusion of oxygen through the tube at the inflow of the column. It is likely, that MCB is sorbed on the iron surface, but a permanent difference between inflow and outflow concentration can only be caused by a constant sorption rate. A permanent sorption occurs, when fresh sorbing surfaces are build, e.g. due to precipitation of iron minerals. Additional investigations are necessary to understand this important effect.
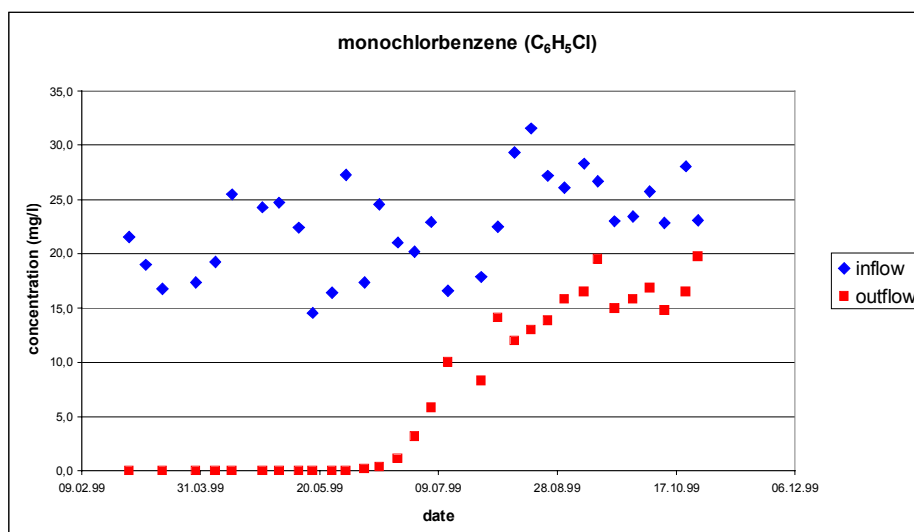

Figure 5   Concentration of monochlorbenzene in the inflow and outflow of the column over time.

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