INHOUD

CHAPTER 4

PHASE I: THE ON-SITE TEST RUNS (INCLUDING LABORATORY TESTS)

4.1 Introduction

The transformation of chlorinated ethenes and chlorinated benzenes was studied separately under anaerobic and microaerobic conditions, respectively. The microaerobic column was initially operated under denitrifying conditions. Whenever necessary, the mode of operation was adjusted according to the scheme presented in figure 11. The anaerobic columns were run at TNO-MEP and the microaerobic column was placed in the on-site unit at the Bitterfeld location. Both columns were run with the same sediment. For practical reasons, the columns which have been used for the anaerobic laboratory experiments are smaller than the column used in the on-site unit at Bitterfeld for the chlorobenzene experiments. However, they have scaled-down dimensions according to the on-site column. Although different systems were used, it is expected that the general outcome of all the experiments can be compared to each other.

The aim of the experiments is to obtain information on the biodegradation processes which are expected to take place under anaerobic and microaerobic conditions. The on-site laboratory column experiments are carried out to determine the amount of electron donor or acceptor necessary relative to the amount of contaminant present in the groundwater. Despite the fact that they are carried out with different column systems, the experiments should still provide enough information on the transformation of the chlorinated ethenes and chlorobenzene under anaerobic and microaerobic conditions, respectively.

4.2 Anaerobic columns

Aim of the experiments

The anaerobic column experiments should provide information on:

- Whether or not complete reductive dechlorination of TCE and DCE in the Bitterfeld groundwater occurs under anaerobic conditions.
- The amount of electron donor needed for complete dechlorination of the chlorinated ethenes. This is especially of interest because of the high amounts of sulphate (around 700 mg l^{-1}) present in the groundwater. It is currently unknown, whether sulphate reduction and dechlorination of the ethenes can occur simultaneously 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 several hundreds of times the amount needed for the complete reduction of the chlorinated ethenes in the groundwater. This would negatively affect the technical and economical feasibility of the anaerobic treatment process in this situation.

Set-up of the experiments

The groundwater for the anaerobic columns was taken from the Safbit 2 sampling well from 28 meters depth, because this groundwater contains TCE. The degradation of TCE in the groundwater was tested in multiport columns (figure 12). The columns were filled with sediment from the Bitterfeld location. A mixture of lactate, acetate, propionate and butyrate (ratio 1:1:1:1, based on electron equivalents) was applied as the electron donor (ED). The initial amount of ED dosed to the columns was enough to sustain complete reduction of all the chlorinated ethenes and the sulphate present. This amount of ED is referred to as 1* ED. The applied hydraulic retention time was 2 days. The columns were run in the dark in a temperature controlled room at 20°C.

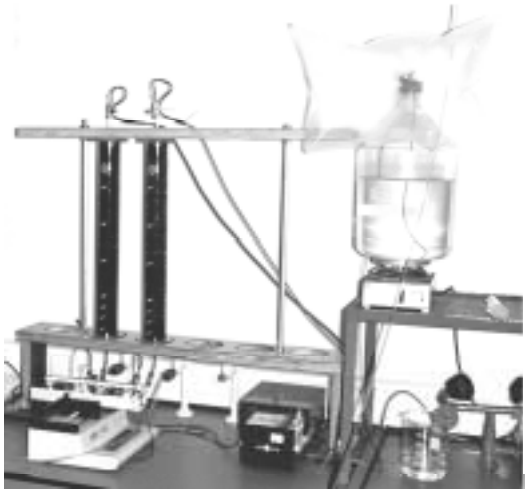

Fig. 12. Set-up of anaerobic columns.

More details on the composition of the groundwater, the set-up of the anaerobic experiments and the analyses carried out are described in Appendix B and Appendix D, respectively.

4.3 Microaerobic column

Aim of the experiment

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 according to the schedule presented in figure 11. It is easier to supply nitrate to groundwater than oxygen. This makes operation under denitrifying conditions an attractive option for future field scale application.

Set-up of the experiments

The microaerobic experiments are carried out with groundwater and sediment from the Bitterfeld location in a stainless steel column (figure 13).

Fig. 13. The microaerobic column in the mobile on-site test unit.

Initially, the groundwater was amended with nitrate at a concentration of 2.4 mM (as KNO_3). More details on the set-up of the column are given in Appendix C.

4.4 **Results of the laboratory and on-site test runs**

4.4.1 *Anaerobic columns*

The anaerobic transformation of chlorinated ethenes present in the Bitterfeld groundwater was tested in two separate column systems. The experiment was divided into four phases (table 2) to test different methods to enhance the reductive dechlorination of the chloroethenes in the groundwater.

Table 2. 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^+

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 (table 3). Small amounts of PCE and TCE are converted to presumably cDCE, but little transformation of higher chlorinated ethenes to lower chlorinated ethenes occurred under these conditions. More than 90% of the VFA and lactate were converted to unknown products. During this period sulphate reduction started, but 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 micro-organisms which are able to degrade chlorinated ethenes.

Table 3 Chlorinated ethenes present in the groundwater and in the effluent of the anaerobic columns with the addition of (in theory) sufficient electron donor to completely reduce the sulphate and chlorinated ethenes present in the groundwater.

Compound	PCE	TCE	cDCE	tDCE	VC	Ethene
Groundwater	3.8	15.6	60.9	17.6	5.9	< DL
Effluent 1	1.8	14.1	63.4	15.7	5.0	< DL
Effluent 2	1.7	13.9	62.4	16.6	5.7	< DL

Concentrations are given as the percentage of the total amount of chlorinated compounds present in the groundwater and effluent after 30 days (DL = Detection Limit).

These options were tested in following phases of the laboratory experiments. The pH of the effluent of the anaerobic reactor throughout the different phases was pH 7.9-8.0. At pH 7.9 to 8.0 less than 4%[1] of the total amount of sulphide-S is present in the toxic form H_2S. The remaining part of the sulphide-S is present as HS^-. Toxicity of H_2S towards the anaerobic bacteria is therefore not a problem.

[1] Based on pKa's of 6.52 and 12.92 of H_2S and HS^-, respectively, at 25°C.

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 14). The dechlorination of TCE to *cis*-1,2-dichloroethene (cDCE) was complete in both columns (figure 15). Also PCE was slightly converted to lower chlorinated ethenes (figure 16). 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) (figures 17 to 19).

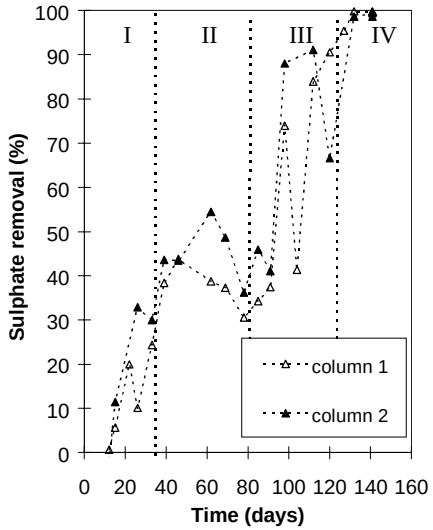

Fig. 14. Sulphate reduction in the anaerobic column treating the TCE containing groundwater.

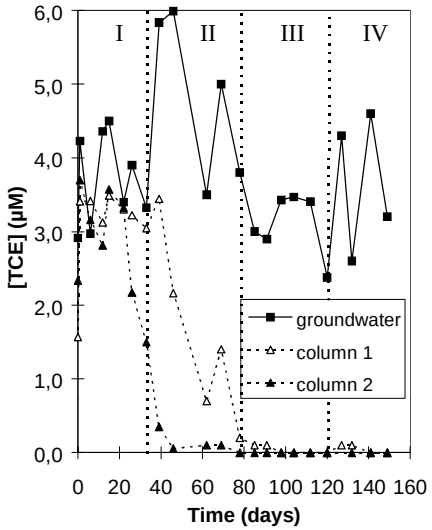

Fig. 15. Transformation of TCE in the anaerobic columns treating the groundwater from Bitterfeld.

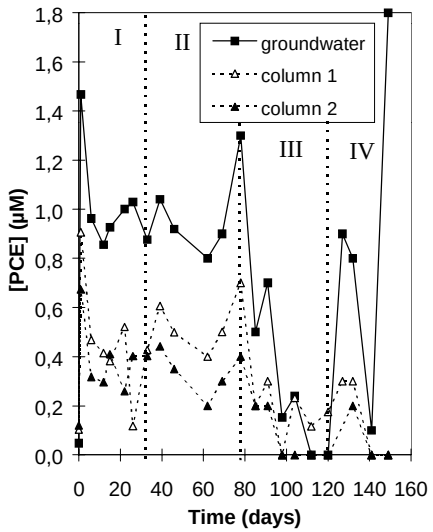

Fig. 16. Transformation of PCE in the anaerobic columns treating the groundwater from Bitterfeld.

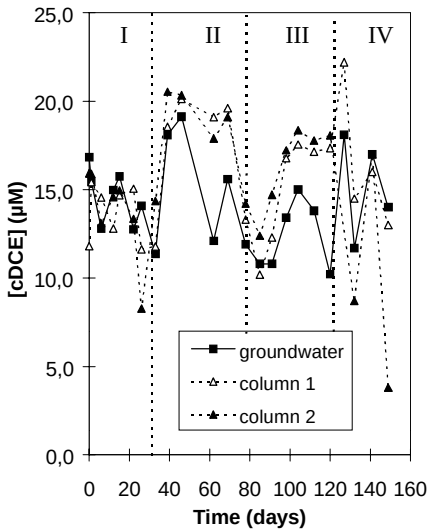

Fig. 17. Transformation of cDCE in the anaerobic columns treating the groundwater from Bitterfeld.

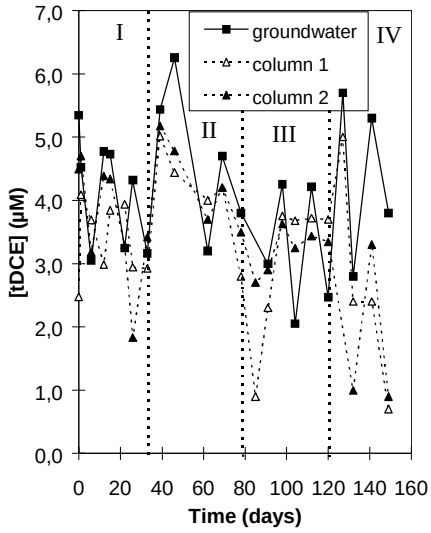

Fig. 18. Transformation of tDCE in the anaerobic columns treating the groundwater from Bitterfeld.

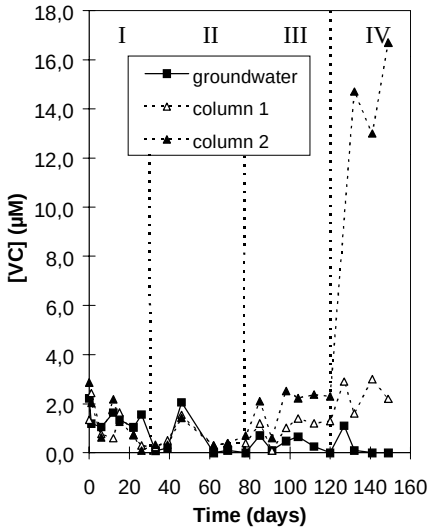

Fig. 19. Transformation of VC in the anaerobic columns treating the groundwater from Bitterfeld.

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 20). 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 (figure 18).

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

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

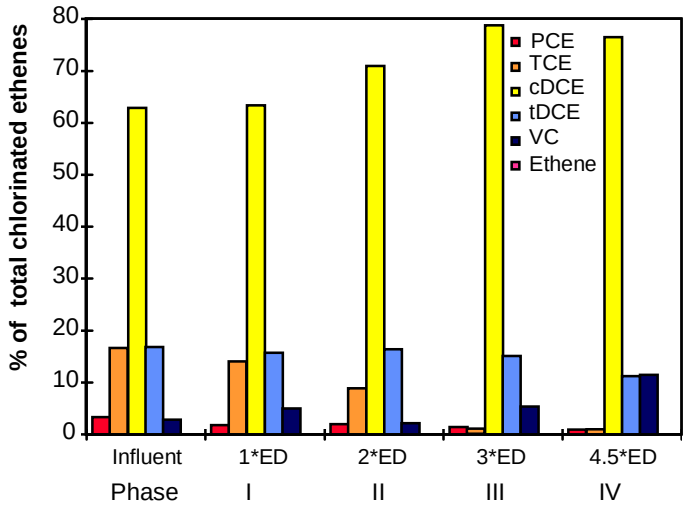

Fig. 20. The effect of increased electron donor concentration on the transformation of TCE in the Bitterfeld groundwater.

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 21). 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 15), 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.

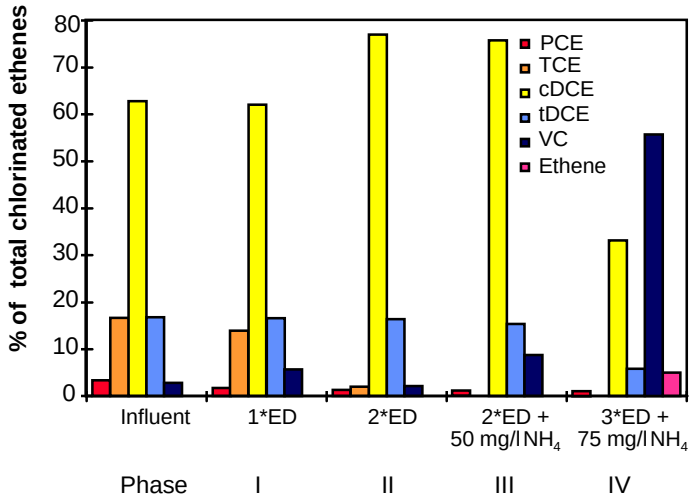

Fig. 21. The effect of increased electron donor concentration and the addition of nitrogen on the transformation of TCE in the Bitterfeld groundwater.

The fate of the electron donor

The electron donor was completely converted during every dosage regime. The fate of the electron donor is not completely clear yet. At least a part of the electrons generated from the VFA and lactate is used to reduce the sulphate present (25% and 32% in column 1 and 2, respectively). Around 53% and 69% of the electrons supplied to the column 1 and 2, respectively are accounted for (table 4). The remaining part of the electron donor is converted to unknown products. The electrons may be present as biomass, methane, unknown reduced products like alcohols, or may be used to reduce the aquifer material. To investigate the second option further, the TOC of the groundwater and the effluent of the column systems will be followed more closely in the future.

Other possible explanations, like leakage of oxygen through tubing or volatilisation of the hydrogen are unlikely because the column system is designed to be airtight and measures are taken to prevent the dissolution of oxygen in the groundwater.

Table 4. Fate of the electron equivalents during the 149 days of operation of the columns.

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

[1] Assuming biomass yields of 0.80 g dry cells (mole eeq)$^{-1}$ for sulphate reducers [36, 37] and 2 g protein (mole eeq)$^{-1}$ for dechlorinating bacteria [38] Biomass formula $C_5H_7NO_2$ [39].

[2] Assuming 10% of the aquifer material consists of Fe.

Implications for scaling up of the process

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 [40] From our laboratory experiments the conclusions can still go both ways. The role of sulphate is under further investigation.

The effect of the addition of complex electron donors on the sequential or simultaneous reduction of sulphate and chlorinated ethenes is also unknown. Obviously, a mixture of different electron donors may stimulate the simultaneous occurrence of the two processes. Also, complex electron donors may be cheaper than the mixture of fatty acids that is used in these experiments.

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).

4.4.2 *The microaerobic column*

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 22). 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 (134.4 mg/ 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. Chlorbenzene removal may also be caused by non-biological processes, like adsorption. However, removal via adsorption to the sediment was not observed (table 5).
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.

Within the SAFIRA framework, research carried out at the department of Environmental Microbiology of UFZ showed chlorobenzene conversion under denitrifying conditions. This transformation was partially attributed to the diffusion of small amounts of oxygen into the system via tubing, and the presence of residual oxygen in the aquifer material [34]. 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 [33, 35]. 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 led to any increase of the chlorobenzene removal in our column system (table 5). This was not expected, but may be explained by the fact that different sediments were used in the experiments.

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 22). The pH of the column effluent was between pH 6.5 to 7.0 throughout the experiment.

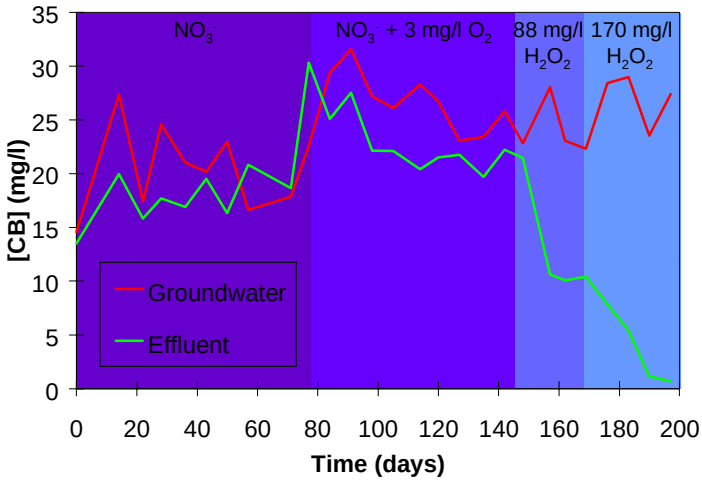

Fig. 22. Transformation of chlorobenzene in the microaerobic column.

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 (table 5). Only half of the chlorobenzene is converted when the oxidant : chlorobenzene ratio is 1:1 (88 mg/l H_2O_2). This is 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.

Table 5. Chlorobenzene concentration (CB) in the groundwater and in the effluent of the microaerobic column. Given are mean values and standard deviation.

Treatment	CB groundwater (mg/l)	CB effluent (mg/)
NO3-	20.3 ± 4.1	17.7 ± 2.3
NO3- + 3 mg/l O2	26.4 ± 2.9	23.3 ± 3.4
88 mg/l H2O2	24.5 ± 3.1	10.4 ± 0.3
170 mg/l H2O2	27.1 ± 2.5	3.8 ± 3.5

4.4.3 *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, because of the high costs and the (volumetric) large amounts that will have to be added.

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 [34, 35]. The lack of transformation of chlorobenzene in our case may have been caused by:

- The differences in aquifer material between the research of Lorbeer [34] and the experiments described here;
- The fact that the research described in this Deliverable was started with the addition of merely nitrate to the groundwater instead of a combination of small amounts of oxygen and nitrate together.

The addition of oxygen in our case was after a period of 70 days during which the reactor was run under denitrifying conditions. This may have to reduced the sediment too much. The subsequent addition of small amounts of oxygen during the on-site test runs may therefore not have led to the desired oxidation of the chlorobenzene. By applying the oxygen already during the start-up of the reactors, this problem may be overcome.

4.4.4 *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.

CHAPTER 5

PHASE II: *IN SITU* REACTOR EXPERIMENTS

5.1 Introduction

In phase I of the Bitterfeld project on-site bench scale and laboratory experiments were carried out to determine the possibilities of combined anaerobic - microaerobic treatment of the groundwater in Bitterfeld which is contaminated with chlorinated ethenes and chlorobenzene. During these on-site (bench) scale experiments the fate of the chlorinated ethenes under anaerobic conditions and of chlorobenzene under microaerobic conditions were investigated (Chapter 4).

From the on-site experiments under anaerobic conditions it was concluded that the addition of electron donor and nutrients (nitrogen as NH_4Cl) is essential for complete dechlorination of TCE to ethene. Evidence is still inconclusive about the necessity of complete sulphate reduction prior to dechlorination of the chloroethenes. Complete sulphate reduction would require the addition of relatively large amounts of electron donor. It is clear that at least some sulphate reduction will occur. Whether partial removal of the sulphate or whether reductive dechlorination can occur under sulphate reducing conditions is under investigation.
Transformation of the chlorobenzene in substantial amounts was found to be induced only by the addition of high concentrations of oxygen only. Degradation under denitrifying conditions did not occur, although small amounts of oxygen were added.

In the *in situ* system the sequential anaerobic/microaerobic treatment of the contaminated groundwater is investigated. The research comprises both the fate of the contaminants, and sulphate. The chlorinated ethenes are planned to be dechlorinated in the first anaerobic step. Partially dechlorinated products that are still present in the anaerobic effluent should be degraded in the second microaerobic step. Sulphide is most likely formed in high concentrations during the first anaerobic phase. Sulphide may precipitate in the anaerobic reactor, which in turn may lead to clogging problems. In the microaerobic reactor, sulphide may be transformed under aerobic conditions both via chemical or microbiological pathways. Biological sulphide oxidation under denitrifying conditions is also known to occur.

The presence of sulphide in the microaerobic reactor may have the following effects:
- increased need for oxygen and/or nitrate;
- deterioration of chlorobenzene transformation.

During the *in situ* trials, more insight should be gained in the contribution of the different pathways to the transformation of the components in the groundwater.

The installation and preparation of the underground reactors was not without problems and required more time than foreseen (see below). The *in situ* test runs were therefore started later than planned.

5.2 The carrier material in the *in situ* reactors

In order to get an environment that is comparable with the situation *in situ*, it was decided that aquifer material originating from the site where the *in situ* reactors are build, would be used as carrier material for the on-site and *in situ* reactors. This sandy aquifer material was stored on-site in containers, which were flooded with groundwater.

The *in situ* reactors were partially filled with this material. Because the amount of properly stored aquifer material was insufficient, also some dry, oxidized aquifer material was used to fill the *in*

situ reactors. This resulted in a severe drop in pH of the reactor. The low pH is most likely caused by a series of chemical reactions in which pyrite reacts with oxygen:

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3(s) + 8SO_4^{2-} + 16H^+$.

After flushing the reactors with groundwater, the pH has increased, but this occurred rather slowly. Original background pH conditions have been achieved finally (in at least three of the four reactors). However, the chemical and microbial condition of the aquifer material will presumably remain different, due to the reactions that have occurred in the material. The effect of the oxidation process and the acidic circumstances on the microbiology on the performance of contaminant degradation processes is unclear. The microbial population in the aquifer material may have changed and died off partially or completely. Also, the chemical composition of the aquifer material has been changed drastically. E.g., metal ions may have leached from the sediment. Therefore, the oxidation and low pH may result in unexpected effects on the microbial processes studied. Therefore, additional lab experiments were carried out to monitor the effect of the oxidation and low pH values on the transformation processes involved in the NA^+ processes. The results of these experiments are described in Appendix G.

Because the pH of part of the aquifer material dropped significantly during storage and during the loading of the *in situ* reactors, it was decided to incorporate an additional equilibration period in the start-up phase of the *in situ* reactors prior to studying the biological processes. During this period the reactors were washed with groundwater to restore proper pH of the reactor contents (figure 23).

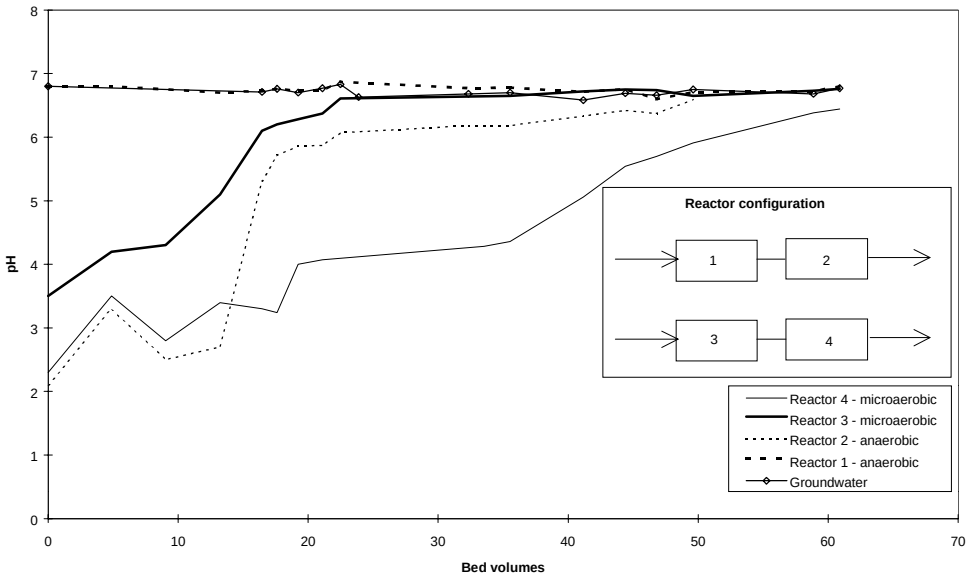

Fig. 23. The pH in the reactor and in the groundwater after start-up of ground water flow.

In three of the four reactors the pH was restored to values, which are acceptable for biological processes within the change of 10 to 25 bed volumes (equal to 3 to 4 months of operation). The pH in reactor 4 reached an acceptable level soon afterwards.

Because of the pH drop in some of the reactors, the set-up of the experiments with the *in situ* reactors was changed to two anaerobic - microaerobic systems that are run parallelly (reactors 1 and 3 as system 1, and reactors 2 and 4 as system 2). The equipment in the shafts was originally not designed for a fresh groundwater flow to both reactors 1 and 2. The "plumbing" of the

system has been adjusted and prepared for such a situation. This required additional time and a later start up of the *in situ* reactors. The biological processes in the *in situ* reactors were started up March 2000.

5.3 General set up of the reactor system

The groundwater is treated in a sequential anaerobic - microaerobic reactor system (figure 24). This system is tested in two sequentially run reactors. The choice was made to use 4 reactors with a volume 4.4 m3 each. This set-up guaranteed maximum flexibility and the possibility to change the reactor set-up at any time as a result of the outcome of the on-site experiments. Engineering of the reactors was not a part of the project, because the NOBIS project was included in the SAFIRA project at a relatively late stage.

Two systems are run in a parallel mode. Reactors 1 (anaerobic) and 3 (microaerobic), exposed to no or a small pH drop function as one system. The reactors 2 (anaerobic) and 4 (microaerobic), which were exposed to much lower pH's than the second system. In this way results can be obtained from at least one two phase system that on forehand was not affected by a low pH period. Insight in the possible effects of low pH values on the biological processes were gained by an additional test program with laboratory columns.

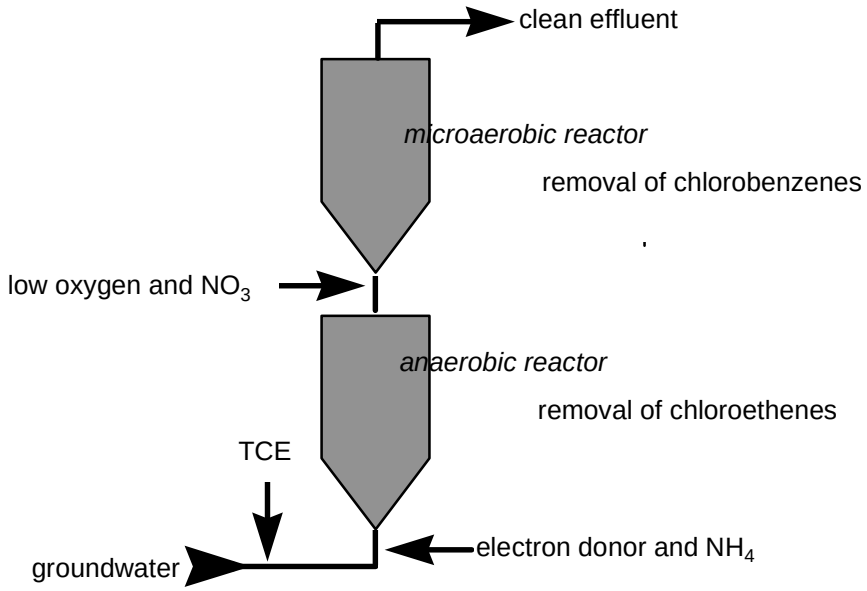

Fig. 24. Sequential anaerobic - microaerobic reactor system for the treatment of the Bitterfeld groundwater.

More information on the set up of the in situ reactors and some preliminary results are given in Appendix F.

CHAPTER 6

COMPARISON OF SAFIRA TECHNOLOGIES

6.1 Introduction

The enhanced bioremediation technology tested in the current NOBIS-SAFIRA project will have to be compared with the results of the other technologies tested in the SAFIRA project. This first evaluation will be focussed on the technical possibilities, limitations and costs of an enhanced in-situ bioremediation variant that may be suitable to be implemented in the Bitterfeld region. A general overview of technologies tested will also be given[2]. Based on the current available information from both the NOBIS-tests and the other SAFIRA-technologies investigated, the comparison of techniques will primarily be focussed on plume management potential.

6.2 SAFIRA technologies: an overview

The SAFIRA (Sanierungs Forschung in Regional kontaminierten Aquiferen) project investigates the development and technological and economical feasibility of technologies that can be used in an integrated plume management approach for the Bitterfeld/Wolfen area. This investigation is performed by testing the techniques at bench scale in *on-site* column reactors or in the laboratory and *in situ* reactors (figure 25) at a pilot plant at the test site at Bitterfeld/Wolfen.

Chlorobenzene is the main contaminant found in the upper aquifer at Bitterfeld, whereas the lower aquifer mainly contains chloroethenes. A difficulty in the composition of the groundwater is posed by the high sulphate concentrations (varying from 600 to 1000 mg/l).

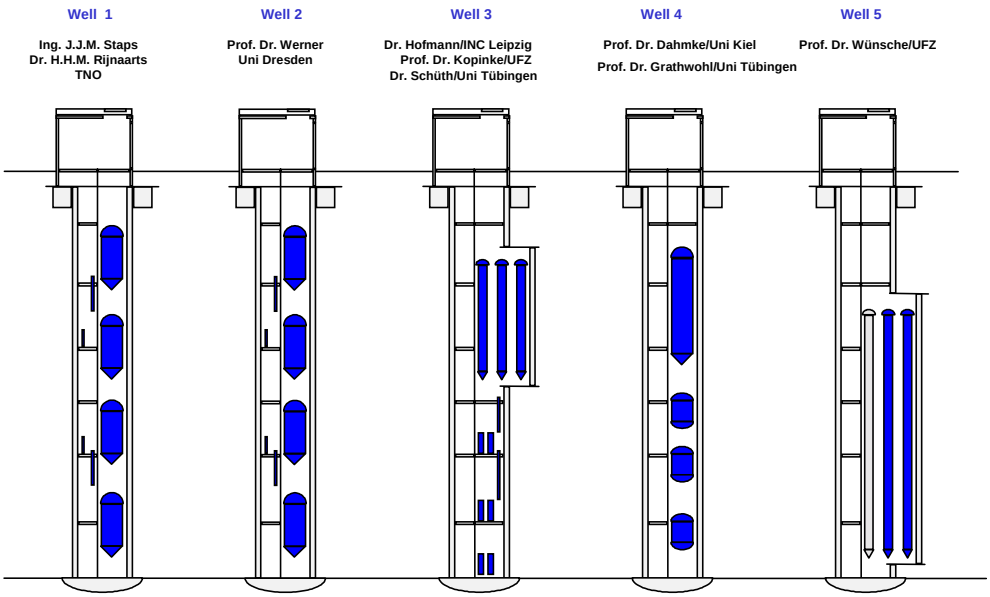

Fig. 25. The SAFIRA technologies tested in the in situ reactors.

[2] See also: Merkel, P., H. Weiss, G. Teutsch, and H.H.M. Rijnaarts (in press). Innovative reactive barrier technologies for regional contaminated groundwater. In: Proceedings of Contaminated Soil 2000 (CONSOIL), September 18-22 2000.

Current SAFIRA technologies tested are (table 6):
- (enhanced) biodegradation (SHAFT I);
- adsorption on activated-carbon (SHAFT II);
- zeolite-supported palladium catalysts, membrane-supported palladium catalysts and oxidative solid metal catalysts (SHAFT III);
- electro-chemical processes (redox) and activated carbon filtration (SHAFT IV);
- anaerobic degradation (SHAFT V).

Table 6. Current SAFIRA technologies tested.

SHAFT	Technology tested	Fill material reactor	Remarks
I	(enhanced) biodegradation	4 reactors filled with aquifer material	both anaerobic and micro-aerobic tests
II	adsorption on activated-carbon	2 reactors filled with activated carbon	both anaerobic and aerobic tests
III	zeolite-supported palladium catalysts membrane-supported palladium catalysts oxidative solid metal catalysts	as technology indicates	-
IV	electro-chemical processes (redox) and activated carbon filtration	ORC's® activated carbon zero-valent iron	both anaerobic and aerobic tests
V	anaerobic degradation	reactors filled with aquifer material	anaerobic testing

SHAFT I

The current NOBIS-consortium uses Shaft I for the (enhanced) biodegradation testing in a two-phase system (figure 26). The first, anaerobic, step is focussed on the degradation of chlorinated ethenes by addition of a mixture of electron donors (lactate and others). The second, micro-aerobic, step aims at a complete mineralisation of (chloro)benzene by addition of nitrate and minimal amounts of O_2. The carrier material for the micro-organisms consists of the aquifer material present at the Bitterfeld site, resembling the (geo)chemical environment in the field.

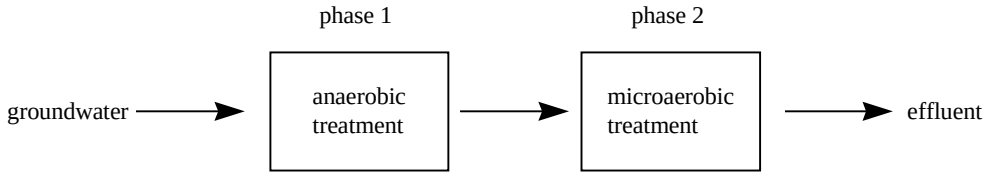

Fig. 26. Biodegradation testing in a two-phase system.

SHAFT II

Universität Dresden uses Shaft II to investigate the adsorption on activated carbon, followed by microbial degradation of contaminants. The experimental set-up is divided into two stages. In the first anaerobic stage, chlorinated ethenes undergo dechlorination to form DCE and VC. The second, aerobic stage comprises the mineralisation of these metabolites and the degradation of the chlorinated aromatics. The creation of the appropriate redox conditions and the addition of substrates to both stages is designed to achieve the simultaneous microbial regeneration of the

adsorbent and thus to considerably prolong the life span of the activated carbon filters. To distinguish the adsorptive and microbial processes a reactor with a non-adsorbing material and a non-stimulated activated carbon reactor will be operated in parallel.

SHAFT III

In Shaft III 3 different types of catalysts are being tested by respectively Universität Tuebingen, Umwelt Forschungs Zentrum (UFZ) Centre for Environmental Research Leipzig-Halle and Universität Leipzig:

- *Zeolite-supported palladium catalysts*
  Using hydrogen as the reducing agent, palladium is able to catalyse the dehalogenation of chlorinated organic contaminants in water. However, the groundwater contains substances, mainly ionic sulphur compounds, which can deactivate ('poison') the catalyst. In order to prevent deactivation, zeolites are used as a support material for the palladium. These zeolites are microporous, highly hydrophobic (water-repellent) aluminium silicates with pore diameters of 0.74 nm into which the palladium is introduced. The pollutants (which are also hydrophobic) and the hydrogen necessary for the reaction can penetrate these pores and react on the surfaces of the palladium. However, the deactivating ionic sulphur compounds cannot enter these pores as they are repelled by the hydrophobic zeolites. Hence the zeolites protect the palladium against deactivation.
- *Membrane-supported palladium catalysts*
  As an alternative for zeolite-support, coating the palladium catalyst with hydrophobic, non-porous silicon material is investigated to keep hydrophilic catalyst poisons such as sulphur ions away from the palladium, while allowing the reactants (chlorinated hydrocarbons, hydrogen, HCl and hydrocarbons) to diffuse through the silicon membrane largely unimpeded. Other positive effects include the enrichment of the hydrophobic pollutants in the membrane and the prevention of valuable and toxic palladium from being discharged into the aquifer. In addition, by using membrane-based catalysts in the form of hollow fibres, a permanent surplus of the reduction agent hydrogen can be kept at the reaction-site.
- *Oxidative solid metal catalysts*
  Ultrasound-based catalytic oxidation is being used in a long-term experiment to demonstrate the *in situ* treatment of groundwater by degrading the organic pollutants. The degradation of the pollutants dissolved in the groundwater takes place via catalytic oxidation on a solid metal catalyst. The solid metal catalyst is a wire mesh specially treated to give it a catalytically active surface coating. Hydrogen peroxide is used as the oxidising agent. The brief periodic application of ultrasound regulates the catalytic activity and hence increases service life.

SHAFT IV

Universität Kiel investigates in Shaft IV a coupled set of a redox-reactor, aerobic reactor (ORC's®) and activated carbon-reactor. Using metallic iron (zerovalent iron) reducible substances such as trichloroethylene can be converted into ethenes and chloride. Non-reducible organic compounds such as monochlorobenzene are adsorbed on activated carbon. Biodegradable products such as benzene or ethene, resulting from the reaction with iron, are degraded by bacteria. The research project is designed to ascertain how the various remediation processes affect one another and the sequence in which the reaction chambers must be installed so that the pollutants can best be removed from groundwater over long periods of time.

SHAFT V

In this Shaft anaerobic degradation is investigated by UFZ. This technique uses the biocatalytic potential of the community of micro-organisms inhabiting the polluted aquifer. The microbial population is stimulated to degrade chlorobenzene under anaerobic conditions by adding the

alternative electron acceptor nitrate. Chlorobenzene and 1,4-dichlorobenzene disappear in the reactor via unknown mechanisms. Recent results (March 2000) indicate a loss of this removal activity and a breakthrough of both dichlorobenzene and chlorobenzene.

6.3 **Current SAFIRA developments**

Since 1998 *on-site* and off site laboratory tests are performed at the SAFIRA test site in Bitterfeld/Wolfen. In 1999 most *in situ* tests programs in the constructed shafts were started up; these tests (see following paragraph) are still running. Based on preliminary test results most physico-chemical methods investigated at the SAFIRA site cannot bring a complete solution for chloroaromatics, nor for the mixture of chloroethenes and chloroaromatics. At least a part of the solution should be provided by biological methods.

Although activated carbon filtration is a standard method in drinking and waste 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. Within the seven months of the experiment, the sorption capacity of the activated carbon was not reached and no breakthrough of contaminants was observed. The preliminary conclusion is that activated carbon filtration is a very effective method to remove chlorobenzene from the Bitterfeld groundwater. However, all in-situ reactors are affected by groundwater-specific processes like plugging and chemo- or biofouling due to precipitation or the growth of biomass, which can reduce the removal efficiency of the systems. These groundwater-specific processes are still under investigation and no relevant results have been obtained so far.

A promising way for the treatment of VOC-contaminated aquifers in passive systems seems to be the stimulation of micro-organisms capable to mineralise the pollutants. The system used in the SAFIRA project combines microbial degradation with adsorption of the VOCs on granular activated carbon. The micro-organisms covering the activated carbon as a biofilm degrade the adsorbed pollutants resulting in a continuous biological regeneration of the adsorbent. The current laboratory investigations focus on the bioavailability of the contaminants adsorbed on activated carbon. In the framework of the SAFIRA project the experiences gained in the laboratory will be transferred to the large-scale subsurface treatment facilities.

Zero valent iron is able to degrade reducible contaminants like chlorinated ethenes. Other contaminants, like benzene and monochlorobenzene, do not react with iron and will not be affected by a wall filled with iron. A secondary effect of the use of zero valent iron 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. Experimental results show that the use of 'iron walls' can be a promising part of a solution. However, contaminants different from the chlorinated compounds (a/o. benzene and monochlorobenzene) will have to be removed or treated using other methods. Different kinds of biological methods are still under investigation.

The research on catalysts is mainly focussed on dechlorination. It was found that 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. Comparable to the zero valent iron, the catalysts are mainly successful in handling chlorinated compounds. Other compounds (a/o. benzene) will have to be removed or treated using different (biological) methods.

Studies performed indicate the presence of micro-organisms for complete anaerobic conversion of chloroethenes to ethene. However it is necessary to supply a nitrogen source, and (at least during the start up phase), high amounts of electron donor. Sulphate reduction started before the first dechlorination of TCE was observed. The amount of electron donor needed for the reduction of sulphate is 500-1000 times higher than the amount needed for complete dechlorination of the chloroethenes present. Complete aerobic degradation of chlorobenzene may be achieved by supplying oxygen as hydrogen peroxide. Relatively high concentrations of hydrogen peroxide are needed. The excess oxidizing equivalents are probably used to oxidize the sediment during the initial phase. After this first high level of oxygenation, a lower supply of oxygen may be possible.

The first results of the SAFIRA research indicate that given the complexity of the mixture of components present in the region, it is expected that biological methods will contribute to the solution of at least a part of the problem.

6.4 **Applicability in relation to plume management**

The current SAFIRA technologies concentrate on plume management using *in situ* technology and/or reactive walls. Primary protection has to be directed towards potentially endangered environmental receptors in the region. These receptors can be split into two main groups:

- Fresh-water ecosystems, i.e. the small river Mulde, the main river Elbe, and nearby lakes and flooded mining pits, that are threatened by groundwater plumes that have started to migrate through the shallow and deep aquifer systems.
- The village of Bitterfeld and neighbouring communities that are threatened by the rising water table and contact with the chemicals emitting from this water: one of the options to be considered is removal and rebuilding of (part of) these villages.

The results of current research show that, because of the complex situation and combination of contaminants, tested physicochemical methods will in any case have to be combined with biological methods in order to meet remedial goals. Therefore the following options for the implementation of remedial concepts are considered:

- Complete (enhanced) *in situ* bioremediation (combined anaerobic and aerobic stages).
- Physiochemical methods (zero valent iron, catalysts, activated carbon) in combination with enhanced bioremediation.

The practical applicability of the different remedial concepts for the Bitterfeld/Wolfen area depends on factors as local situation (source-path-object, hydrogeological constraints, area involved), costs and technical feasibility and reliability. The technologies may be implemented using *in situ* reactors, reactive walls, funnel-and-gate approaches or activated (biostimulated) zones. Based on Dutch and international experiences with aquifer clean-up and groundwater treatment, *in situ*-technologies (including reactive walls) appear to be the most viable option. Complex technical installations will increase the possibility of technical failure especially in long term operation. Sensitivity and cost analysis may result in a more thorough view on this subject.

CHAPTER 7

A FIRST STEP TOWARDS PLUME MANAGEMENT FOR THE BITTERFELD REGION

7.1 Introduction

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

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

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

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

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

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

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

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

The Bitterfeld area can be characterised as an infiltration area. On a regional scale water that infiltrates will partially flow through the Quaternary aquifer towards the Mulde and discharge in this river, another part will infiltrate even deeper to the underlying tertiary aquifer [41]. In fact two hydrogeological systems exist (apart form groundwater extractions and man made drainage systems). A relatively shallow system (the Quaternary aquifer) consists of an area around the river Mulde and a deeper system (the Tertiary aquifer) consists of an area bordered by the watershed upstream of the village Bitterfeld (to the west) and the border between the deeper and shallow system (figure 27).

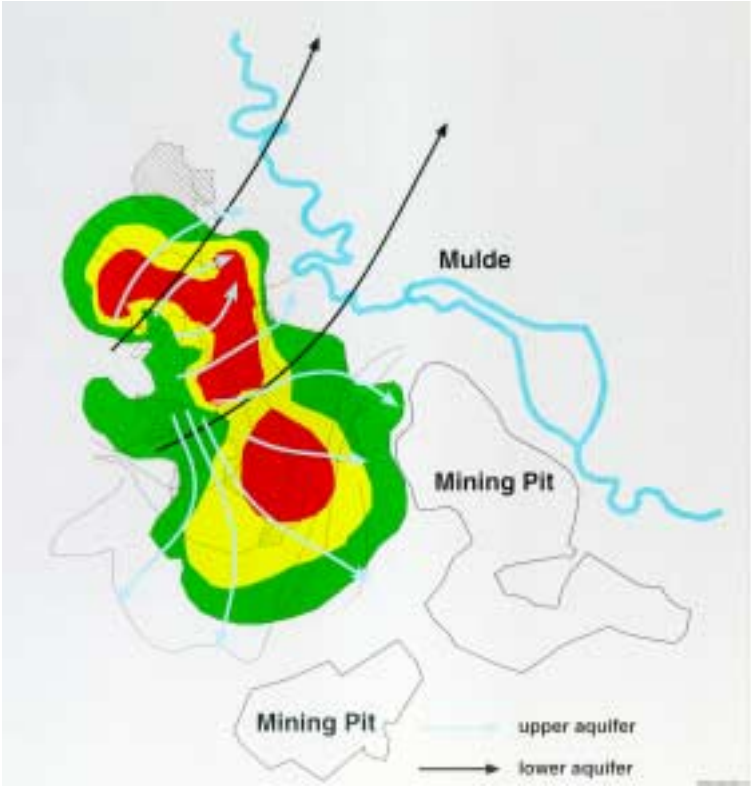

Fig. 27. The current contaminant situation, the isohypses, from which the direction of the groundwater flow can be deduced, and the pit and river Mulde. When the pit is replenished, the general groundwater flow will be from west to east in the direction of the Mulde.

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

7.3 Jig-saw pieces for scaling-up

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

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

River Mulde: active or passive treatment

One of the objects at risk is the river Mulde (figure 28). This has been the case even before closure of the mining wells, although the flux of contaminated groundwater towards the river was less at that time. Prevention of exposure of the river ecosystem can be achieved by in-situ treatment of the contaminant groundwater travelling towards the river. Groundwater discharging into the river Mulde originates from the shallow Quaternary aquifer. The interception and treatment of groundwater travelling towards the river Mulde should focus on the Quaternary aquifer and the main contaminants in the shallow aquifer.

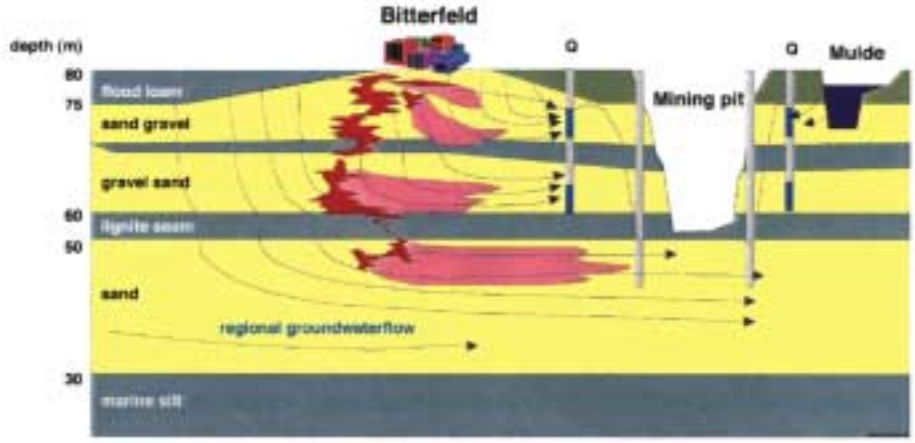

Fig. 28. The floodplain of the river Mulde and the contaminant plume.

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

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

The most active way to collect the groundwater for treatment would be pump-and-treat. Treated groundwater has to be discharged on the river Mulde or injected into the subsurface. Both possibilities have to deal with geochemical and biological processes hindering injection or surface water discharge due to ex-situ treatment. The different redox status between the effluent and the receptor (the subsurface or the river Mulde) forms a specific research item. Problems like for example possible clogging and precipitation of oxides are related.
The concept of funnel-and-gate seems more feasible to protect the river. The gate can be placed parallel to the river downstream of the contaminated groundwater plume. In this way groundwater is treated in-situ. The volume of groundwater that has to be treated in the 'gate' depends on the degree of funnelling. To assure that all contaminated groundwater is trapped and treated in the gate, some pumping may be necessary. A cost optimum has to be found between the effort of funnelling and the volume of groundwater to be pumped towards the gate. If pumping has to be avoided by all means, a reactive wall could act as gate. Again a cost optimum has to be found between the degree of funnelling and the required extent of the gate. Funnelling could be done by hydrological means (groundwater extraction), sheet piling or physical or chemical isolation. These funnel systems are probably even or more expensive than the gate and will have to be replaced in due time.

A more cost-effective solution would be a reactive wall or biological treatment zone, optionally in combination with groundwater extraction systems. Groundwater may be funnelled towards a biological treatment zone by groundwater extraction downstream of the wall. The extracted groundwater originates from the wall and doesn't need further treatment. This 'clean' groundwater could be injected upstream between reactive walls in order to create a hydrological barrier. In this way the extent of the active zones could be largely reduced, no funnels are required and groundwater is passively treated in-situ within the walls.
A similar extensive approach is to use the natural hydrological discharge to funnel contaminated groundwater towards the floodplains along the river. Biodegradation of contaminants could be facilitated by using degradation capacity of those wetlands (helofyte filters). This approach requires careful management of those areas.

For all the options mentioned above, the summed volume of contaminated groundwater to be treated and or extracted is the same. However, the options differ with respect to the effort put in the funnel & gate or reactive walls. If the cost of funnelling groundwater is less than the cost of the gate, options with the emphasis on large funnels and small gates should be preferred. This is the case if clean groundwater extraction downstream of the reactive wall is used as a funnel. The cost of this hydrological funnel is low compared to traditional downstream groundwater extraction or sheet piles as funnel because the extracted groundwater is clean and doesn't have to be treated. As already mentioned a proper estimation of the volume of contaminated groundwater to be treated can only be made when the hydrological system is characterised. A hydrological model is most useful for this purpose. Based on a rough estimate of the contaminated area of 100 km^2, one millimetre recharge per day and the educated guess that 10-30% of water infiltrating in this area will discharge into the Mulde, about 1.10^4 till 3.10^4 cubic meters a day have to be treated. The rest of the infiltrating groundwater within the 100 km^2 penetrates the Tertiary aquifer.

Deeper aquifer: few or no objects at risk
Probably the largest part of the contaminated groundwater will infiltrate towards the deeper, tertiary aquifer, due to the small capacity of the river Mulde to discharge deeper groundwater. Contaminants in the deeper aquifer will migrate over large distances (>100 km) before they eventually discharge to surface water. Due to adsorption and degradation it may take thousands of years before surface water (e.g. river Elbe) is contaminated by this deeper groundwater.

Within this time frame risks for exposure of humans to this contaminated groundwater are small. Exceptions are of course extraction of groundwater from the deeper aquifer for drinking water purposes. The migration of contaminants could be monitored to support planning and future risk assessment. Treatment of the deeper aquifer seems not cost-effective due to the absence of objects at risk and other priorities.

Former mining pit (artificial lake): funnel &gate

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

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

7.4 Possible limitations of current technologies for plume management

Within the funnel-and-gate or the reactive wall approach as described in the previous paragraphs, an *in situ* treatment process should be implemented. Most viable alternatives (see Chapter 6) seem to be:

- complete (enhanced) *in situ* bioremediation (combined anaerobic and aerobic stages);
- physiochemical methods (zero valent iron, catalysts, activated carbon) in combination with enhanced bioremediation.

Limitations of the proposed funnel-and-gate systems could be both technical and financial. Besides technical limitations of the treatment technologies currently under investigation, technical problems could also arise when groundwater has to be infiltrated after extraction and treatment (e.g. clogging effects). Especially combined hydrological funnel-and-gate systems seem to be susceptible for these kind of technical problems. Passive techniques like biological treatment zones or reactive walls are less susceptible for clogging, because groundwater passes those walls at natural flow rate (except if groundwater is funnelled towards the wall).

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

7.5 Concluding remarks on plume management

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

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

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

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

It is recommended to assess the flux of contaminated groundwater towards gates. The volume of groundwater to be treated at the gate and its contaminant load are key figures for estimation of the remediation costs and design. These costs are necessary to decide on the feasibility of the proposed concepts for plume management for the Bitterfeld contamination. Special attention should be given to subsurface heterogeneity [42].

CHAPTER 8

CONCLUDING REMARKS AND RECOMMENDATIONS FOR FURTHER RESEARCH

The overall aim of SAFIRA and of the NOBIS/SKB participation is to obtain cost-efficient technologies that can form elements in a regional integrated plume management approach for the Bitterfeld region and similar large scale contaminated areas. Integration of feasible (biological and physicochemical) technologies into regional redevelopment plans is therefore also part of the project.
More specifically, the research deals with finding a biological remediation method for the treatment of both chlorinated aliphatic and chlorinated aromatic compounds present in the groundwater in Bitterfeld. The chlorinated ethenes and chlorobenzene are transformed in a sequential anaerobic-aerobic process, because chloroethenes are more easily removed under anaerobic conditions, whereas chlorobenzene (so far) has only been found to be degraded under microaerobic or completely aerobic conditions.
The choice was made to use the so called "natural attenuation plus" principle, in which the biological processes are stimulated via the addition of electron donors and electron acceptors.

Currently the natural attenuation plus principle is tested at the location. The results thus far indicate that:

- The micro-organisms for complete anaerobic conversion of chloroethenes to ethene are present, but need to be supplied with a nitrogen source, and (at least during the start up phase), with high amounts of electron donor.
- Complete aerobic degradation of chlorobenzene can be achieved by supplying oxygen as hydrogen peroxide, but needs (at least during the start-up phase) a supply of high amounts of hydrogen peroxide. The high amounts of hydrogen peroxide are probably needed to oxidise the sediment during the initial phase.
- Other physicochemical methods tested within SAFIRA cannot bring a complete solution for chloroaromatics (benzene is formed as a dead-end product), nor for the mixture of chloroethenes and chloroaromatics. At least a part of the solution should be provided by a biological method.

The bottlenecks in the project consist of the following:

- Large scale application, with all the consequences involved (clogging, high costs, practical applicability) as a part of a regional plume management approach.
- High sulphate concentrations (700 mg/l), which may interfere with the anaerobic process (competition for electron donor, dechlorinators must be able to sufficiently compete with sulphate reducers; otherwise high electron-donor demand due to sulphate reduction).
- High sulphate concentration interfering with the aerobic process: high sulphide concentrations formed in the anaerobic step that influence the aerobic step (high oxygen demand due to sulphide oxidation and influence on pH).
- The high oxygen demand thus far needed for complete chlorobenzene degradation, which can probably be reduced to microaerobic levels after the initiation phase.

Operation of the in situ reactors will have to be continued to assess long term in-situ performance. Several aspects like costs, but also clogging problems and scaling up issues will have to be investigated in order to be able to make a translation from the in situ reactors to the real scale situation in Bitterfeld. At the end of the operation period, the results from the other technologies tested in the SAFIRA project have to be compared to come up with a well fundamented approach to deal with the real problem.

The operation of the column experiments will be continued to assess the long term performance of the systems. Although they do not form part of phase II anymore, TNO has decided to continue the columns up to phase III, in order to make it possible to use them for gaining insight into optimisation and long term effects.
These systems are suitable to test several optimisation aspects relatively quickly. The electron donor concentration has to be minimised to reduce costs. Also, cheaper but suitable electron donors have to be found. This involves making an inventory of available electron donor sources in the Bitterfeld region.
For the microaerobic step the amount of oxygen that is necessary will be minimised for economic and practical reasons.

Also, the research will focus on whether an initial reduction of the sediment material is enough to sustain the dechlorination, and how sulphate reduction can be controlled (minimised). This aspect is important because the operation of the anaerobic process will be directed towards prevention of sulphate reduction and subsequent sulphide formation. The sulphate concentration in the groundwater is very high and sulphate reduction requires large amounts of electron donor. Consequently, high sulphide concentrations require large amounts of oxidizing equivalents in the microaerobic reactor and may also lead to the formation of precipitates.
The role of the sulphate reduction in the anaerobic process as a whole will be clarified. It is unclear if sulphate reduction can occur simultaneously with dechlorination in the anaerobic phase or if complete sulphate reduction is required before dechlorination can take place.
On the other hand for the aerobic step, the option for initial complete oxidation of the sediment material will have to be assessed.

The consequences of connecting the microaerobic reactor to the anaerobic reactor will also be investigated. This concerns:
- The fate of the (chlorinated) products of the anaerobic conversion processes in the microaerobic reactor.
- The fate of chlorobenzene, mineralisation or just partial conversion.
- The fate of sulfide (formed in the anaerobic reactor) under microaerobic conditions. The presence of sulfide could lead to a high oxygen and/or nitrate demand in the second microaerobic step. More insight should be gained in the occurrence of these oxidation processes.

To get more insight in the nature of the compounds present, regular Gas Chromatographe / Mass Spectrometry (GC/MS) screening of the groundwater and effluent is necessary.
The sediment is still considered to be a black box system. Some of the research questions could be solved by clarifying the composition and other characteristics of the aquifer material. This is of importance for, among others, the oxidizing and reducing capacity of the sediment material, which will influence the initial start-up of the process.

The research aspects described above form a part of the research proposal for phase III of this project ("Bitterfeld: Bioremediation of regional contaminated aquifers. Phase III: Long term performance and feasibility"). This project proposal has been approved by SKB.

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APPENDIX A

GEOCHEMICAL ANALYSIS OF THE GROUNDWATER

Table A1. Geochemical analysis of the groundwater used in the on-site mobile test unit (data obtained from UFZ).

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

Concentrations are given in mg/l units unless stated otherwise. The "June-August 1998" data are given as the data for the groundwater which will be used in the mobile on-site test unit. The data from June 1998 and 1997 are ranges measured in several different groundwater sampling wells (different depths).

APPENDIX B

SET UP OF THE ANAEROBIC EXPERIMENTS AND COMPOSITION OF THE GROUNDWATER

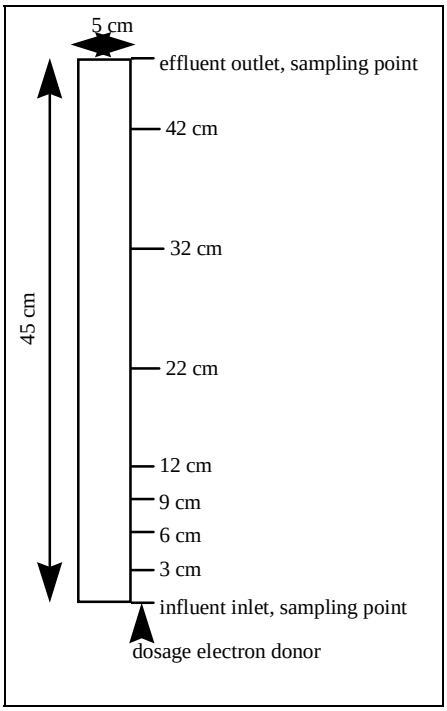
Set-up of the experiments

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 and transported to TNO in glass flasks (volume 2 l) which were air tight and completely filled. The composition of the groundwater was analysed after it was received in the lab. The analysis was carried out in 15 bottles, which were randomly picked from the stock supply of 150 bottles. The TCE concentrations were somewhat lower than the results reported earlier (table B1) [42]. The sediment was delivered in glass flasks and covered with groundwater.

Table B1. Concentrations of pollutants (mg l^{-1})in the groundwater used in the anaerobic column (DL = Detection Limit).

Component	Groundwater experiments Anaerobic column	Safbit 2/96 28 meters [42]
chlorobenzene (CB)	0.0002 ± 0.00001	0.16
benzene	0.014 ± 0.003	0.19
tetrachloroethene (PCE)	<DL	n.q.[1]
trichloroethene (TCE)	1.3 ± 0.4	8.64
cis-1,2-dichloroethene (cDCE)	2.8 ± 0.6	6.70
trans-1,2-dichloroethene (tDCE)	1.0 ± 0.2	3.62
vinylchloride (VC)	0.28 ± 0.03	n.q.
ethene	0.08 ± 0.04	
trichloroethane	0.033 ± 0.015	n.q.
chloroethane	<DL	
ethane	<DL	
toluene		0.01
methane	2.2 ± 0.2	
chloride	665 ± 55	1207
nitrite		<DL
nitrate	0.44 ± 0.28[3]	4.1
sulphate	706 ± 97	738
bromide	2.1 ± 0.3[2]	4.9
Na	473 ± 79	241
Al		0.28
B		0.20
Ba		0.07
Ca	476 ± 42	582
Fe		2.40
K	87 ± 28	45
Mg	82 ± 10	73
Mn		1.9
Ni		<DL
P		<DL
Zn		0.14
pH	6.7 ± 0.0	7.0
Redox	225 ± 4	

[1] Not Quantified.



[2] Mean value of two sample bottles.

The degradation of TCE in the groundwater is tested in duplicate in multiport columns, which are made of air-tight PVC. The columns have a volume of 880 ml (figure B1). 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 groundwater.

The column was filled with the sediment from the Bitterfeld location and TCE containing groundwater was infiltrated. In this way, the sediment was equilibrated. Originally, plans were to use compost extract together with lactate, because both are known to sustain reductive dechlorination [17, 43, 44]. However, since a constant quality of the extract could not be guaranteed, the choice was made to use the main (known) components of the compost extract, being the volatile fatty acids.

Fig. B1. Set-up of anaerobic column.

A mixture of lactate, acetate, propionate and butyrate (ratio 1:1:1:1 based on electron equivalents) was applied as the electron donor. Previous investigations and literature show that this mixture should be able to sustain dechlorination.

The mixture of electron donor is added to the columns in amounts larger than necessary for complete reduction of the oxidised compounds present in the groundwater (sulphate, chlorinated ethenes). As soon as dechlorination is observed the concentration of the electron donor will be decreased as far as possible to avoid problems due to clogging etc, and to minimise losses to non-dechlorination processes like sulphate reduction.

The influent of the columns consists of anaerobic groundwater amended with electron donor. The groundwater containment vessel is closed airtight and connected to a gas bag filled with N_2 to prevent the influx of oxygen (figure 12).
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.

This means that the dechlorination obtained in the laboratory will probably be faster than in the *in situ* reactors, since temperatures are lower in the shafts (14°C). The factor by which the rates can be increased depends upon the micro-organisms involved. The rates could be around 2 to 3 times higher at 20°C compared to rates at 14°C.

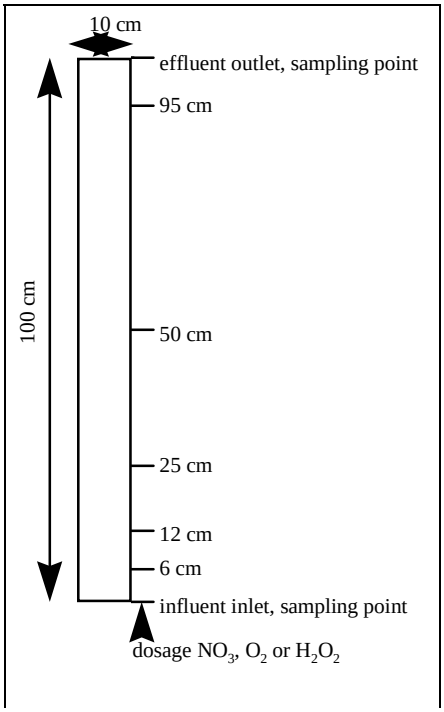
Firstly, the column was fed with groundwater during 4 retention times to establish a steady state situation. Thereafter, the electron donor was added to the influent groundwater. A mixture of lactate, acetate, propionate and butyrate is currently dosed at equal electron equivalent base, which

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). The influent and effluent of the columns is analysed twice a week until TCE was no longer detected in the effluent.

APPENDIX C

SET UP OF THE MICROAEROBIC REACTOR EXPERIMENTS AND COMPOSITION OF THE GROUNDWATER

Set-up of the experiments



The column is run with groundwater from the location. The composition of the groundwater used for the experiments is given in table C1. This column is operated by the people from UFZ.

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 (figures 13 and C1). 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 column is operated with an initial hydraulic retention time of 2 days (groundwater flow around 65-70 ml h^{-1}).

Fig. C1. Set-up of micro-aerobic column.

The column is run in the mobile on-site test unit. In this unit the temperature is controlled at 20°C. The influent and effluent of the column are analysed on a weekly basis with a more frequent analysis of vital parameters during the first three weeks.

Table C1. Concentrations of pollutants (mg l^{-1})in the groundwater used in the aerobic column in the mobile on-site test unit (Storage tank sampling date: 15-03-99; Mean of duplicate measurements) (DL = Detection Limit)

Component	Groundwater Aerobic Column
1,4-dichlorobenzene	0.23 ± 0.01
1,2-dichlorobenzene	0.045 ± 0.005
chlorobenzene (CB)	16.8 ± 0.32
benzene	0.09 ± 0.00
hexane	0.08 ± 0.00
bromobenzene	<DL
2-chloortolueen	0.03± 0.00
tetrachloroethene (PCE)	<DL
trichloroethene (TCE)	<DL
cis-1,2-dichloroethene (cDCE)	<DL
trans-1,2-dichloroethene (tDCE)	<DL
vinylchloride (VC)	0.01 ± 0.00
1,1,2,2-tetrachloroethane	0.03 ± 0.00
chloride	497
nitrite	<DL
nitrate	<DL
ammonium	5.23
sulphate	745
phosphate	9.1
Fe	<DL
Mn	0.122
Cu	<DL

APPENDIX D

ANALYSIS OF VOLATILE COMPOUNDS

Chlorinated ethenes, ethene and ethane

TCE, DCE, VC, ethene, ethane, and chlorobenzene were measured in the waterphase by injecting a 1 ml sample into a 7 ml MiliQ water containing 22 ml headspace vial. The vials are closed with 3 mm Teflon lined butyl rubber septa, and placed in a Tekmar 7000 headspace autosampler. The vials are heated for 1 h at 85 °C. Subsequently, 1 ml of the headspace is injected into a Varian Genesis 3800 GC equipped with a Pora Bond Q column (25 m x 0.32 mm x 5 µm) connected to a Flame Ionisation Detector (FID). The detector temperature was 300°C. The GC oven was heated with a temperature program: 3 minutes at 35°C, 10°C/minute to 250 °C, 5.5 minutes at 75°C. Helium is used as a carriergas (1.4 ml minute^{-1}). The retention times (in minutes) were 17.9 for TCE, 15.6 for cDCE, 14.6 for tDCE, 9.6 for VC, 3.5 for ethene, 3.0 for ethane and 21.6 for chlorobenzene. The concentrations were determined with an external standard using a 4 points calibration curve.

Chlorobenzene and benzene

Chlorobenzene and benzene were measured in the waterphase. The components are adsorbed a solid phase via Solid Phase Micro Extraction (SPME). The solid phase is heated and the components are separated on a StabilWax DB column (0.32 mm, length 30 m, thickness of the film 1 µm) in a Varian Star 3600 CX GC connected to a Photo Ionisation Detector (PID). The detector temperature was 200°C. The concentrations were determined with an external standard using a 4 points calibration curve.

APPENDIX E

TRANSFORMATION OF CHLORINATED ETHENES IN THE GROUNDWATER FROM BITTERFELD UNDER ANAEROBIC CONDITIONS-COMBINED RESULTS

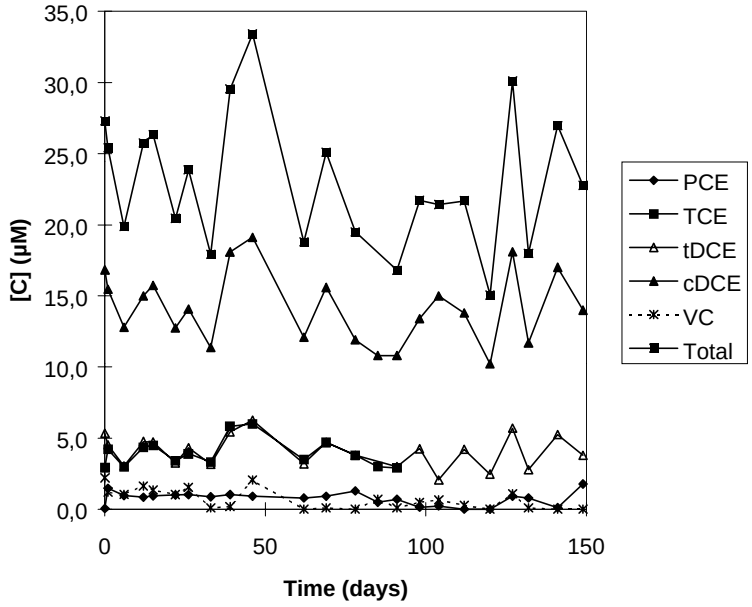


Fig. E1. Composition of the groundwater during the anaerobic experiments.

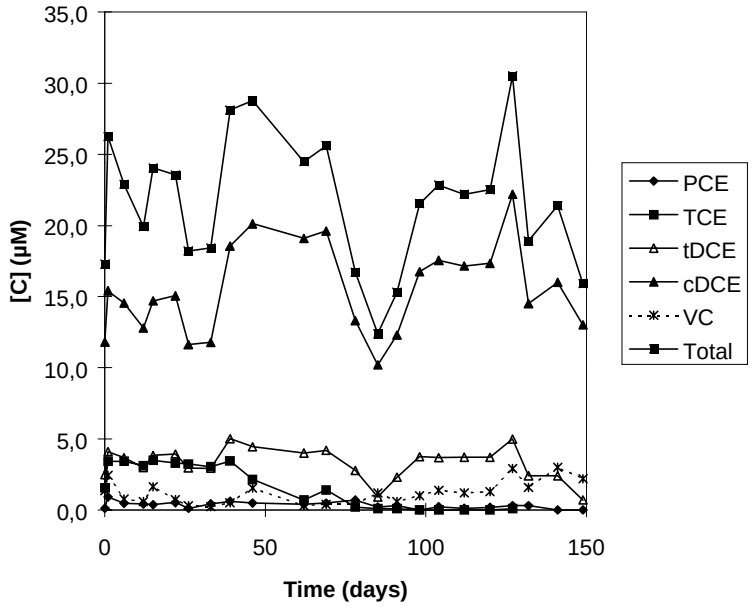


Fig. E2. Composition of the effluent column 1.

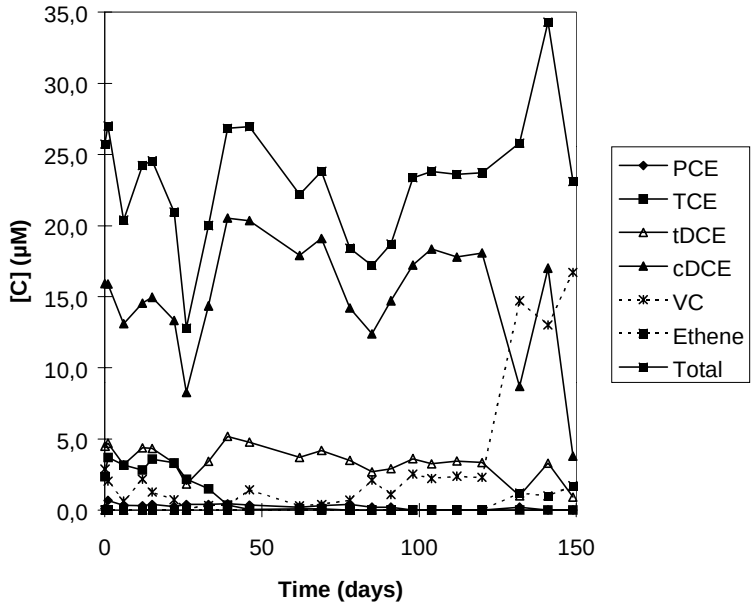


Fig. E3. Composition of the effluent column 2.

APPENDIX F

SET UP OF THE IN SITU REACTORS AND PRELIMINARY RESULTS

Anaerobic reactors

Since the Bitterfeld groundwater from the upper aquifer which is used in the *in situ* experiments does not contain any TCE or lower chlorinated ethenes, TCE is added to the groundwater. This TCE amended groundwater is then distributed to the reactors 1 and 2.

TCE is added as TCE saturated solution with tap water which is supplied to the groundwater. The tap water is saturated with TCE in a separate tank (volume 50 litres), which contains pure TCE at the bottom. This tank is flown through with tap water. The tap water is slowly stirred in the tank to optimise the contact between the water and the TCE, and maximise the amount of TCE dissolved. The retention time (around 8.3 days) of the tap water in the tank is long enough to ensure saturation of the water with TCE. Preliminary experiments have shown that in a similar system on lab scale a hydraulic retention time of 1 day is enough to reach saturation of the water. TCE will be added at a final concentration of around 10 mg l^{-1}.

The electron donor of the first test period consists of a mixture of lactate and volatile fatty acids (acetate, propionate, and butyrate) and is at first be added at two times the amount needed for complete removal of sulphate and chlorinated ethenes (2 * ED) based on the presence of 750 mg/l sulphate in the groundwater. The reactor is started up with this electron donor mixture. The search for cheaper and better electron donors (preventing sulphate reduction) will continue.

Nitrogen is added as NH_4Cl (50 mg NH_4 l^{-1} groundwater).

The reactors are run with a retention time of 2 days (per reactor).

Operational parameters for reactors 1and 3 are the following:

Initial flow of the groundwater:		575 l/day
Estimated TCE concentration in saturated water:		1000 mg/l
Desired TCE saturated water flow:		5.75 (or 6) l/day
Composition of electron donor-N-source (E-N) solution (200 times concentrated):		
	sodium lactate	74.8 g/l
	sodium acetate	82.4 g/l
	sodium propionate	54.8 g/l
	sodium butyrate	44.0 g/l
	NH_4Cl	29.6 g/l
Desired E-N solution flow:		2.9 l/day

Microaerobic reactors

At first, nitrate and a small amount of oxygen are dosed to the effluent of the anaerobic reactors. Possibly phosphate will be added in future to the reactor influent as well, however, whether this is necessary depends on the outcome of the experiments with the on-site reactor in the very near future. Oxygen may be added via saturation of a part of the influent with the modules which are present in the *in situ* shaft. The aim is an oxygen concentration of around 3 mg/l in the influent of the microaerobic reactor together with 2.4 mM of KNO_3, which is two times the amount needed (in theory) for complete removal of the chlorobenzene present in the groundwater (based on a concentration of 20 mg l^{-1}).

The total groundwater stream is led through the gas module and the oxygen concentration is fixed at 3 mg/l.

If high oxygen concentrations are needed H_2O_2 will be added to the groundwater instead.

Operational parameters for reactors 3 and 4:

Initial flow of the groundwater:	575 l/d
Composition of potassium nitrate solution (100 times concentrated):	20.2 g/l
Desired concentration of nitrate in the influent	2.4 mM
Desired nitrate solution flow:	5.75 (or 6) l/day

Preliminary results

During the equilibration period of the reactors, the groundwater and effluent of the reactors was regularly monitored (Table F.1). Some removal of 1,4-dichlrobenzene (14DCB), 1,2-dichlorobenzene (12DCB) and 2-chlorotoluene was shown. However, the results do not show any significant transformation of the target (compounds). Chlorobenzene is hardly degraded. The addition of TCE to the groundwater started in January, which explains the presence of this compound in the effluent of reactor 1 and 2.

The concentrations of the cations and H_2S in the groundwater remain stable during passage through the reactors. The conductivity also remains the same.

Table F1. Composition of the groundwater and the effluent of the 4 reactors during the equilibration period. During this period, reactor 1 and 2 were operated as one system as well as reactor 3 and 4.

		Groundwater		Reactor 1		Reactor 2		Reactor 3		Reactor 4	
		AVG[1]	STD[1]	AVG[1]	STD[1]	AVG[1]	STD[1]	AVG[1]	STD[1]	AVG[1]	STD[1]
pH[2]		**6.72**	0.08	**6.30**	1.72	**5.86**	1.19	**6.13**	1.34	**4.74**	1.50
14DCB	mg/l	**0.216**	0.043	**0.191**	0.033	**0.106**	0.031	**0.163**	0.038	**0.064**	0.037
12DCB	mg/l	**0.038**	0.043	**0.035**	0.007	**0.013**	0.15	**0.030**	0.014	**0.012**	0.011
CB[3]	mg/l	**4.980**	0.501	**5.154**	0.361	**4.295**	0.467	**4.979**	0.669	**3.552**	1.842
Benzene	mg/l	**0.003**	0.003	**0.004**	0.004	**0.003**	0.004	**0.004**	0.004	**0.005**	0.004
Cyclohexane	mg/l	**0**	0	**0**	0	**0**	0	**0**	0	**0**	0
Br-benzene	mg/l	**0**	0	**0**	0	**0**	0	**0**	0	**0**	0
2-Cl-toluene	mg/l	**0.146**	0.015	**0.137**	0.010	**0.073**	0.032	**0.118**	0.034	**0.046**	0.035
PCE	mg/l	**0.001**	0.004	**0.000**	0.001	**0.001**	0.002	**0.000**	0.001	**0.001**	0.002
TCE[4]	mg/l	**0**	0	**0.045**	0.085	**0.021**	0.040	**0**	0	**0**	0
cDCE	mg/l	**0**	0	**0**	0	**0**	0	**0**	0	**0**	0
tDCE	mg/l	**0**	0	**0**	0	**0**	0	**0**	0	**0**	0
VC	mg/l	**0**	0	**0**	0	**0**	0	**0**	0	**0**	0
1122TeCA	mg/l	**0.015**	0.042	**0.046**	0.058	**0**	0	**0.059**	0.057	**0.07**	0.029
Na	mg/l	**110.8**	6.8	**119.5**	3.4	**120.8**	5.7	**119.3**	3.2	**111.4**	12.8
Ca	mg/l	**296.9**	5.4	**305.9**	12.5	**314.5**	26.1	**284.5**	12.4	**304.7**	13.4
Mg	mg/l	**39.5**	1.7	**40.6**	1.6	**39.5**	0.3	**40.0**	1.1	**34.2**	1.6
K	mg/l	**91.6**	13.1	**95.3**	1.6	**95.9**	4.2	**97.7**	1.3	**95.5**	6.8
H_2S	mg/l	**1.37**	0.35	**0.18**	0.12	**0.19**	0.15	**0.28**	0.17	**0.10**	0.11
Conductivity	mS/cm	**2.35**	0.02	**2.24**	0.62	**2.38**	0.50	**2.21**	0.46	**2.42**	0.67

[1] AVG = Average; STD = Standard Deviation.

[2] Large standard deviation due to the increase of the pH in the reactors during the equilibration period.

[3] The chlorobenzene concentration is 4 to 5 times lower than the concentration in the groundwater fed to the on-site column systems.

[4] Large standard deviation due to the feeding of low concentrations of TCE to the groundwater during the last two weeks of January as part of the full operation of the *in situ* reactors.

APPENDIX G

BITTERFELD: BIOREMEDIATION OF REGIONAL CONTAMINATED AQUIFERS ADDITIONAL COLUMN EXPERIMENTS

Summary
This report describes additional research carried out within the framework of the project "Bitterfeld: Bioremediation of regional contaminated aquifers". In the project the combined biotransformation of chlorinated ethenes and chlorobenzene is carried out in a sequential anaerobic-microaerobic system. The additional experiments were performed to determine the effect of exposure of the aquifer material to air and subsequent oxidation and low pH values on the performance of the biological processes occurring in the sequential anaerobic-microaerobic system.

The sediment material which was initially oxidized and exposed to low pH was placed in upflow columns and allowed to be neutralised by feeding the columns with fresh groundwater prior to the experiments. The effects of low pH exposure are summarised in the table below. The results were compared to the results obtained in the column experiments with unaffected aquifer material [Chapter 4 of the final report]. Overall it can be stated that low pH exposure affects both the anaerobic and the microaerobic processes. The anaerobic dechlorination of the chloroethenes started up much slower. Possible reasons for this effect are higher a higher electron donor demand of the oxidised aquifer material or an effect on the anaerobic microbiology. The microaerobic processes on the other hand started up much faster. A possible explanation may be the increased oxidation level of the sediment.

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

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

Samenvatting
Dit rapport beschrijft aanvullend onderzoek dat is uitgevoerd in het kader van het project "Bitterfeld: Bioremediation of regional contaminated aquifers". In dat project wordt de gecombineerde biologische afbraak van chloorethenen en chloorbenzeen in een sequentieel anaëroob - microaeroob systeem onderzocht. Het aanvullend onderzoek is uitgevoerd om het effect vast te stellen van oxidatie van het bodemmateriaal en een lage pH op de biologische processen die optreden in het sequentiële anaërobe - microaërobe systeem.

Het bodemmateriaal dat aanvankelijk was blootgesteld aan lage pH-waarden werd geneutraliseerd door spoelen met grondwater voorafgaand aan de optimalisatie van de milieuomstandigheden (toevoegen van elektrondonor of elektronacceptor) ten behoeve van de afbraak. De effecten van de lage pH-waarden zijn weergegeven in onderstaande tabel. Algemeen kan worden gesteld dat blootstelling aan lage pH-waarden de stabiliteit van zowel het anaërobe als het microaërobe proces verlaagt. De anaerobe dechlorering van de chloorethenen begint veel langzamer dan die in de kolommen met bodemmateriaal dat niet was blootgesteld aan lage pH-waarden [Hoofdstuk 4 van het eindrapport]. Het microaërobe proces echter, start gemakkelijker op. Een mogelijke verklaring hiervoor kan de hogere oxidatiegraad van het materiaal zijn.

Effect van blootstelling aan lage pH-waarden op de biologische processen in de kolommen (vergeleken met kolommen met ongestoord sediment)

Onderzoeksdeel	Anaëroob proces	Microaëroob proces
Opstart	Langzamer	Sneller
Additieven	Meer elektronendonor nodig voor opstart	Proces kan wellicht worden opgestart met NO_3^- en kleine hoeveelheden zuurstof
Long term performance	• capaciteit reductieve dechlorering onzeker • sulfaatreductie langzamer • processtabiliteit onbekend • langere periode nodig om de hoeveelheid elektronendonor te verlagen	• capaciteit chloorbenzeenafbraak onzeker • processtabiliteit onbekend

1. Introduction

The research described in this report is additional to the NOBIS research project "Bitterfeld: Bioremediation of regional contaminated aquifers".
This NOBIS project is part of the SAFIRA project, in which several technologies are being tested for their applicability to remediate contaminated groundwater at a regional scale. The remediation concepts are tested in two phases. During the first phase on site and laboratory scale reactor experiments have been carried out, while during the second phase the different remediation concepts will be tested in in-situ reactors.
The concept of the NOBIS project is the application of a NA^+ (Natural Attenuation plus) concept, which deals with the contaminants (chloroethenes and chlorobenzene) in a sequential anaerobic-aerobic reactor system. To ensure that the reactor system will resemble the situation in situ as much as possible, aquifer material was chosen as a carrier material in the reactors. In this way, the results from the on site and in situ reactor experiments can be compared and the results can be extrapolated to the contaminated aquifers. The various reactors were placed in shafts. The NOBIS project has one shaft with four reactors at its disposal.

Results of the column and laboratory experiments that were originally proposed for the Bitterfeld project are presented in "Bitterfeld : Bioremediation of regional contaminated aquifers - Deliverable no. 2"[3] [Chapter 4 of the final report]. The in situ reactors were filled with aquifer material in July 1999. The aquifer material, which was removed from the site during the building of the shafts, was stored in containers, soaked in groundwater and covered with liners and soil, until packing of the material in the in situ reactors. The demand for aquifer material was higher than originally expected. Therefore, aquifer material from another place on the site was taken for further use in the in-situ reactors. This material had been stored in open heaps. Possibly due to oxidation of the aquifer material prior to the filling of some of the reactors, very low pH values (pH 2-3) have been measured during the first period of flushing with groundwater. The low pH is presumably caused by a series of chemical reactions in which pyrite reacts with oxygen:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3(s) + 8SO_4^{2-} + 16H^+.$$

Since then the pH in the reactors has increased, but this occurred rather slowly. Original background pH conditions have been achieved finally (in at least three of the four reactors). However, the chemical and microbial condition of the aquifer material will be changed, due to the reactions that have occurred in the material. The effect of oxidation of the solids and acid circumstances on the microbiology on the performance of contaminant degradation processes is unknown. The microbial population in the aquifer material may have changed or died off partially or completely. Also, the chemical composition of the aquifer material will have changed drastically due to the low pH values. E.g., metal ions will be leached from the sediment. Therefore, the oxidation and low pH exposure may result in an extended lag phase before anaerobic transformation of the chlorinated compounds commences. Also, other products may be formed or the product formation rate may be lower compared to the experiments carried out in phase I of the main project. On the long term, the microbial processes could also remain unaffected, in which case, the results of the in situ experiments may be translated to large scale situation without restraints.
For this reason, additional column experiments were carried out to determine possible effects of oxidation/low pH on the biodegradation processes.

[3] Eekert, M. H. A. van, J. J. M. Staps, W. N. M. van Heiningen, and H. H. M. Rijnaarts. 1999. Bitterfeld: Bioremediation of regional contaminated aquifers.
Deliverable no.2 TNO-MEP - R99/. TNO-MEP.

In this report the results of these column investigations are discussed and put into perspective with respect to the on site and laboratory tests.
The results obtained in this research lead to insight in the effect of low pH values on the processes planned for the main project. Based on the results, it will be determined whether the material that is present in the reactors is sufficiently representative for the in-situ aquifer material. Thus, it can be determined whether or not the present reactor material is suitable for the research that is planned within the framework of the main project. In general, the results will give insight into the effects of oxidation/acidification due to contact with oxygen on microbial and other processes. Oxygen supply is used in various SAFIRA treatment zone technologies. Therefore, the results from the experiments described here are relevant to all SAFIRA research groups.

The additional column experiments are financially supported by NOBIS, UFZ, and TNO.

2. Set-up of the experiments

2.1 Introduction

The total set-up of the system consists of two columns that are run under anaerobic conditions to investigate the transformation of the chlorinated ethenes and two columns, which are run under microaerobic conditions to study the degradation of chlorobenzene. Groundwater containing chlorinated ethenes or chlorobenzene was sampled from different wells in Bitterfeld, namely Safbit 16-97 and Safbit 30-98, respectively. The composition of the groundwaters is similar to the groundwaters used in the on site and laboratory column tests in Bitterfeld and Apeldoorn. The groundwater was sampled with a procedure to prevent contact with oxygen and transported to TNO in glass flasks (volume 2 l) which were air tight and completely filled. The groundwater was stored at 4°C until further use. The composition of the groundwater was analysed after it was received in the lab (table 2.1).

Table 2.1. Chlorinated hydrocarbon composition of the groundwater (mg/l) used in the experiments.

Component	Safbit 16-97 Anaerobic column	Safbit 30-98 Microaerobic column
Trichloroethene	5.3	<DL[1]
cis-1,2-dichloroethene	7.1	<DL
trans-1,2-dichloroethene	1.8	<DL
Chlorobenzene	0.7	4.6

[1] DL=Detection Limit.

Sediment from heaps of aquifer material still present at the Bitterfeld site was used for both the anaerobic and the microaerobic column. This sediment was exposed to the same conditions as the sediment used in the in situ reactors no. 2 and 4 and therefore was thought to be a suitable material for the experiments. The pH of the aquifer material in the reactors 1 and 3 is reasonably high, while the pH of the reactors 2 and especially nr. 4 remained lower for longer periods[4] [Chapter 5 of the final report].

2.2 Set-up of the experiments

The experiments are carried out in column systems with the same dimensions and general set-up as the anaerobic column used for the laboratory experiments [Chapter 4 of the final report] (figure 2.1). The columns were packed with sediment from the upper aquifer at Bitterfeld, which is primarily contaminated with chlorobenzene. This sediment was also used for the experiments with the undisturbed laboratory column systems. The sediment was continuously saturated with groundwater to assert the degassing of the soil and uniform packaging of the column. The up-flow columns were fed with groundwater with a hydraulic retention time of 2 days. The groundwater used was taken from two sampling wells. The anaerobic columns were fed with groundwater from sampling well 16-97, and the microaerobic columns were fed with groundwater from well 30-98.

After approximately four weeks the groundwater of the anaerobic reactors was amended with a mixture of lactate and fatty acids. The composition of this electron donor solution was described earlier [Chapter 4 of the final report]. At the same time nitrate (two times the amount needed for complete chlorobenzene removal as described in Deliverable 2) was added to the groundwater and fed to the micro-aerobic reactor.

[4] Eekert, M. H. A. van, J. J. M. Staps, W. N. M. van Heiningen, and H. H. M. Rijnaarts. 1999. Bitterfeld: Bioremediation of regional contaminated aquifers Deliverable no.3 TNO-MEP - R99/. TNO-MEP.

The columns are 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.

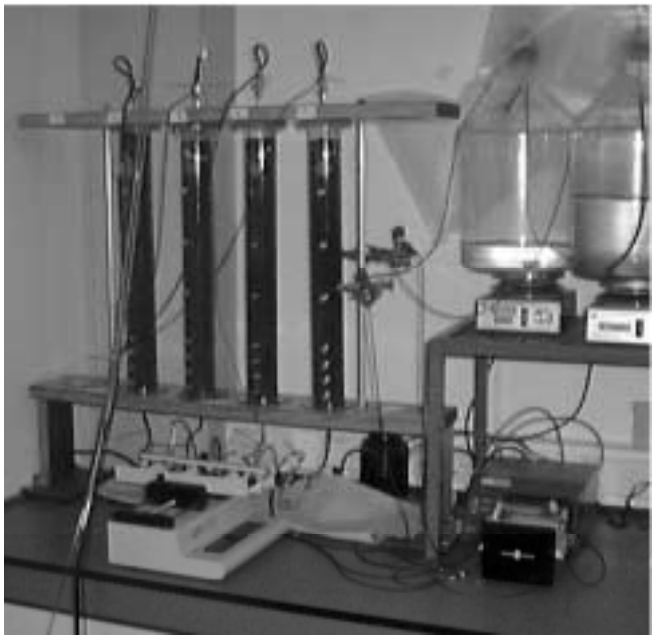


Fig. 2.1 Set-up of anaerobic and microaerobic columns.

The column systems were operated under similar conditions as the "undisturbed" columns according to the schedule described in table 2.2. The microaerobic reactors were initially run under denitrifying conditions. In the case that transformation of the chlorobenzene would not take place within 30 days, small amounts of oxygen would be added to the groundwater (most likely in the form of H_2O_2) (table 2.2).

Table 2.2 Operating conditions of the two anaerobic columns.

Phase	Days	Anaerobic Columns 1	Microaerobic Columns
0	0-28	Groundwater	Groundwater
I	29-56	1 * ED	NO_3^-
II	57-96	2 * ED	NO_3^- + trace oxygen
III	97-113	2 * ED + 50 mg/l NH_4^+	NO_3^- + trace oxygen

The influent and the effluent of the column systems were analysed regularly to measure the pH, the concentration of the chlorinated contaminants, and the concentration of sulphate (in the anaerobic columns) and nitrate (in the microaerobic columns). The columns were run for a period of about 12 weeks.

3. Results and discussion

3.1 pH of the column systems

During the 28 days the columns were washed with groundwater. Two columns were washed with groundwater from well 30-98, which is primarily contaminated with chlorobenzene. The other two columns were washed with groundwater from sampling well 16-97 that mainly contains chloroethenes. The pH of the effluent of the reactors was low as was expected from the measurements on the in situ reactors [Chapter 5 of the final report] (figure 3.1). The pH slowly increased during the first 28 days of operation (14 bedvolumes). After the start of the addition of electron donor or nitrate at day 28, the pH increased further and faster (figure 3.1). This however was not linked to the dosage of the supplements. The pH pattern in the in situ reactors showed the same course with and without any addition (figure 3.2).

The time scale needed for the restoration of the pH is comparable in both column and reactor systems (40 to 60 days, which is 15 to 30 bedvolumes). The column systems were operated separately, whereas the in situ reactors were run in two parallel two reactor streets. Especially, the second reactors in each connected reactor pair regenerate slower. This is probably due to the lack of fresh groundwater flowing through the reactors 2 and 4. Clearly, separately run column systems show a faster recovery of pH independent of the groundwater used for washing. Whether the prolonged low pH in e.g., reactor 4 has a more damaging effect compared to the performance of reactor 3 or reactor 2 can only be found out during the in situ test runs. Results from the in situ reactors were not available, at the time this report was written.

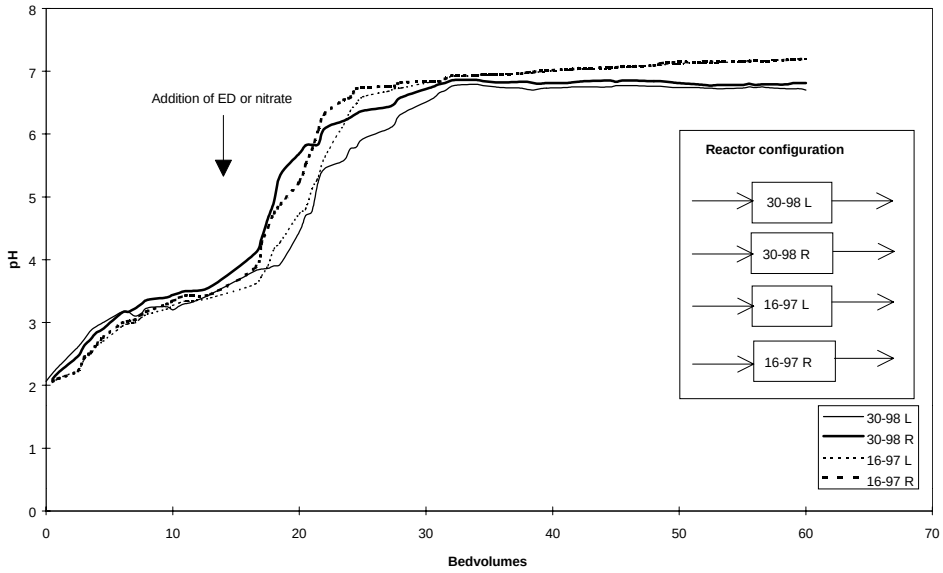


Fig. 3.1 pH in time of the effluent of the anaerobic (16-97 L and 16-97 R) and the microaerobic reactors (30-98 L and 30-98 R) as a function of the bedvolumes passed through the reactors.

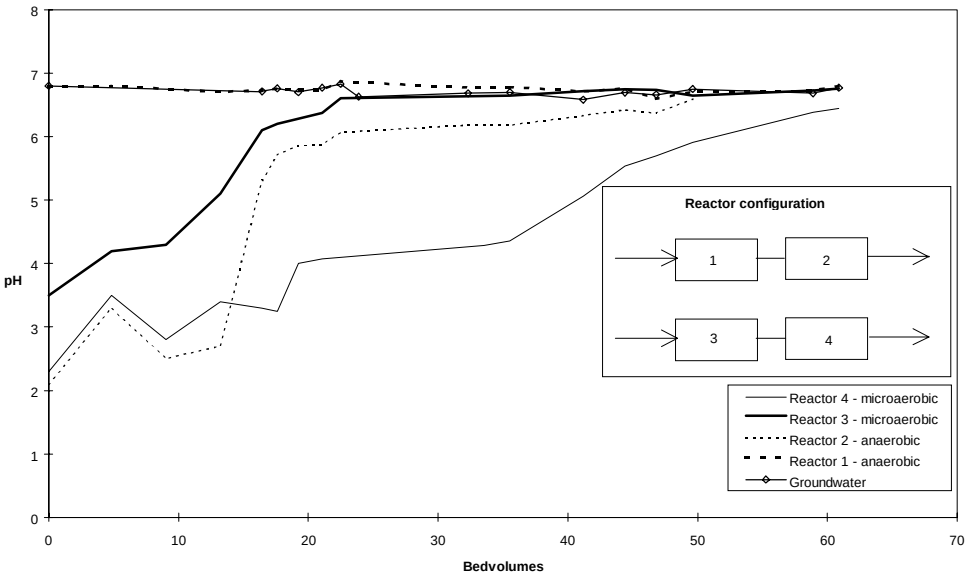


Fig. 3.2 pH in the in situ reactors during the equilibration period as a function of bedvolumes passes through the reactor.

3.2 Anaerobic columns

Under anaerobic conditions the transformation of the chlorinated ethenes in the groundwater of Bitterfeld should take place. The presence of high concentrations of sulphate gives rise to difficulties in carrying out this process, due to the high demand for electron donor. The transformation of chlorinated compounds was investigated according to the schedule presented in table 2.2. In the experiments with the undisturbed sediment material it was found that sulphate reduction was the first process to occur in the columns, followed, after short periods of time, by TCE dechlorination. Complete dechlorination was achieved after increasing the electron donor concentration and the addition of nitrogen to the groundwater.

Sulphate reduction

The sulphate reduction in the sediment, which had been exposed to low pH, started at a relative late stage compared to the undisturbed columns. Whereas sulphate already was reduced in phase I of the start-up in the undisturbed columns (figure 3.4), the low pH columns showed start up of sulphate reduction in phase II (that is after the electron donor concentration was increased to 2*ED) (figure 3.3). The undisturbed columns reached 60 to 90% sulphate reduction after the addition of a nitrogen source. Only 50% of the sulphate present was reduced in the columns with initial low pH. The amount of sulphate reduced may however, increase during this phase.

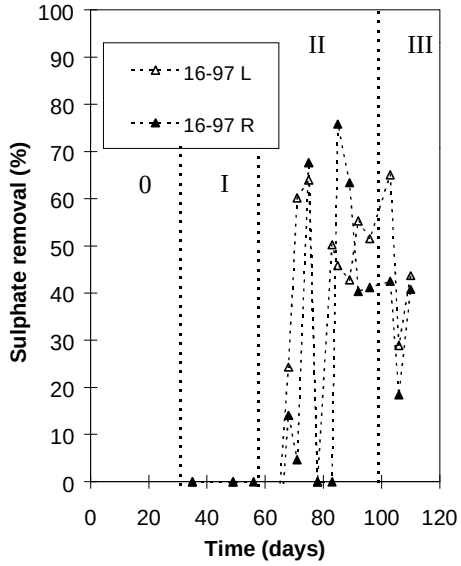


Fig. 3.3 Sulphate reduction in the anaerobic columns with initial low pH.

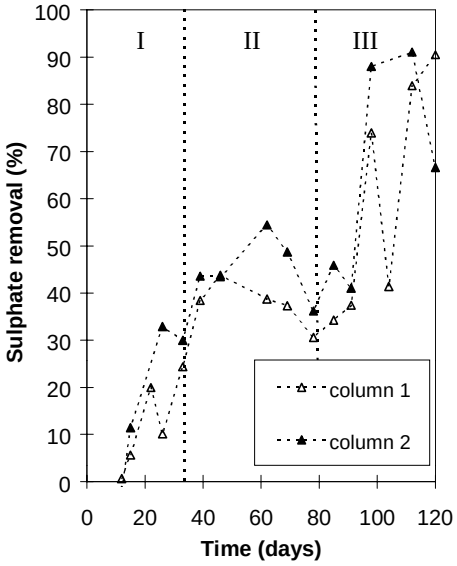


Fig. 3.4 Sulphate reduction in the undisturbed anaerobic columns.

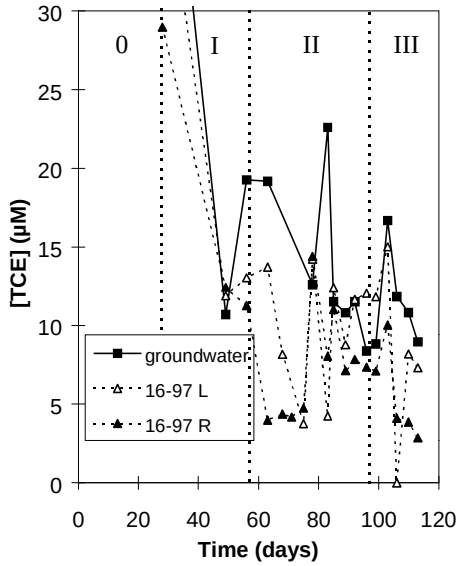


Fig. 3.5 Transformation of TCE in the anaerobic columns with initial low pH.

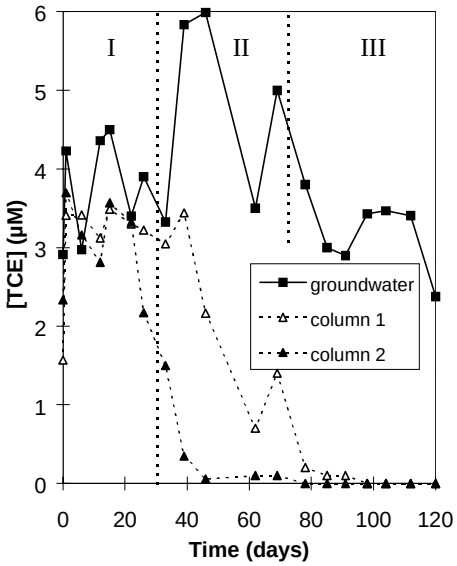


Fig. 3.6 Transformation of TCE in the undisturbed anaerobic columns.

Chlorinated ethenes

The TCE and cDCE concentration in the groundwater used for running the undisturbed columns was somewhat lower than the TCE concentration in the groundwater used for the pH experiments. This however, will not have affected the results, because the concentrations of chlorinated ethenes are far below the maximum solubility and are not expected to be toxic.

In the undisturbed columns TCE was removed slightly during phase I (1*ED addition), and the TCE concentration in the effluent of the column systems further decreased during phase II (figure 3.6). TCE was converted to cDCE by the undisturbed sediment. In the columns which were exposed to low pH, TCE dechlorination started at the end of the experimental period in phase III (figure 3.5). The results however, are not clear. Also, like with the sulphate reduction, the reduction process seems to have been destabilised. Effluent concentrations fluctuate drastically, which is in contrast with the results obtained with the undisturbed column systems.

cDCE, tDCE and VC are hardly formed or transformed during phase III of the experimental period (table 3.1). After 120 days of column operation TCE dechlorination to cDCE already occurred in the undisturbed columns. During phase III lower chlorinated ethenes like vinylchloride were found in the effluent of these column systems. VC was not formed in substantial amounts in the columns initially exposed to low pH (figure 3.7). A minor increase in cDCE concentration was observed in the effluent of the "low pH" columns.

From the results obtained during the first 120 days of operation it is clear that exposure to low pH before start up of the column systems resulted in a delay in the TCE dechlorination. The start-up of sulphate reduction was also delayed. The effect of the initial low pH exposure on the anaerobic microbiological processes on the long term is not clear.

Table 3.1 Concentrations of the chlorinated ethenes given as percentages of the total amount of chlorinated ethenes present.

Phase I	PCE	TCE	cDCE	tDCE	VC
Groundwater	0.0±0.0	19.6±1.7	65.9±3.2	14.0±1.2	0.6±0.6
16-97 L	0.1±0.1	18.7±3.1	69.2±3.0	11.6±4.2	0.4±0.6
16-97 R	0.0±0.0	18.3±2.9	67.4±2.7	13.7±1.2	0.5±0.8

Phase II - 2*ED	PCE	TCE	cDCE	tDCE	VC
Groundwater	0.1±0.1	14.3±8.8	70.7±7.3	14.5±4.7	0.6±0.9
16-97 L	0.1±0.2	15.8±7.2	68.8±11.6	13.9±4.4	1.4±1.3
16-97 R	0.0±0.0	16.3±3.8	68.3±4.6	13.8±1.6	1.6±1.7

Phase III - 2* ED + NH_4	PCE	TCE	cDCE	tDCE	VC
Groundwater	0.3±0.2	18.6±2.2	72.9±4.7	8.2±6.7	0.1±0.2
16-97 L	0.1±0.1	13.7±2.9	75.7±6.9	9.9±6.4	0.8±0.5
16-97 R	0.1±0.1	9.3±3.9	78.9±8.3	10.2±5.5	0.7±0.4

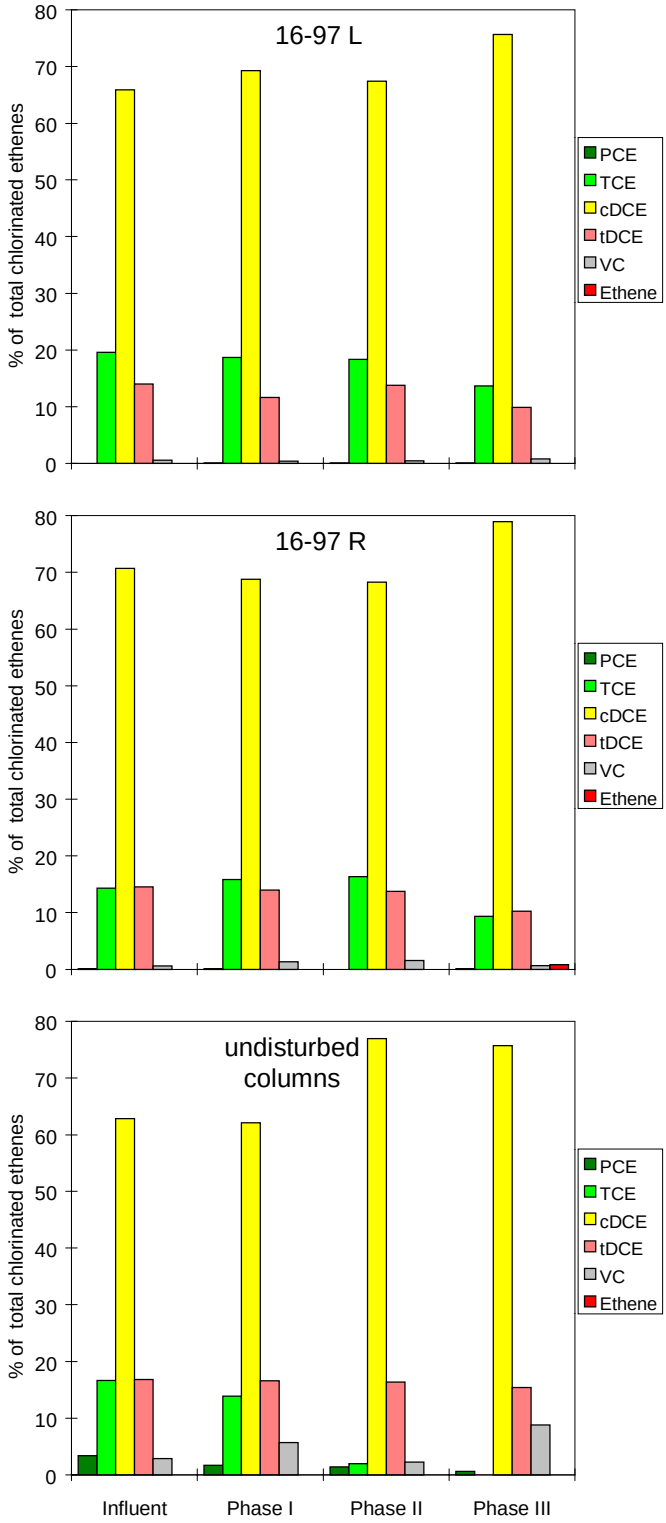


Fig. 3.7 The effect of increased electron donor concentration and the addition of nitrogen on the transformation of TCE in the Bitterfeld groundwater in the columns which were initially at low pH (16-97 L and 16-97 R) and the undisturbed anaerobic columns.

3.3 Microaerobic columns

The transformation of chlorobenzene during start-up of the microaerobic column was investigated with two column systems operated according to the scheme presented in table 2.2. The mean chlorobenzene concentration found in the groundwater during the experiments was 5896 ± 1624 µg/l. Originally, it was planned that phase III would consist of an operational period under complete aerobic conditions. In that case H_2O_2 would be dosed at a concentration which would be sufficient to oxidise the complete amount of chlorobenzene present. However, since the experiments with the undisturbed column showed, that it is relatively easy to obtain removal of chlorobenzene under aerobic conditions, this phase was not executed in the pH experiment.

The results obtained in with the columns initially exposed to low pH are not unequivocal. Chlorobenzene was not removed in the column containing undisturbed sediment material (figure 3.8, lower graph).

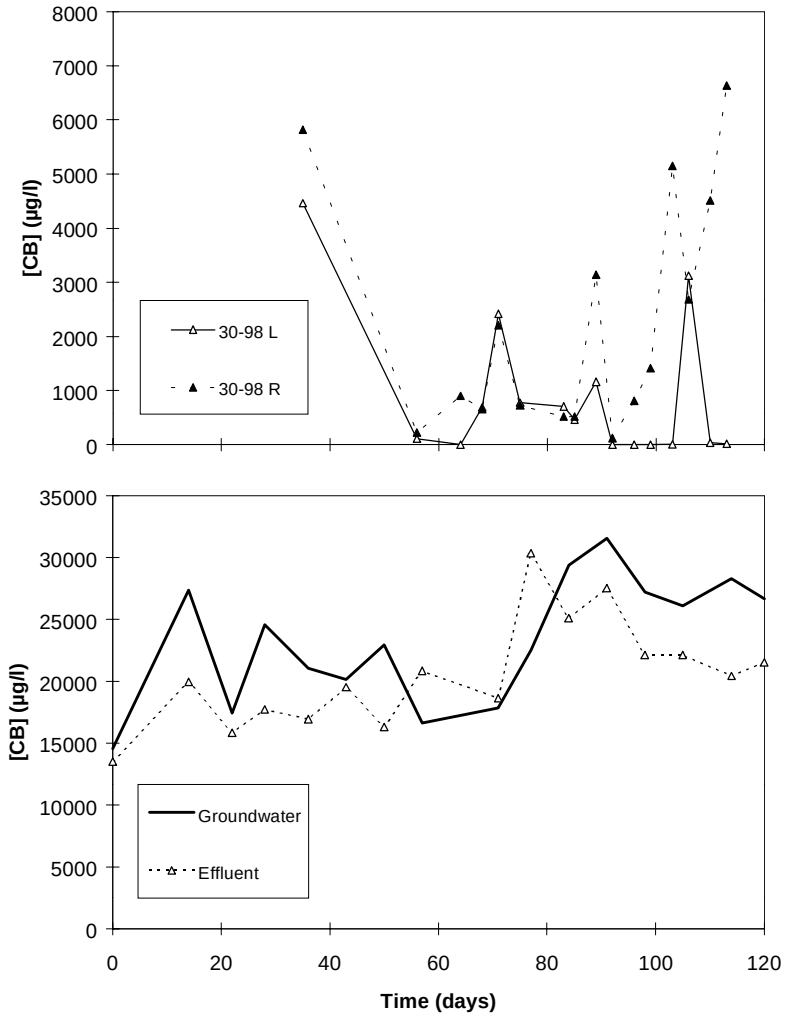


Fig. 3.8 Chlorobenzene removal in the column initially exposed to low pH (upper graph) and the undisturbed column system (lower graph).

During phase I both columns with the disturbed material already show a removal of chlorobenzene (Figure 3.8, upper graph). This was not observed in the column with undisturbed material (figure 3.8, lower graph), and also in contrast with the believe that complete chlorobenzene transformation under denitrifying conditions is not possible. After the addition of 3 mg/l oxygen chlorobenzene removal was almost complete in both columns (phase II, figure 3.8, upper graph).

In phase III (no changes in experimental set-up) the chlorobenzene removal in column 30-98 L continued to be nearly complete, whereas chlorobenzene removal in the other (30-98 R) column slowly deteriorated. A clear indication of the cause of this discrepancy was not found. Operational conditions of both columns are the same. One reason may be the initial pH drop in the sediment, which may have been inhomogeneous thus leading to different results in both columns. However, if this were the case, these major changes would have resulted in differences much earlier in the experiment. Other unknown effects can not be excluded.

Around 30 to 50% of the nitrate was converted in the columns with the undisturbed sediment material. In contrast with the columns with disturbed sediment material between 50 and 100% of the nitrate was converted.

3.4 Reduction-oxidation capacity of the sediment material

On forehand it was not clear what the effect of the low pH exposure and subsequent oxidation of the sediment material would be. Unlike the experiments with the undisturbed sediment, chlorobenzene was removed very early after start-up of the experiment while only minor amounts of oxygen were supplied to the groundwater. Comparable results by another group participating within SAFIRA, where chlorobenzene degradation was reported immediately after start-up of the experiments. Without addition of oxygen, this degradation gradually declined and eventually ceased [Chapter 6 of the final report, Shaft 5]. This may explain the rapid transformation of chlorobenzene after a suitable pH was reached and the addition of an electron acceptor (nitrate) was started. As a result of the chemical oxidation of the sediment material on forehand, there was no need for oxidating equivalents to change the environmental conditions of the sediment. All the oxidizing equivalents could immediately be used for chlorobenzene oxidation.

In contrast with this, the dechlorination of the chlorinated ethenes and the reduction of sulphate occurred relatively late in the oxidised and pH disturbed column systems. This may be explained by the fact that a large amount of the electron donor is required for the reduction of the oxidised sediment material. Therefore, more time is needed to establish favourable conditions for the reduction processes in the column systems. The oxidation/low pH may thus have influenced the processes in a negative way, especially during the initial phase of operation of about 100 days. Long term effects could not be demonstrated yet.

4. Implications for the in situ reactors

The experiments with the column systems exposed to low pH have shown that the effects of oxidation/low pH exposure of sediment components on the biological processes are diverse. The initial stability and efficiency of the anaerobic processes decrease, whereas a positive effect on chlorobenzene transformation was found. The effects on the anaerobic and microaerobic processes are summarised in table 4.1.

The development of the pH, however, shows a similar pattern in the in situ reactor compared to the column systems. Most likely the biological processes in the in situ reactors will show a performance comparable to the column systems, thus initial disturbance of the anaerobic processes and possible enhancement of the microaerobic processes.

For the anaerobic reactors this means higher initial costs for electron donor addition and longer start-up periods followed by a long period during which the electron donor concentration can be reduced. The role of sulphate reduction in the whole process remains unclear. The long term stability of both the anaerobic and the microaerobic processes is unknown. Especially for the large in situ reactors, the long term effects are important. A continuation of the runs with the oxidation/low pH column systems should provide more information concerning these matters.

Table 4.1 Effect of low pH exposure on the performance of the biological processes in the column systems.

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

5. Conclusions and recommendations

- Based on a comparison of the results of both the anaerobic and microaerobic columns with both the original columns and reactors, it can be concluded that the aquifer material that was investigated, had a relatively high status of oxidation and a low pH.
- Therefore, it can be assumed that there is a direct relation between the way of storing the material and the oxidation level and thus the chemical and biological behaviour in the columns and that heterogeneities of for example the pyrite content do not play a substantial role.
- The most important effects of the oxidation/low pH values are:
    - the chemical situation has been changed;
    - the start-up period of the reductive dechlorination process is longer (a delay of about 100 days);
    - more electron donor is necessary for the initial anaerobic phase (which can have substantial cost consequences);
    - less oxygen necessary is necessary for the initial microaerobic phase;
    - the initial stability of the processes has been decreased;
    - long term effects on especially the anaerobic processes are unknown. A continuation of the experiments is required.
- To date, it is not possible to confirm these results with in-situ results.

APPENDIX H

ABBREVIATIONS USED

AOX	adsorbing organic halogens
CB	chlorobenzene
cDCE	cis-1,2-dichloroethene
DDT	dichlorodiphenyltrichloroethane
HCH	hexachlorocyclohexane
NA	natural attenuation
PCB	poly chlorinated biphenyl
PCE	tetrachloroethene
SAFIRA	Sanierungs Forschung in kontaminierten Aquiferen
TCE	trichloroethene
tDCE	trans-1,2-dichloroethene
TOC	total organic carbon
UFZ	Umwelt Forschungs Zentrum
VC	vinylchloride