In situ groundwater remediation research in the Bitterfeld region in eastern Germany (SAFIRA)

HOLGER WEISS, BIRGIT DAUS, PETER FRITZ, FRANK-DIETER KOPINKE, PETER POPP & LOTHAR WÜNSCHE
UFZrCentre for Environmental Research Leipzig-Halle, Permoserstraße 15, D-04318 Leipzig, Germany

Abstract The SAFIRA project has been set up to examine and further develop in situ groundwater decontamination techniques. The Bitterfeld region was selected as the model location for investigations into developing in situ technologies for the remediation of complex contaminated groundwater. The principal site-specific investigations have been completed and the main contaminants characterized. The location was found to be suitable for a pilot plant and the fundamental mechanisms for removing the “pollutant cocktail” are now known; degradation experiments have been scaled up. The methods tested successfully in the laboratory and in the mobile decontamination unit to prove their chemical and hydrological long-term stability will be competitively optimised in a pilot plant under real-world conditions.

INTRODUCTION

The industrial region of Leipzig-Halle-Bitterfeld in eastern Germany is characterized by the overlapping environmental impacts of the chemical industry and extensive landscape devastation and groundwater drawdown as a consequence of lignite mining. Among the different tasks of landscape reclamation the management of hazardous waste deposits and groundwater contamination are the most urgent in this region.

Underground and open-cast mining since 1830 and the concentration of chemical industry sites led to an extensive groundwater drawdown and a change in groundwater dynamics. The affected area exceeds 1100 km²; the groundwater deficit is $5.6 \times 10^9$ m³. Most of the industrial waste deposits are in contact with the groundwater. As a consequence of the present hydrogeological situation and the low flow velocities ($< 50$ m year$^{-1}$) the landfills are currently showing stagnating emissions which could and would be activated through changing groundwater regimes.

Today, an area of about 235 km² in the Bitterfeld region is degraded, 50% due to open-cast mines, 4% due to abandoned industrial sites, 1% is taken up by waste sites and about 15% of the area shows significant groundwater contamination covering an area of about 25 km² containing a volume of about $200 \times 10^6$ m³ (Peter et al., 1995).

The restoration of pre-mining groundwater conditions is the major task in redevelopment of post-mining landscapes. This will have considerable consequences for the assessment of the polluted areas and landfills. Northwest of Bitterfeld, several former open cast lignite mines have been used as landfills for chemical wastes. Due
to the fact that the deposits are not sealed, effluents have direct contact with the local groundwater.

The "Antonie" landfill, for example, contains $5-6 \times 10^6$ m$^3$ of various industrial residues, including waste material from pesticide production (Walkow, 1996). The groundwater under the site is seriously polluted by hexachlorocyclohexane (HCH) isomers. Downgradient, however, the pollution is characterized by the more mobile contaminants like chlorinated aliphatic and aromatic hydrocarbons. The concentrations reach several hundred milligrams per litre, exceeding the effluent standards by several orders of magnitude. Conventional pump-and-treat technologies are not economically feasible due to the continuous output from the landfills of about $4 \times 10^6$ m$^3$ per year. At present, the groundwaters are discharging into the "Goitsche" open cast mine. However, this excavation will be flooded and from there water will infiltrate the entire flood-plain area, including parts of the urban centre of Bitterfeld. The ecological and social/economic consequences of the changing groundwater regimes have not yet been fully assessed. However, it will be necessary to look at novel remediation technologies.

The SAFIRA ("SAnierungs-Forschung In Regional kontaminierten Aquiferen"—Remediation research in regionally contaminated aquifers) project has been set up to develop in situ remediation technologies for complex contaminated groundwaters at a model site. To create the necessary basis for this model project, a preliminary study was carried out by the UFZ in cooperation with the Universities of Dresden, Halle, Leipzig, Stuttgart and Tübingen. During the course of this preliminary study, the hydrogeological and hydrogeochemical conditions at a selected field site were investigated and various technologies for the design of the in situ pilot plant were examined and tested. The goal is to construct a pilot plant ("reactive barrier") inside the aquifer for competitive testing and optimisation of several physico-chemical and microbiological techniques. The results of the feasibility study for the experimental site are presented in Weiss et al. (1998).
Table 1 Concentrations of contaminants in the groundwater at the test site (July 1997).

<table>
<thead>
<tr>
<th>Concentrations (mg l(^{-1}))</th>
<th>Quaternary aquifer</th>
<th>Tertiary aquifer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorobenzene</td>
<td>8-51</td>
<td>0.1</td>
</tr>
<tr>
<td>Dichlorobenzene</td>
<td>0.7-1.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>1,2-Dichloroethene</td>
<td>0.01-0.04</td>
<td>4.6</td>
</tr>
<tr>
<td>c,1,2-Dichloroethene</td>
<td>0.03-0.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>0.05-0.2</td>
<td>10.0</td>
</tr>
<tr>
<td>Sulphate</td>
<td>550-1000</td>
<td>740</td>
</tr>
<tr>
<td>Chloride</td>
<td>100-400</td>
<td>1250</td>
</tr>
</tbody>
</table>

GEOLOGY OF THE PILOT PLANT LOCATION

The contaminated area is situated in the flood plain of the Mulde River and can be described by the following generalized geological model: (a) Quaternary sands and gravels, (b) Upper Oligocene lignite, (c) Upper Oligocene micaceous sands, and (d) Middle Oligocene clays. The latter unit is a regionally distributed aquitard and corresponds to the base of the groundwater pollution. The sandy and gravelly units represent the aquifers, separated by the lignite seam which acts as a local aquitard. The Quaternary unit can be divided into a lower part, represented by lower terrace sediments of the Weichselian Mulde, and overlying sediments, built up by alluvial fan/braided river deposits of a smaller tributary stream. Both are separated by a hydraulically effective clay layer. Figure 1 shows a geological section of the area under investigation.

POLLUTION

Groundwater

Contamination of the groundwater by inorganic pollutants (e.g. heavy metals, arsenic etc.) has proved to be minor at the experimental site; the only noteworthy aspects are the high concentrations of sulphate and chloride (Table 1).

To characterize the organic pollution of the groundwater, several samples from different levels were examined. The "main components" of the organic contamination were found to be chlorobenzene, 1,2-dichlorobenzene, 1,4-dichlorobenzene, benzene, trichloroethene, cis-1,2-dichloroethene and trans-1,2-dichloroethene. Mass spectrometry screening detected other substances but in very low concentrations.

Although high organic pollution with halogenized hydrocarbons was confirmed in both the upper and lower aquifers, contamination varied considerably between the two in both quality and quantity (Table 1). The lower aquifer is dominated by aliphatic chlorinated hydrocarbons (trans-1,2-DCE, cis-1,2-DCE and TCE), whereas the main component of the upper aquifer is chlorobenzene. During depth-oriented sampling of the upper aquifer, a significant stratification of contamination was encountered: samples from a depth of 7-8 m contain only very low amounts of
pollutants, samples from depths between 16 and 20 m contain high levels of chlorobenzene (8–51 mg l\(^{-1}\)), as well as substantial concentrations of dichlorobenzenes (up to 1 mg l\(^{-1}\)).

**Solid samples from the cores**

In addition to the water samples, core material was also examined. The core samples from one borehole were subjected to headspace-screening over the entire profile between 0 and 48.5 m. The relative sensitivities, which are proportional to the concentration of the substances in the sample show clearly the influence of the lignite seam on the contaminant distribution.

One striking aspect is that the aliphatic halogen hydrocarbons and benzene chiefly occur in the strata between 19.5 and 24.5 m, whereas chlorobenzene and the dichlorobenzenes are found in higher concentrations in the strata, between 12 and 22.7 m. The main components are trans-1,2-dichloroethene, cis-1,2-dichloroethene, chlorobenzene, trichloroethene and benzene. Bromobenzenes and perchloroethene were also identified by mass spectrometry.

**DEGRADATION TECHNIQUES**

**Bioremediation**

The basic requirements for deciding whether microbiological in situ remediation techniques can be used are first of all the determination of microbial density and the pollutant degradation capacity of the autochthonous microbial biocoenoses under in situ conditions. Thereafter, ways of boosting the degradation capacities of the autochthonous microbial biocoenoses have to be investigated in order to develop technically and financially feasible measures for in situ remediation procedures.

The groundwater and aquifers are inhabited by bacteria down to the maximum drilling depth (50.5 m below the surface). Nitrate-, iron- and manganese-reducing bacteria predominate in the autochthonous biocoenoses. As expected, a lack of yeasts and mycelium-forming fungi were lacking in most habitats. A tiny abundance (<5 x 10\(^{2}\) g\(^{-1}\)) was detected in the coal-bearing strata, individual horizons of the Quaternary aquifers (at 6, 16–17 and 19–21 m) and the Tertiary aquifer at 48 m.

The pollutants found to be the main contaminants in the Quaternary aquifer were selected for degradation studies. These were monochlorobenzene (MCB, 30 mg l\(^{-1}\)), 1,2-dichlorobenzene (1,2-DCB, 10 mg l\(^{-1}\)) and 1,4-dichlorobenzene (1,4-DCB, 10 mg l\(^{-1}\)). Benzene (100 mg l\(^{-1}\)) was also included in the investigation as its formation is expected after an abiotic dehalogenation of chlorobenzenes.

The three primary pollutants, MCB, 1,2- and 1,4-DCB (as well as benzene) were removed from the autochthonous bacteriocoenoses under simulated in situ conditions within technologically relevant periods of times. However, the extent and speed of removal significantly differed, depending on the pollutant’s chemical structure, the type of metabolism of the ecophysiological groups involved, as well as the availability of electron acceptors and additional carbon substrates (Fig. 2).
Of the three chloroaromatics, 1,2-DCB proved to be the hardest compound to degrade; in fact, under anaerobic conditions no decomposition whatsoever was possible without the availability of additional carbon substrates. After adding non-resident carbon substrates (a mixture of acetate and lactate), the 1,2-DCB was, however, almost completely removed after just 20 days under nitrate-, sulphate- and iron-reducing conditions. Under these conditions other pollutants were no longer detectable, i.e. totally degraded.

Under aerobic conditions, the 1,2-DCB in all experiments was only degraded very slowly (if at all). The residual concentrations found after an incubation time of
40 days were usually 40–50%, and in just one case about 30% of the initial concentration. Thus, on the whole, they were only slightly below the residual concentration of 50% defined as the evaluation limit for biological removal.

Assuming that sufficient quantities of terminal electron acceptors and carbon substrates were available, the pollutants were, somewhat surprisingly, broken down relatively quickly in the anaerobic environment under nitrate-, sulphate- and iron-reducing conditions.

The findings of the screening programme indicate that the microbiological in situ remediation of the contaminated aquifers is in principle possible under the anaerobic conditions prevailing at the location. Furthermore, the in situ removal capacities can be increased by stimulating autochthonous anaerobic groups via the addition of electron acceptors and utilisable carbon substrates.

**Abiotic pollutant removal**

Physical and chemical methods for pollutant reduction in the groundwater are grouped together within the SAFIRA project under the term abiotic techniques. Starting from the familiar process of dehalogenizing aliphatic chlorinated hydrocarbons with Fe⁰ (Gillham & O’Hannesin, 1994; Matheson & Tratnyek, 1994), new methods were surveyed which enable the removal of chloroaromatics and are suitable as in situ techniques. Initial possibilities are seen in electrochemical techniques, sonochemical methods and bimetal systems. In addition, activated carbon adsorption was tested, which could, in particular, be interesting as an in situ method if the residence times were extended by microbial inhabitation. In the following, the findings of electrochemical removal studies are presented as an example; it should be pointed out that other approaches also yielded very promising results (see Weiss et al., 1998).

A distinction was made between two different techniques for electrochemical removal.
dechlorination: systems using palladium as a catalyst for hydrogen activation and systems without palladium. The former represent the current state of research, whereas the latter have not previously been described for chlorobenzene.

Water electrolysis produces molecular hydrogen, which is activated at the surface of the Pd. Pd was either precipitated electrochemically on the carbon cathode or mixed with the cathode material as a carrier catalyst (e.g. 5% Pd on activated carbon). The main difference between the two methods is that in the first case the Pd is on the electrode potential, whereas in the second it is not conductively linked to the electrode.

The concentration of chlorobenzene in the electrolytes (Bitterfeld groundwater) in these experiments was 50–150 ppm. In many cases, chlorobenzene was completely removed. Figure 3 shows a typical graph of concentration versus time for a mixture of mono-, di- and trichlorobenzenes. The constancy of the chlorobenzene concentrations was measured up to 450 h to record sorption and other losses. After starting water electrolysis, most of the chlorobenzenes were removed within about 50 h. The regular arrows indicate the renewed addition of the chlorobenzene mixture; the jagged arrows mark the beginning of electrolysis. This sequence can be repeated several times without a drop in activity. The only reaction products found were benzene and chloride (>90% of the converted chlorobenzenes). Similar results were obtained when Pd on different carriers (activated carbon, soot) was freely suspended as powder in the groundwater.

SCALING UP

In the first phase of activity the principal site-specific investigations have already been completed. The location has been found suitable for the proposed work, and fundamental processes able to remove the “pollutant cocktail” are known. The investigations still underway are mainly designed to refine the database for hydraulic and transport modelling, and to test and optimise additional removal techniques. Moreover, the technical principles for structural planning are being worked out.

The next stage is to scale up the laboratory experiments. A mobile decontamination unit has been designed for this purpose as a “window in the aquifer”. Groundwater from a depth of about 20 m is pumped into a storage tank without coming into contact with oxygen from the air. This polluted water will then be used to charge five possible test columns with the physico-chemical conditions of the aquifer being preserved (T = 14°C, pH = 7, Eh = -150 mV, Χ = 2 mS cm⁻¹, AOX = 30 mg l⁻¹).

The methods tested successfully in the laboratory and in the mobile decontamination unit have to prove their chemical and hydrological long-term stability and will be optimised in a pilot plant. Several vertical experimental columns of up to 2 m in diameter will be installed to a depth of 20 m directly into the aquifer. Numerous sampling and process controlling facilities as well as a variable design of the reaction columns, will enable the analyses of relevant chemical and hydraulic processes during operation and competitive development in technology under real-world conditions. Operation of the pilot plant is expected to start by the end of 1998.
REFERENCES


