Chloroaromatics in groundwater: chances of bioremediation
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Abstract The potential for biodegrading of mono-, di- and trichlorobenzenes in a contaminated aquifer in Bitterfeld (Saxony-Anhalt) was tested both in the laboratory and using on-site column experiments. Under the prevailing anaerobic conditions, the reductive dechlorination of 1,4-dichlorobenzene (1,4-DCB) takes place very slowly. Under aerobic conditions the indigenous micro-organisms are able to mineralize monochlorobenzene (MCB) and 1,4-DCB. The degradation rates for the other two isomeric dichlorobenzenes and for 1,2,4-trichlorobenzene (1,2,4-TCB) under aerobic conditions are significantly lower. Indications were found that once the oxygen has been consumed, Fe(III) species can be used as alternative electron acceptors.

Keywords Biodegradation · Chlorobenzenes · Groundwater

Introduction
In the Bitterfeld region, the groundwater is extensively contaminated in the area of a disused chemical factory that once produced and processed large quantities of halogenated compounds. High concentrations (up to 50 mg/l) of chloroaromatics, especially monochlorobenzene (MCB), have been detected downstream from the contaminated area.

The UFZ has launched a research programme known as SAFIRA to develop and test suitable in-situ remediation procedures for contaminated aquifers. The site of the SAFIRA project is located south-east of Bitterfeld, downstream from the contaminated area. The hydrogeological situation is characterized by a quaternary and a tertiary aquifer separated by a lignite seam 4–8 m thick (Fig. 1). The quaternary groundwater is highly contaminated by chlorobenzenes (CBs), chiefly MCB with an average concentration of 25 mg/l. The concentrations of 1,4- and 1,2-dichlorobenzene (DCB) are two orders of magnitude lower, whereas trichlorobenzenes (TCB) and higher chlorinated aromatics are not detectable. The main contaminants in the tertiary aquifer are chloroaliphatics, primarily trichloroethene and dichloroethenes. The lignite has adsorbed and accumulated large quantities of these contaminants, causing their concentrations in the groundwater to decrease (Dermietzel and others 1998, Christoph and Dermietzel 2000).

Initial studies revealed that groundwater and sediments in the research area have been populated by both aerobic and anaerobic micro-organisms at up to 10^5 cfu/ml and 10^6 cfu/g dry weight, respectively (Wünsche and others 1997).

Biodegradation of CBs has been studied under both aerobic (Reinecke and Knackmuss 1981) and anaerobic (Sahm 1986) conditions. The ability of micro-organisms to degrade CBs is believed to closely depend on their long-term adaptation to the contaminated habitat (van der Meer and others 1998).

The bottleneck in the complete mineralization of chloroaromatics is the separation of the C–Cl bond(s). According to current knowledge of the aerobic reaction mechanisms (Reinecke 1999), dechlorination takes place before or immediately following the split of the aromatic ring system. As the number of substituted chlorines increases, the π-electron system becomes more resistant to oxidative degradation. By contrast, reductive attack by anaerobic micro-organisms is preferred. The anaerobic degradation pathway consists of phased dechlorination, with benzene being the theoretical end product. In practice, the reaction pathway stops at the MCB level (Holliger and others 1992).

Consequently, remediating a contaminated water that contains different chlorobenzenes should involve two steps: the anaerobic dechlorination of multiple chlorinated benzenes, followed by aerobic treatment to degrade the remaining low-chlorinated aromatics. This principle was
successfully tested in fluidized-bed reactors with spiked water (Nowak and others 1993) and actual contaminated groundwater (Meierling and Hegemann 1997). The main objective of this paper was to ascertain whether this strategy is suitable for the in-situ remediation of the groundwater at Bitterfeld.

The ratio of aromatic concentrations in the quaternary groundwater (large quantity of MCB accompanied by smaller amounts of DCBs and benzene) suggests that an anaerobic degradation process takes place in the aquifer with MCB as the preliminary end product. Therefore, a promising approach would appear to be to stimulate the oxidative degradation potential.

**Experimental procedures**

**Laboratory experiments**

Groundwater samples were taken at 11 different sites of the test field representing different degrees of contamination (Fig. 2, Table 1). The filters of all the groundwater-monitoring wells are located directly above the base of the quaternary, with the exception of GWM 19/91, which extends down to the tertiary aquifer. The column experiments (see below) were performed with groundwater from SB 7/97, which was analysed weekly. Its CB concentrations varied considerably over time, but had average levels of 25 mg/l MCB, 0.3 mg/l DCBs and benzene at ≤ 0.1 mg/l.

**Cross-Section**

![Geological section at the SAFIRA test field in Bitterfeld (Ruske and others 1999)](image1)

![Site map of the SAFIRA test field showing a schematic cross section of the MCB plume (Ruske and others 1999) and the location of the used groundwater monitoring wells, but without SB 18/97 (south of SB 17/97) and GWM 19/91 (north-west of the test field)](image2)