

# POTENTIALS AND LIMITATIONS OF BIOREMEDIATION OF A DIESEL FUEL CONTAMINATED SITE

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## ABSTRACT

*In situ* bioremediation relies on the stimulation of microbial activity and enhancement of the mass transfer rate of contaminants from nonaqueous phase liquids (NAPL) into the aqueous phase. Over a period of four years, a sandy aquifer contaminated with residual constituent compounds of aged diesel fuel was infiltrated with H<sub>2</sub>O<sub>2</sub> and nutrient-amended water. The release and biodegradation of the hydrocarbons was improved by a factor of about 20 - 50. However, it became apparent through soil analysis that the mass transfer kinetic was the limiting factor. The conclusion was reached that the soil clean-up levels are too far below the levels which are perceived to be technically and economically feasible. Nevertheless, GC-analysis showed that the more soluble aromatic compounds, which have been widely regarded as the primary contaminants affecting groundwater, had been completely removed. Evidence gathered while monitoring the groundwater for one year following the bioremediation process indicated that the established water clean-up levels could easily be maintained through the *in situ* treatment.

## INTRODUCTION

The *in situ* bioremediation of the described diesel oil contamination started in the beginning of 1992, ended 4 years later, and was in a final monitoring phase in the beginning of 1997. In 1992, the authorities established limiting values (clean-up levels) for total petroleum hydrocarbons (TPH) of 500 mg/kg dry weight for soil and 500 µg/L for groundwater. In order to evaluate the efficiency of the remediation, an attempt was made to follow the reduction of hydrocarbons in groundwater and soil. In general, the balancing of the degradation during an *in situ* bioremediation and the demonstration of the remediation success afterwards is very difficult, due to several problems in monitoring a 'black-box' system (Madsen, 1991).

## MATERIAL AND METHODS

### Description of the Contaminated Site

The contamination caused by a leaking pipeline 45 to 50 years ago was assumed to be associated with diesel oil. The estimated amount of leaked diesel oil was 15,000 to 17,000 L, and most of the oil floating on the groundwater was removed at the end of the 1970s, leaving approximately 5,700 kg. The subsoil of the contaminated area is characterized as a pleistocene aquifer with fine- and medium-grained sands. The average permeability ( $k_f$ ) is 10<sup>-4</sup> to 5 x 10<sup>-4</sup> m/s. The highest concentration of TPH was about 18,000 mg/kg dry weight (see Figure 2, at a depth of 6 to 7 m). The pollution is distributed to a depth of 4 to 9 m below ground level, thus lying in the aquifer (the groundwater level is approximately 4.5 m below ground level). Gaschromatographic profiles of water and soil extracts showed no typical *n*-alkanes, thus indicating that these compounds had already been degraded. Details concerning the chemistry of the contamination (Steiof, 1993) and the inorganic parameters of this bioremediation (Steiof & Dott, 1995) have been described previously. A top view of the contaminated area, illustrating the positions of the production and infiltration wells, all observation wells, and the distribution of the hydrocarbons is given in Fig. 1.

### Remediation Design

The *in situ* remediation design included two infiltration wells, two production wells, and an on-site groundwater processing plant. This groundwater treatment-plant consisted of an iron-removal filter, an oxygenator (using technical oxygen gas), a manganese-removal filter, and an air stripping column. Before the reinfiltration of the treated groundwater, it was possible to add electron acceptors and nutrients. To meet the electron acceptor demand, hydrogen peroxide and nitrate were added to the reinfiltrated water. Phosphate was added to meet the nutrient demand. During the four years of operation, the following amounts were added to the infiltration water:

H<sub>2</sub>O<sub>2</sub>: 33 t (about 15 t O<sub>2</sub>); NaNO<sub>3</sub>: 5 t; (NaPO<sub>3</sub>)<sub>n</sub>: 0,4 t (about 0,3 t PO<sub>4</sub>).

The two production wells had a joint average production rate of 5-10 m<sup>3</sup>/h and the two infiltration wells a joint average rate of 3-6 m<sup>3</sup>/h during the four years of operation. The groundwater velocity during operation was about 2 m/d, in contrast to 0.4 m/d without operation. The average residence time of the circulated groundwater in the aquifer was about 15 days (Battermann & Meier-Löhr, 1996).

## RESULTS AND DISCUSSION

### Hydrocarbons in Soil

The hydrocarbon concentrations in the soil samples of ram boring S3 during the remediation are given in Figure 2. The samples '-100 days' represent the concentrations 100 days before the bioremediation was started. Afterwards samples were taken from the same location with a horizontal shifting of 10 cm each year. Some samples from later ram borings contained higher TPH concentrations than earlier samples. After 1340 days of remediation TPH concentrations higher than the limiting value remained in some samples. The soil samples of the ram borings S1, S2 and S4 showed similar results.

Because of the heterogeneity of the subsoil and the typical inhomogeneous distribution of the contaminants, soil samples can not be regarded as representative. A significant reduction of the contaminants was observed only in an advanced stage of the remediation process. Obviously, the homogeneity and the permeability of the aquifer have a decisive influence on the success or failure of an *in situ* remediation.

### Hydrocarbons in Groundwater

The TPH concentrations in groundwater samples from three observation wells are given in Figure 3. During the first year of bioremediation, no effect from addition of electron acceptors and nutrients could be observed. The highest TPH concentration was about 2,100 µg/L in well B5 (in most observation wells <1,000 µg/L) and there was no significant decrease during this time. However, a decrease was not expected because a permanent re-solubilization of hydrophobic fuel oil compounds from the soil matrix into the water matrix occurred. After two years of bioremediation, the TPH concentrations in all observation wells settled down below the given limiting value of 500 µg/L.

The gaschromatographic profile of the hydrocarbons in the groundwater of observation well B5 (exemplarily for all observation wells within the contaminated zone) in the beginning of the remediation process is given in Figure 4. In contrast to the GC-MS analysis of the hydrocarbons in soil, only aromatic hydrocarbons could be identified in the groundwater extracts. Iso-alkanes could not be identified. After about 3.5 years of operation, the typical aromatic compounds (see Figure 4) were completely removed and the TPH concentrations declined below the clean-up level of 500 µg/L.

### Methodical Approach to the Quantification of Hydrocarbon Degradation

Because of the lacking representativity of the soil samples and the lacking correspondence of TPH in soil and groundwater samples, a different approach to balance the success of the fuel oil degradation was made (Meier-Löhr, 1997). For this indirect attempt, the consumption of added electron acceptors (oxygen from hydrogen peroxide; nitrate) as well as the production of inorganic carbon species (free carbon acid and hydrogencarbonate) had to be determined in groundwater samples. Unfortunately, the complete quantification of these compounds is complicated (Zeyer et al., 1995) since additional sources (e.g. mobilization of mineral lime) and sinks (oxydation of inorganic compounds) are difficult to estimate. A balance applying this approach (consumption of electron acceptors and production of inorganic carbon species, measured as acid- and base-capacity) showed that about 3,500 to 3,700 kg (60 to 65% of the starting amount) of the hydrocarbons were degraded.

### Registration of the Risk Potential

Experiences with different *in situ* bioremediations showed that the given limiting values often were not reached in all soil samples. Nevertheless, there is not enough knowledge to estimate the risk potential of these remaining hydrocarbons at the end of a bioremediation. On the other hand, a bioremediation usually leads to a reduction of the contaminants and the toxicity in the groundwater (Dasappa & Loehr, 1991) and, as a consequence, the risk potential will be lowered or eliminated.

It is generally accepted, that the mobility and bioavailability of contaminants have a crucial influence on the risk potential of a polluted site (Rippen et al., 1994). Therefore, it is more important to monitor the TPH concentrations in the groundwater than in the soil. In addition, the application of toxicity tests is necessary (DECHEMA, 1995). Chemical analysis of environmental samples usually does not lead to reasonable predictions of biological or ecological effects. Toxicity tests, however, integrate the effects of all mobile and bioavailable contaminants and complement

the chemical analysis of a contaminated site. We conducted the bioluminescence test assay with *Vibrio fischeri* according to the German Standard Methods (1991). The EC<sub>50</sub>-values of the groundwater samples of the remediation zone and downstream of the contaminated area did not reach toxic levels (data not shown here).

## CONCLUSIONS

During a final control phase, the groundwater was examined with special attention given to the TPH concentration and the toxicity. Although the TPH concentration in some soil samples exceeded the limiting values, the authorities agreed to bring the remediation to an end. The TPH concentration in the groundwater in combination with the results of the toxicity tests seemed to verify, that the risk potential of this contamination has been eliminated.

However, it became apparent through soil analysis that the mass transfer kinetic from the NAPL attached to the soil surface in the groundwater was the limiting factor. The conclusion was reached that the soil clean-up levels are too far below the levels which are perceived to be technically and economically feasible. Nevertheless, GC-analysis showed that the more soluble aromatic compounds, which have been widely regarded as the primary contaminants affecting groundwater, had been completely removed. Also, the dissolution of the remaining low soluble aliphatic hydrocarbons did not reach detectable levels and therefore did not affect the groundwater quality. Evidence gathered while monitoring the groundwater for one year following the bioremediation process indicated that the established water clean-up levels could easily be maintained through the *in situ* treatment. Given that the main objectives are the clean-up and protection of water resources, the application of an *in situ* remediation technology is technically and economically effective.

## ACKNOWLEDGEMENTS

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## REFERENCES

- Battermann, G. and M. Meier-Löhr. 1996. „Erfahrungen aus zwei *in situ* Sanierungen in der gesättigten Bodenzone“. In Kreysa, G. u. Wiesner, J. (Eds.): *In-Situ Sanierung von Böden, 11. DECHEMA Fachgespräch Umweltschutz*, DECHEMA, Frankfurt a.M., 163-190.
- Dasappa, S. M. and R. C. Loehr. 1991. "Toxicity Reduction in Contaminated Soil Bioremediation Process." *Wat. Res.* 25(9): 1121-1130.
- DECHEMA (Dott, W. and K. Hund). 1995. "Bioassays for Soil" In G. Kreysa and J. Wiesner (Eds.), *4th Report of the Interdisciplinary DECHEMA Committee „Environmental Biotechnology - Soil“*; *Ad-hoc-Committee „Methods for Toxicological / Ecotoxicological Assessment of Soils“*, 46 pages, DECHEMA e.V., Frankfurt a.M.
- German Standard Methods. 1991. "Testverfahren mit Wasserorganismen, Bestimmung der Hemmwirkung von Abwasser auf die Lichtemission von Photobacterium phosphoreum - Leuchtbakterien-Abwassertest mit konservierte Bakterien." *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung DIN 38412 Teil 34*, L34.
- Madsen, E. L. 1991. "Determining *in situ* Biodegradation." *Environ. Sci. Technol.* 25(10): 1663-1673.
- Meier-Löhr, M. 1997. „Bilanzierung und Modellierung von biologischen und physikalisch-chemischen Prozessen bei der *In-Situ* Sanierung von kohlenwasserstoffverunreinigten Grundwassersystemen“, PhD Thesis, Technical University of Dresden, Germany.
- Morgan, P. and R.J. Watkinson. 1992. "Factors Limiting the Supply and Efficiency of Nutrient and Oxygen Supplements for the *in situ* Biotreatment of Contaminated Soil and Groundwater". *Wat. Res.* 26(1): 73-78.
- Rippen, G., T. Held, and P. Ripper. 1994. "Microbiological Remediation of Waste-Oil Polluted Soils - Ecotoxicological and Toxicological Considerations." *Environ. Sci. Poll. Res.* 1(3): 185-189.
- Steiof, M. 1993. "Biologische *in situ* Sanierung eines mit Dieselloh kontaminierten Aquifers." Ph. D. Thesis and Publication from the Department of Hygiene, Technical University of Berlin, Germany.
- Steiof, M. and W. Dott. 1995. "Application of Hexametaphosphate as a Nutrient for *In Situ* Bioreclamation". In R. E. Hinchee, J. A. Kittel, and H. J. Reisinger (Eds.), *Applied Bioremediation of Petroleum Hydrocarbons*, pp.301-310. Battelle Press, Columbus, OH.
- Zeyer, J., P. Höhener, D. Hunkeler and D. Hahn. 1995. "*In situ* Bioremediation of Mineral Oil Contaminated Soils and Aquifers: Quantification of Degradation Rates and Fate of Hydrocarbons." In W. J. van den Brink, R. Bosman and F. Arendt (Eds.), *Contaminated Soils '95*, pp. 319-326. Kluwer Academic Publishers, Netherlands.

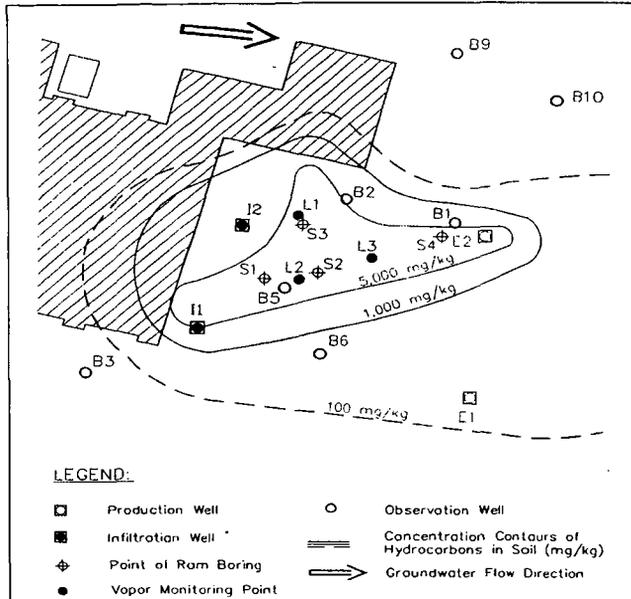


FIGURE 1. Top view of the contaminated area with TPH concentration and the position of all wells and points of ram boring with open sided tube.

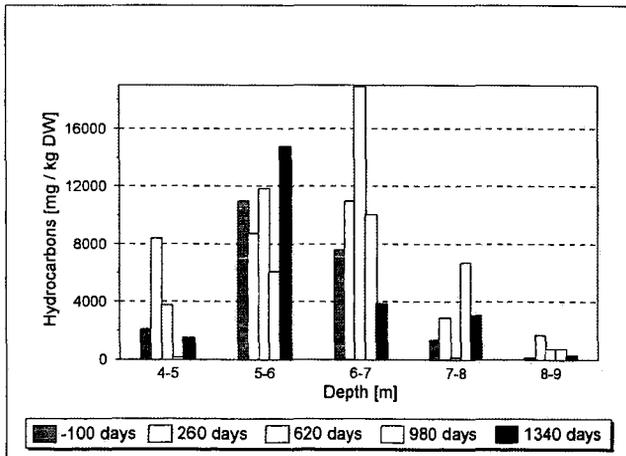


FIGURE 2. Hydrocarbon concentrations in the soil of ram boring S3.

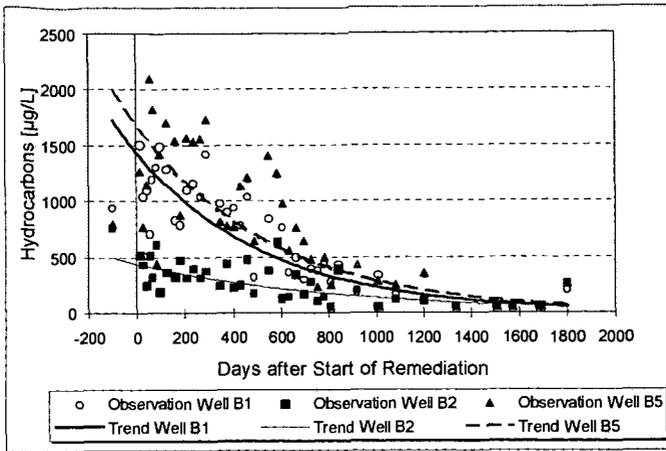


FIGURE 3. Hydrocarbon concentrations in the groundwater of the observation wells B 1, B 2 and B 5.

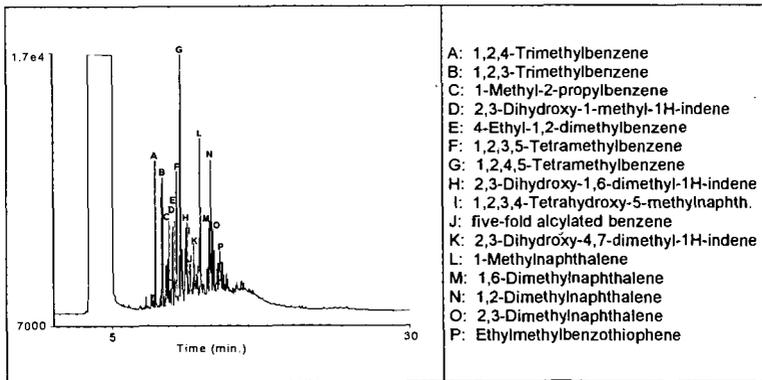


FIGURE 4. Gaschromatographic analysis of the hydrocarbons in the groundwater of observation well B 5 (TPH-concentration: 1,800 µg/L).