

# NITRATE BASED ENHANCED NATURAL ATTENUATION IN-SITU TECHNOLOGY FOR HYDROCARBON

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## Summary

Pumping and in-situ bioremediation has been applied as the first and second remediation tiers at a former refinery site, mainly contaminated by BTEX compounds, and has led to a cost effective removal of about **2460** tons of hydrocarbons, **98%** of the initial contamination respectively. At that remediation level, declining degradation rates and hydrocarbon concentrations in groundwater imply the prevalent kinetic constraints and limitations of technical remedial action, with respect to their potential to comply with established groundwater quality guidelines. By a risk assessment, based on mass transfer and groundwater transport modelling, Natural Attenuation is assumed to be feasible as final third tier of the site remediation, enabling the containment of the plume as well as the removal of residual hydrocarbons within a reasonable time frame.

## 1. Introduction

Hydrocarbon contaminations generally comprise complex mixtures of constituent components that are effectively immiscible with groundwater. Coupled to their low solubility in groundwater the effectiveness and progress of established remediation techniques, e.g. pumping and bioremediation, are kinetically controlled by mass transfer mechanism.

Prevailing kinetic constraints and limitations of pumping and in-situ bioremediation operations are often indicated by declining degradation rates and hydrocarbon concentrations in groundwater.

As alternative for further remediation natural attenuation has to be thoroughly evaluated with respect to their potential to control plume extent and exposure pathways as well as to comply with groundwater quality criteria removal. The implementation of appropriate and cost-effective remedial strategies requires a good understanding of the governing processes and suitable methods to evaluate the mass transfer, transport and transformation behaviour of the constituents, which will be presented in this paper.

## **Compounds of concern**

### ***Mineral oils***

Mineral oils are a mixture of different compounds where properties vary with respect to solubility, toxicity, adsorbability and biodegradability. The properties depend on the number of C-atoms and the length of the C-chains. The longer the chain the less biodegradability to compound is. The biodegradability of the mineral oils decrease according the following ranking:

Alkanes – Iso-Alkanes – Alkenes – Alkines – Cycloalkanes

Many inventions confirm this behaviour and in some site samples under going natural attenuation processes the alkane fraction disappeared completely which the other compounds are still existing (Handbuch der mikrobiologischen Bodenreinigung, Materialien zur Altlastenbearbeitung, Band 7, LfU Karlsruhe 1991).

In general mineral oils are readily biodegradable under aerobic conditions and oxygen is the limiting factor. But biodegradation could be proved under anoxic conditions with electron acceptors other than oxygen, too, (Bregnard et al 1997, Ackersberg et al 1991, Rueter et al 1994).

### ***Monoaromatic compounds***

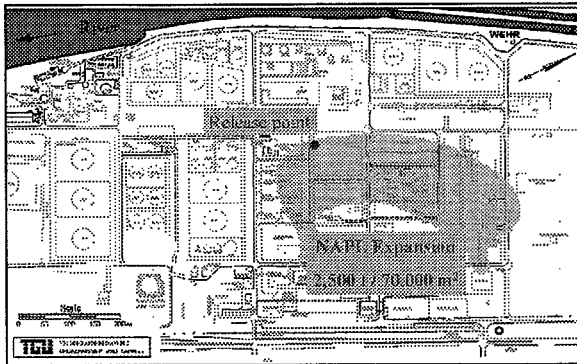
This group of contaminants comprises benzene, toluene, ethylbenzene and xylenes. They are moderately soluble in water, readily biodegradable and weakly absorbable. Benzene is highly toxic and carcinogenic, but best biodegradable among this group.

Under aerobic environmental conditions the kinetic of biodegradation of all those compounds is very high. Moreover they are biodegradable under anoxic and even under methanogenic conditions, too (Vogel and Grbic'-Galic' 1998). Some research group could prove the mineralisation of BTEX-compounds under sulphate reducing conditions (Edwards et al 1991, Beller 1992, Weiner et al 1998). Edwards et al describe a ranking in the biodegradation also follows: toluene, p-xylene and o-xylene. No transformation in the presence of sulphate could be observed for benzene and ethylbenzene on the other hand. Loveley et al (1995 and 1996) could prove the degradation of benzene during sulphate reducing conditions. Even under iron-reducing conditions BTEX compound can be oxidised. It is remarkable that the rate of mineralization under these conditions is almost as high as that under aerobic conditions (Loveley et al 1994).

The microorganism can use the iron oxides existing in the subsurface for the oxidation of the monoaromatic compounds in the frame of a natural attenuation process. According Baedecker et al 1993, Bennet et al 1993 and Eganhouse et al 1993 this process is predominant for the oxidation of benzene, toluene, ethylbenzene and xylenes during a case study at a refinery site. Iron reduction is present in environments where nitrate and sulphate is depleted.

Wilson (1986) as well as Vogel and Grbic'-Galic' (1987) observed a slow mineralization of benzene, toluene and O-xylene even under methanogenic conditions.

## 2. Site Description



The site is located in the Hessian Rhine-valley and has been used as refinery from 1966 to 1986. In 1974 a corrosion hole in a subsurface production pipe led to the release of about 2500 t of NAPL spreading out as mobile phase on the groundwater surface over an area of about 70.000 m<sup>2</sup>. Benzene and BTEX has been detected as the predominant contaminants with a mass fraction of 15% and 50%, respectively, on the NAPL.

fig. 1: site map and NAPL expansion

The upper aquifer mainly consists of sand, gravelly sand, or sandy gravel sediments, characterized by a hydraulic conductivity from  $5 \cdot 10^{-4}$  to  $2 \cdot 10^{-3}$  m/s. As shown by fig.2 the aquifer is limited by a silt/clay layer at a depth of 20 m bgs. The NAPL's are located in the upper part of the aquifer from 6 to 10 m bgs. The hydro-geological cross sections illustrates the hydraulic containment to protect the adjacent water wells.

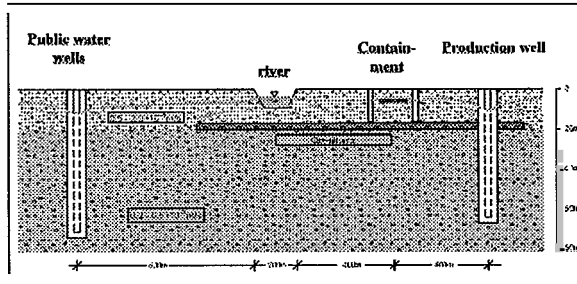


fig.2: hydrogeological cross section

## 3. Remediation Tier 1 – Pumping and Product Recovery

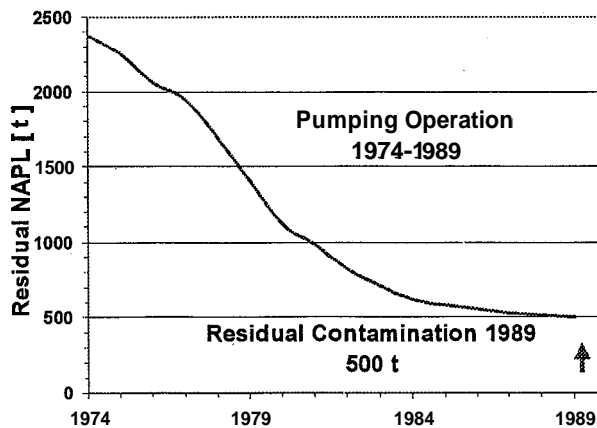
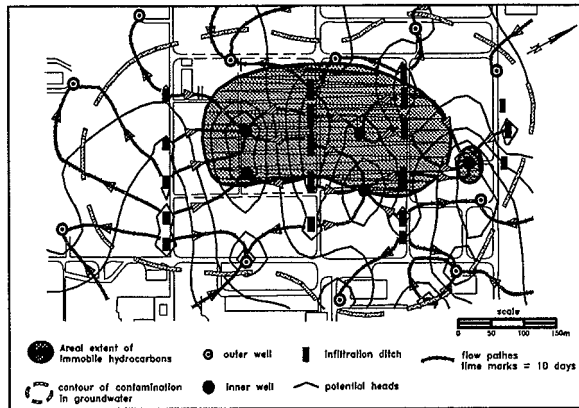


fig.3: NAPL removal during pumping operation

The first remediation tier focused on the recovery of mobile NAPL and the hydraulic containment of the contaminated area in order to protect the adjacent water wells by pumping and bailing. 15 years of pumping operation from 1974 to 1989 led to the removal of about 2000t of hydrocarbon, mainly as mobile phase (see fig.3). Remaining were about 500 t of immobile residual hydrocarbons, which could not efficiently removed by pumping. The decreasing slope of the removal graph (fig.3) indicates the kinetical constraints of the pumping operation.

#### 4. Remediation Tier 2 - Stimulated In-Situ Bioremediation

As the removal of the residual NAPL (500 t) could not efficiently be achieved by pumping, laboratory test, pilot field study and groundwater modelling has been performed to assess the feasibility of a in-situ bioremediation



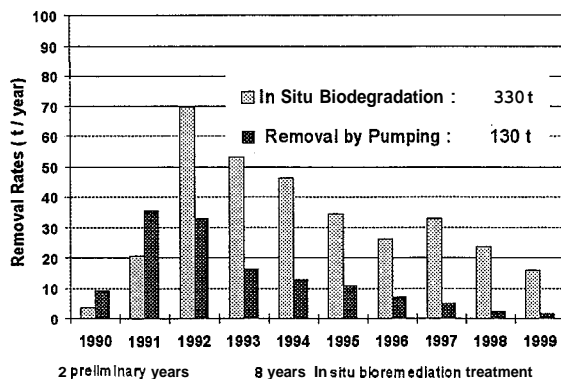
(Battermann et al, 1993), stimulated by nitrate and nutrients. Based on the result of the feasibility study a large scale in situ bioremediation applying nitrate as electron acceptor was initiated as second tier in 1992. The hydraulic system of recovery wells and recharge trenches (fig.4) enabled a groundwater circulation of 400 m<sup>3</sup>/h for intensive flushing and effective distribution of nitrate and nutrients and the hydraulic containment of the subsurface treatment area of about 18 ha (Battermann et al,

1995).

fig.4: hydraulic system of in-situ bioremediation

#### 4.1 Mass Balances

For process control and evaluation of the in-situ biodegradation mass balance calculations have been performed. Relevant compounds of mass balancing were the electron acceptors NO<sub>3</sub><sup>-</sup>, O<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, Fe(III), Mn (IV), the inorganic carbon and alkalinity, the alkaline and alkaline-earth metals and the dissolved organic carbon. The attribution of mass balances to biological and geochemical



reactions for quantification of hydrocarbon degradation has been evaluated by inverse modelling procedures (Meier-Lohr, 1998) adjusting „measured“ and „calculated“ mass balances of inorganic carbon and alkalinity. Applying about 1100 t nitrate and 200 t oxygen during eight years of operation the removal of hydrocarbons from residual nonaqueous phase liquids has been quantified of about 460 t of hydrocarbons.

fig.5: quantification of hydrocarbon degradation and removal

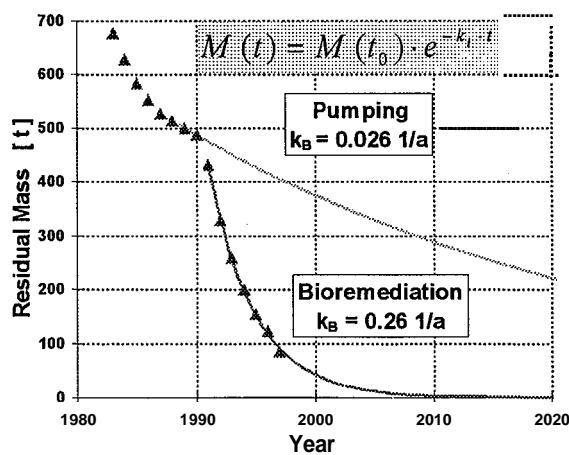
As shown in fig. 5 about 70 % of the mass removal, i.e. 330 t, has been contributed by biological transformation and mineralization of hydrocarbons, evaluated from mass balances and adjusted stoichiometric relationships. Considering biological oxidation of reduced minerals sensitivity analysis reveals a loss of electron acceptors in the ranges of 10 to 15% .

## 4.2 Mass Transfer and Biodegradation Kinetics

In-Situ bioremediation relies on the stimulation of the microbial activity and enhancing the mass transfer rate of contaminants from NAPL phases into aqueous phase. For evaluation of multicomponent NAPL mass transfer and biodegradation kinetics an integral hydraulic modelling approach (Meier-Lohr et al, 1998) has been applied. The mathematical model of the hydraulic system is based on an **advection-dispersion-reaction** incorporating a first-order mass-transfer relationship and first-order biodegradation kinetics for the BTEX-compounds benzene, toluene, and xylene. On the assumption that the enhancement of the NAPL-compounds dissolution caused by microbial activity relies mainly on the increase in water solubility  $C_{weq}^1$  at interfaces, a solubility factor  $f_{K1}$  was introduced and evaluated by calibration.

Due to the model calculations the enhancement of NAPL mass transfer by a factor of about 10 to 15, compared with pumping operation, was mainly affected by the biological influence on hydrocarbon solubility in groundwater, indicated by solubility factor  $f_{K1}$  of 4 to 6. As far as biodegradation kinetics of the BTEX compounds are concerned model calibration led to the following rate constants  $K_B^1$ : benzene 0,003-0,03 1/d; toluene 0,15-0,25 1/d; m-p xylene 0,03 - 0,07 1/d. Benzene, only slightly biodegradable under the denitrifying conditions, was mainly removed from NAPL by flushing, because of its high solubility in water.

## 4.3 Remarks on the Efficiency of in-situ Bioremediation



The enhancement of dissolution and subsequent degradation of aromatic hydrocarbons from residual multicomponent NAPL by a factor of about 10 compared with pumping operations gave evidence to the efficiency of the in-situ bioremediation (fig.6). However, at a remediation level of 98 % NAPL-removal, declining degradation rates and hydrocarbon concentrations in groundwater indicate the prevalent kinetic constraints and limitations of the in-situ treatment with respect to their potential to comply with established groundwater clean-up criteria for BTX-compounds.

fig.6: Evaluation of mass removal by pumping and bioremediation

## 5. Evaluation of Natural Attenuation as Tier 3

Natural attenuation processes are mainly governed by the availability of suitable electron acceptors, the mass transfer kinetics of constituent contaminants and the fate and transport properties of dissolved constituents. Therefore implementation of natural attenuation as remediation alternative requires a comprehensive characterization and evaluation of the attenuation processes with respect

to their potential to control plume extent and exposure pathways as well as to complete the source removal.

### 5.1 Methodological Approach

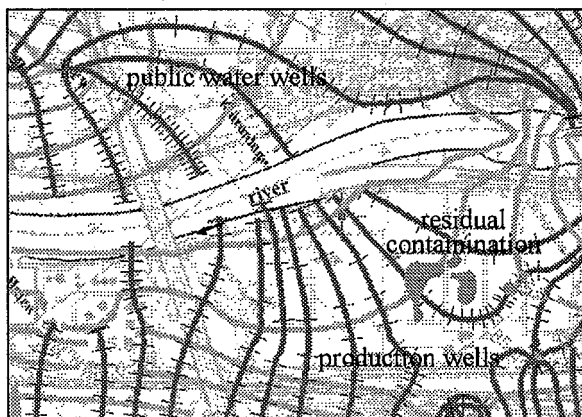
The feasibility of Natural Attenuation as final remediation action has been investigated by a risk assessment, including inventory analysis, exposure pathway evaluation, elaborate mass transfer and groundwater flow and transport modelling of the contaminants of concern. Mass transfer and transport characteristics were derived from the site and accomplished by literature data.

### 5.2 Inventory Analysis

The inventory analysis of the constituent hydrocarbons (total: 40 t) reveals, that benzene is still the most relevant contaminant of concern. Due to the relatively high solubility the benzene concentration or fraction in groundwater (25 %) is ten times higher than in the residual NAPL (2.5 %), which stands in line with the partitioning derived from Raoult's law.

By balancing the available electron acceptors, the capacity of natural degradation of hydrocarbons at the site, has been calculated to about 1000 kg/year. As proven by groundwater analysis during the pumping operations, sulfate will be the pre-dominant electron acceptor at background concentrations of 100 mg/l. Mn(IV) and Fe(III) attached to the soil matrix, will also provide considerable electron accepting capacity for natural biological hydrocarbon mineralization.

### 5.3 Exposure Pathway Evaluation



According to the risk assessment, the migration of dissolved hydrocarbons, in particular benzene, in groundwater is the relevant pathway under natural conditions. By elaborate groundwater flow modelling different hydrological conditions and discharge scenarios are evaluated with respect to an exposure of the potential receptors. As illustrated on fig.7, an exposure of the adjacent public water work can be excluded, as the river is an effective natural boundary for the catchment area of the water wells on the opposite river bank.

fig.7: groundwater flow at mean hydrological conditions

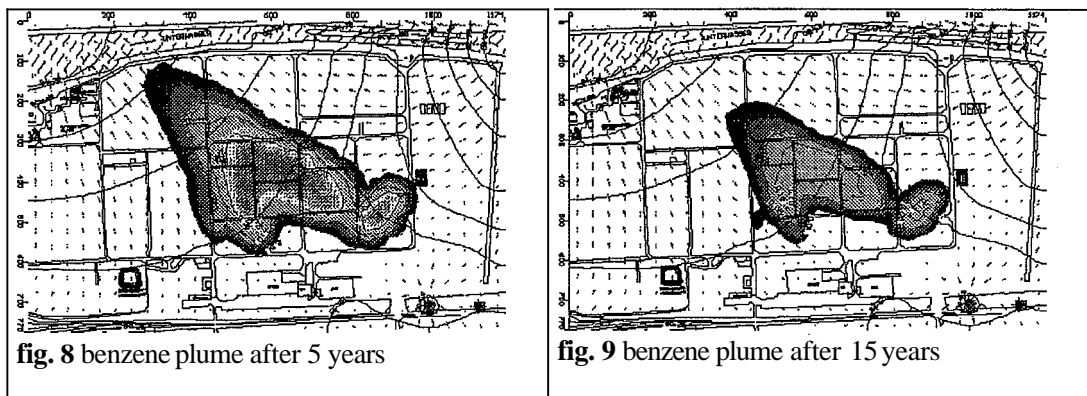
### 5.4 Mass Transfer Calculations

For quantification of hydrocarbon exposure, the mass transfer model, calibrated to site conditions and data, shows, that the mass-transfer rate will decrease after closure of bioremediation by a

factor of about 25 in all likelihood. That means a total hydrocarbon outflow at the border of residual contamination of about 500 kg/year total hydrocarbons, including 125 kg/year benzene.

### 5.5 Fate and Transport Modelling

The fate and transport modelling leads to the assertion that benzene will be naturally degraded under sulfate and iron/manganese reducing conditions to concentrations of about 10 µg/l at the exposure point at the river bank. A considerable reduction of the benzene plume expansion by Natural Attenuation, NA, is expected within 15 years (fig.8 & fig.9).



## 6. Conclusions

Pumping and product recovery is acknowledged as an essential first tier in aquifer remediation that focused on the removal of mobile NAPL. In-situ bioremediation has been proven as efficient technology to enhance the remediation of residual immobile hydrocarbons. Natural Attenuation is assumed to be feasible as final process for site remediation, enabling the containment of the plume as well as the removal of residual hydrocarbons within a reasonable time frame. Applied Natural Attenuation will require an elaborate groundwater monitoring and groundwater modelling to verify the calculations and to ensure the protective status of the site.

The applied mass balance calculations, the mass transfer and groundwater transport modelling give considerable support for the development of a cost effective remediation strategy.

All organic compounds present at hydrocarbon contaminated sites under a naturally occurring biodegradation process which is controlled by the following factors:

- availability and acceptance of electronacceptors (Mainly oxygen, nitrate, sulphate, Fe(III), Mn(IV))
- Toxicity of the compounds
- Composition of the contaminants cocktail
- competitive biodegradation of the compounds
- environmental conditions (e. g. pH-value, temperature, humidity)

Aerobic and anoxic degradation of the compounds is predominant for natural attenuation process. Methanogenic processes only play a minor role in the elimination of the contaminants.

The interactions between the different compounds under the different environmental conditions are highly complex and not enough elucidated so far. The knowledge on the processes occurring in the subsurface is still very weak and a reliable prediction modelling requires still a lot of research activity.

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