Evidence of natural attenuation at a MTBE contaminated site at Leuna (Germany)

Different technologies to enhance the natural process

Marion Martienssen, Holger Fabritius, Stefan Kukla, Gerd U. Balcke, Eyk Hasselwander, Mario Schirmer
methyl tert-butyl ether (MTBE)

\[
\begin{align*}
\text{CH}_3 & \quad | \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{O} \quad \text{CH}_3 \\
\text{CH}_3 & \quad |
\end{align*}
\]

gasoline additive
(up to 14 % in German Super Plus)

- octane enhancer
  research Octane number 117
- anti knocking agent
- oxygenate

decreases ozone and CO concentrations
methyl tert-butyl ether (MTBE)

- Low acute toxicity
- Highly soluble (50 g/l)
- Henry’s Law constant of 0.03 at 25 °C
- Low threshold concentrations for taste and odour
- Difficult to biodegrade
The test site at Leuna
The chemical plant in Leuna (Germany)
Oil phases at the source area

- Refinery oil
- Parex parafines

Ground water flow direction
G.U.T.
GERICHTSRAIN 1
06217 MERSEBURG

**BTEX plume**

**MTBE plume**

(11/2003)
# Groundwater contamination at the Leuna site

<table>
<thead>
<tr>
<th>parameter</th>
<th>dimension</th>
<th>overall site contamination</th>
<th>Pilot site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>min-max</td>
<td>average</td>
</tr>
<tr>
<td>MTBE</td>
<td>µg/l</td>
<td>0 - 300 000</td>
<td>36 - 67 000</td>
</tr>
<tr>
<td>Ammonia</td>
<td>mg/l</td>
<td>0,9 – 110</td>
<td>9 – 110</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/l</td>
<td>0 – 29</td>
<td>0 – 15</td>
</tr>
<tr>
<td>Sulfate</td>
<td>mg/l</td>
<td>0,8 – 1100</td>
<td>130 - 940</td>
</tr>
<tr>
<td>Sulfide</td>
<td>mg/l</td>
<td>0 – 7,3</td>
<td>0 – 2,2</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/l</td>
<td>0,1 – 28</td>
<td>0 - 5,2</td>
</tr>
<tr>
<td>Iron(II)</td>
<td>mg/l</td>
<td>0 – 19</td>
<td>0 - 15</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/l</td>
<td>0,2 - 2,2</td>
<td>0,1 - 1,6</td>
</tr>
<tr>
<td>Mineral oil hydrocarbon</td>
<td>mg/l</td>
<td>0 – 32</td>
<td>0 - 0,2</td>
</tr>
<tr>
<td>PAH</td>
<td>µg/l</td>
<td>0 – 33</td>
<td>0 – 0,4</td>
</tr>
<tr>
<td>BTEX</td>
<td>µg/l</td>
<td>1 - 147 200</td>
<td>9 – 288</td>
</tr>
</tbody>
</table>
Does Natural Attenuation of MTBE occur at the Leuna site?
Laboratory testing
Estimation of the degradation potential in microcosm studies

- Efficient MTBE degradation in all cultures (in Borden aquifer 3 out of 16 cultures only)

- Lag Phase about 70 days (compared to 18 moths in Borden)

MTBE degrading bacteria available in comparable high numbers
Aerobic MTBE degradation

Enrichment culture from MTBE contaminated ground water

Enrichment culture 6a: utilizes MTBE as sole source of carbon and energy

Aerobic degradation without accumulation of TBA

yield: 0.1 to 0.2 mol-C Biomass per mol-C MTBE

Two isoates: one degrading MTBE and TBA

R. H. Müller & T. Rohwerder
Department Umweltmikrobiologie
Cometabolic MTBE-degradation by resting cells

**Culture conditions:** 20°C, 40 mg/l MTBE, BTS 0,3 g/l

Isolation of methane, propane, buthane and also 1-propanol degrading bacteria.

Controls (without additional substrate): degradation started 3 months later
Evidence for naturally occurring MTBE degradation from field results
Development of the MTBE plume during the last years
MTBE and different intermediates from the MTBE degradation along the groundwater flow direction.
Potential electron acceptors for MTBE degradation

![Graph showing concentration and redox potential vs. distance from source](image)
Utilization of iron and sulfate as electron acceptors
First conclusions from lab and field work

- Biodegradation of MTBE can be proofed at the site.
- MTBE can be mineralized as the sole source of carbon and energy.
- MTBE can be degraded cometabolically with different primary substrates. (n-alkanes, iso-alkanes, 1-propanol)
- Some evidence for anaerobic degradation (nitrate).
- MTBE is also degraded at natural conditions.
- At least at the site in Leuna, the degradation is an aerobic process.
- The plume length is the result of MTBE transport and degradation. It is controlled by the natural oxygen supply.
Accelerating the natural MTBE degradation

The ENA approach in the METLEN-Project

aim
encouraging and accelerating the naturally occurring processes in the aquifer through deliberate dosing of e.g. electron acceptors, nutritive solutions, catalysts and microorganisms in conditioning units
Single Conditioning Unit (mixing and/or treatment)

- GOK
- GW flow
- Aquifer
- Aquitard
- Sheet pile gravel
- Conditioning chamber
- Reaction zone in situ
the test site (overview)
Upstream sheet piles
The conditioning unit
The conditioning chambers
Down stream stripes and sampling wells
Dividing the down stream stripes by sheet piles
accelerated MTBE degradation by oxygen supply
accelerated degradation of BTEX by oxygen supply

accelerated degradation of TBF by oxygen supply
Summary

- MTBE is difficult to degrade under field conditions.

- Addition of pure oxygen can accelerate MTBE degradation, but the added oxygen is used primarily for the degradation of byproducts and intermediates. MTBE degradation is accelerated thereafter by enhancing the amount of available natural oxygen for the MTBE degradation.

- Addition of specialized microorganisms or cosubstrates is not necessary at the site.
Technical problems for the ENA approach at Leuna

• Sufficient oxygen supply for aerobic degradation (pure oxygen and/or H₂O₂, more than 150 mg/l are needed for complete MTBE degradation)
• High concentrations of ammonia (additional oxygen demand for nitrification, but nitrate can be used as a source for anoxic MTBE degradation)
• Action of iron and manganese (catalytic action, clogging)
The research partners

• Andreas Dahmke, Torsten Wachter (University Kiel)
• Peter Grathwohl, Martin Bittens, Dai Chen (University Tübingen)
• Peter Werner, Axel Fischer, Michael Selle, Claudia Oehm (Technical University Dresden)
• Erik Arvin and Rasmus Krag (DTU, Denmark)
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