REDUCING COSTS BY QUANTIFYING NATURAL SOURCE ZONE DEPLETION PROCESSES IN RISK-BASED REMEDIATION

Dr. Michael Schubert, RSK Alenco, Germany
Project/site description

- Industrial site in Eastern Germany
- More than 50a of industrial history
- Leakage of approximately 500m³ of a mineral oil product (medium C-fraction) in 2013 through an underground pipeline
- Soil contamination in the vadose zone of ~ 500m³
- LNAPL in an area of ~ 40,000m², ~ 2/3 on private land
- Groundwater contamination with BTEX/TMB and TPH
- No use of groundwater, no water protection zone, no emissions into buildings, no risk to human health
Hydrogeological setting

- Fluvialite sediments, sands and gravel, medium to high permeability
- Depth to groundwater 4 to 7m
- High fluctuation of groundwater levels caused by adjacent river (~ 500m NW) created a smear zone of ~ 2m
- Change of flow directions depending on river levels
Previous measures – authority requirements

- Intense investigation of the contaminated area
- Recovery of free product as long as technically feasible and proportional
  - Recovered product volume ~ 150 m³
  - Stopped in 2018
- Containment of dissolved plume (ongoing)
- Active measures in source zone (leakage point) impossible due to existing infrastructure
- Further remediation required
  - Remediation of residual contamination

7 October 2019
Regulatory background

Authority expectations

- Remediation under German law comprises decontamination and containment (BBodSchG)
- Contaminations younger than 1st March 1999 shall be eliminated, only in case decontamination is unproportional, containment can be accepted
- Natural source zone depletion (NSZD) / monitored natural attenuation (MNA)
  - Is not accepted as a remedial measure!
  - MNA can only be applied in combination with or after active measures
  - Rates and prognosis required!
- Regulator required active measures to actively treat the residual contamination by, e.g.
  - Excavation and ex-situ treatment or deposition
  - Thermal measures incl. hot water flushing and steam injection
  - ISCO
- Expected costs for active measures do exceed 10 Million Euros
Strategy

Identification and quantification of NSZD processes and comparison with active measures

- **Hydrochemistry**
  - Providing initial information on potential biodegradation processes, consumption of electronic acceptors, methanogenesis

- **BACTRAPs**
  - Providing evidence that the environment is able to degrade contaminants of concern

- **CO₂ Traps**
  - Quantification of biodegradation processes, prognosis of ongoing processes and their duration

- **Synthesis**: Cost-benefit analysis of active measures vs. natural biodegradation including sustainability criteria
BACTRAPs – Technical Background

Sensitive and direct proof of biodegradation capability within a contaminant plume with *in situ* microcosms

- Direct monitoring of *in situ* biodegradation in a groundwater system by using microcosms (BACTRAPs) that are loaded with a isotopically ($^{13}\text{C}$)-labelled contaminant

- After recovery, incorporation of $^{13}\text{C}$ into the biomolecules of microorganisms will demonstrate that contaminant degradation can take place within the contaminant plume

- Application over a period of 2-4 months

Source: Isodetect GmbH
BACTRAPs - Application

- m-Xylene (one of the main constituents of concern) as labelled substance
- Two campaigns in 2015 and 2016, 5 months each
- Application in total 5 new and existing wells
  - Area under treatment (biosparging/-venting)
  - Untreated area
# BACTRAPs - Results

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>F</th>
<th>G</th>
<th>H</th>
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<tbody>
<tr>
<td>Alanin</td>
<td>817</td>
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<td>Glycin</td>
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<td>212</td>
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<td>83</td>
<td>124</td>
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<td>264</td>
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<td>112</td>
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<td>82</td>
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<td>Valin</td>
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<td>143</td>
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<td>Prolin</td>
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<td>Methionin</td>
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<td>n.d.</td>
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<td>13</td>
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<td>Glutamin</td>
<td>962</td>
<td>532</td>
<td>105</td>
<td>221</td>
<td>313</td>
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<tr>
<td>Lysin</td>
<td>565</td>
<td>332</td>
<td>76</td>
<td>103</td>
<td>199</td>
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</tbody>
</table>

Total Biomass: 6,560 µg AS/bactrap

n.d. = not detected
BACTRAPs - Results

The environment is able to degrade m-Xylene in all areas of the site, regardless if NA is enhanced or not. However, microbiological activity seems higher in the stimulated area.
CO₂ Traps – Technical Background

CO₂ is end product of all biodegradation

**Anaerobic Degradation (Methanogenesis):**

\[ C_8H_{18} + 3.5 \text{ H}_2\text{O} \rightarrow 6.25 \text{ CH}_4 + 1.75 \text{ CO}_2 \]

**Aerobic degradation:**

\[ C_8H_{18} + 12.5 \text{ O}_2 \rightarrow 9 \text{ H}_2\text{O} + 8 \text{ CO}_2 \]

\[ \text{CH}_4 + 2 \text{ O}_2 \rightarrow 2 \text{ H}_2\text{O} + \text{CO}_2 \]
CO₂ Traps – Technical Background

Installation method:

a) Installation of CO₂ traps by simple direct push (example)

b) Absorption of atmospheric and soil CO₂ in two different absorbent elements (Sodasorb®) over a period of approximately 2-4 weeks

Absorption is the reaction of CO₂ with soda lime:

\[ \text{CO}_2(g) + \text{Ca(OH)}_2(s) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \]
CO₂ Traps – Technical Background

Lab procedure:

a) **Calculation of CO₂ production in LNAPL area**
   - Weighing of absorbed CO₂
   - Calculation of total CO₂ mass produced during application period

b) **Calculation of CO₂ production outside LNAPL area**
   - Weighing of absorbed CO₂
   - Calculation of total (natural) CO₂ mass produced during application period

c) **Analyses of carbon isotope ¹⁴C**
   - Differentiation between fossil und recent carbon C*
   - Calculation of natural and LNAPL induced CO₂ production
   * Fossil Carbon: Mineral Oil
   Recent Carbon: Younger organic material

d) **Synthesis**
   - Calculation of CO₂ as produced by LNAPL biodegradation
   - Calculation of degradation rates
CO₂ Traps - Application

- Two campaigns in winter 2015 and summer 2016, 2 weeks each
- Application at 10 locations, 2 thereof background
- Subsurface installations to prevent manipulation by third parties
### CO₂ Traps - Results

#### Deployment Dates

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Deployment Period 1</th>
<th>Deployment Period 2</th>
<th>Total Days</th>
<th>Moisture</th>
<th>Dry Sorbent Mass (g)</th>
<th>Number of Replicates</th>
<th>Avg CO₂±</th>
<th>CV CO₂±</th>
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<tbody>
<tr>
<td>SGER-R2-CO2-TB</td>
<td>8/20/16 8:55</td>
<td>8/20/16 12:31</td>
<td>NA</td>
<td>13.9%</td>
<td>44,402</td>
<td>2</td>
<td>1.00%</td>
<td>1.95%</td>
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<tr>
<td>SGER-R2-CO2-01</td>
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<td>8/30/16 6:10</td>
<td>NA</td>
<td>11.7%</td>
<td>46,227</td>
<td>2</td>
<td>4.14%</td>
<td>0.67%</td>
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<td>SGER-R2-CO2-02</td>
<td>8/20/16 10:13</td>
<td>8/30/16 12:39</td>
<td>NA</td>
<td>17.9%</td>
<td>46,163</td>
<td>2</td>
<td>3.33%</td>
<td>2.35%</td>
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<td>SGER-R2-CO2-03</td>
<td>8/20/16 9:27</td>
<td>8/30/16 12:50</td>
<td>NA</td>
<td>12.7%</td>
<td>45,012</td>
<td>2</td>
<td>5.44%</td>
<td>0.86%</td>
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<td>8/20/16 10:31</td>
<td>8/30/16 13:13</td>
<td>NA</td>
<td>17.6%</td>
<td>46,173</td>
<td>2</td>
<td>7.91%</td>
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<td>45,023</td>
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<td>16.6%</td>
<td>46,366</td>
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<td>8/28/16 12:55</td>
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<td>16.2%</td>
<td>46,263</td>
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<td>8/28/16 12:55</td>
<td>NA</td>
<td>16.5%</td>
<td>44,542</td>
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<td>8.45%</td>
<td>1.68%</td>
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#### Blank Corrected Results and δ¹³C Analysis (Fossil Fuel)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Carbon Content</th>
<th>CO₂ Flux (µM/m²/sec)</th>
<th>Modern Carbon, As Reported</th>
<th>Std. Dev. Modern</th>
<th>Modern CO₂ Flux (µM/m²/sec)</th>
<th>Contemporary Fossil Fuel CO₂ (g)</th>
<th>Fossil Fuel CO₂ Flux (µM/m²/sec)</th>
<th>Equivalent Fossil Fuel NAPL Loss Rate (gallons/acre/yr)</th>
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</thead>
<tbody>
<tr>
<td>SGER-R2-CO2-TB</td>
<td>0.0%</td>
<td>-</td>
<td>-</td>
<td>66.6%</td>
<td>0.21%</td>
<td>-</td>
<td>36.6%</td>
<td>-</td>
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<td>SGER-R2-CO2-01</td>
<td>3.1%</td>
<td>1.45</td>
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<td>80.9%</td>
<td>0.25%</td>
<td>6.12</td>
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<td>SGER-R2-CO2-02</td>
<td>2.3%</td>
<td>1.07</td>
<td>4.01</td>
<td>57.5%</td>
<td>0.24%</td>
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<td>SGER-R2-CO2-03</td>
<td>4.4%</td>
<td>2.00</td>
<td>9.11</td>
<td>93.6%</td>
<td>0.31%</td>
<td>6.02</td>
<td>11.1%</td>
<td>0.11</td>
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<tr>
<td>SGER-R2-CO2-04</td>
<td>6.9%</td>
<td>3.19</td>
<td>14.57</td>
<td>90.7%</td>
<td>0.25%</td>
<td>13.06</td>
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<td>0.21%</td>
<td>4.36</td>
<td>33.3%</td>
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<td>SGER-R2-CO2-06</td>
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<td>8.73</td>
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<td>8.15</td>
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<td>7.84</td>
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<td>SGER-R2-CO2-08</td>
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<td>3.31</td>
<td>15.40</td>
<td>74.8%</td>
<td>0.30%</td>
<td>11.14</td>
<td>28.7%</td>
<td>0.91</td>
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<td>SGER-R2-CO2-09</td>
<td>3.5%</td>
<td>1.62</td>
<td>7.50</td>
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<td>SGER-R2-CO2-10</td>
<td>7.4%</td>
<td>3.32</td>
<td>15.43</td>
<td>67.6%</td>
<td>0.33%</td>
<td>13.29</td>
<td>16.6%</td>
<td>0.46</td>
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</tbody>
</table>

#### Note

1/ CO200507_v1.09, 2019

**Green:** High loss rate  
**Blue:** Medium loss rate  
**Red:** Low loss rate

**Average loss rate:**
~ 1 l per m² and year
Conclusions

Remedial alternative analysis (RAA) including MNA accepted by the regulator

- Residual contamination on the client’s property
  - Authority agrees, that further cost intensive unsustainable measures like excavation, hot water flushing and steam injection are not appropriate and proportional

- Monitored Natural Attenuation (MNA)
  - Is the appropriate method to further manage the contaminated area
  - Natural degradation rates are currently at 1l per m² and year
  - MNA to be continued to verify present results and prognosis

- Active measures to be continued as long as required, technically feasible and proportional:
  - Containment of the dissolved plume
  - Biosparging/-venting in source zone
Thank you!