Predicting Natural Attenuation of a large urban CHC-plume to aid regulatory decision making

Grant WN 0367-69 of the BMBF KORA funding priority

3rd European Conference on Natural Attenuation and In-situ Remediation at DECHEMA / Frankfurt M.

Topics

• The contamination source
• Case history + plume development
• Spatial distribution of CHC-metabolites and Fe in 3d
• Case hypotheses: the controlling factors
• Sorption on low C\textsubscript{org} - sands and gravels

Session "Processes" at 17:30: Dethlefsen et al. in more detail

• The reactive transport model
• Significance of model prediction results
• Conclusions: transfer and decision making
The location

Hannover-Suedstadt

Lower Saxony

Central Station

Study Area

Source

Not to scale

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The contamination source

- whole sale dealer for chemicals from 1920's - 1984
- groundwater contamination reports from 1976
- **CHC**, BTEX, HC, acids
- Estimated cumulated spill: >250 tons of solvents
- pump & treat on site started in 1979
- pump & treat in plume area 1988 - 1993
- **Slurry wall** and water management scheme on site from 1993
- DNAPL recovery approx. 200 tons CHC
1976 Contamination discovered

- Depression of groundwater table \( \geq 2 \text{ m} \)
- \( > 1400 \mu \text{g/L} \Sigma \text{CHC} \)

**NW extension of plume**

- \( t \) subway construction (from 1972)
- \( S \) active source
- \( b \) water tapping for industry

(L artificial lake has sealed bottom)
1979 NNW-SSE subway construction

- Depression of groundwater table
  \[ \geq 7 \text{ m} \]
  \[ > 1300 \mu g/L \Sigma \text{CHC} \]

  \[ \rightarrow \text{large volumes of the aquifer were drained} \]

  W extension of plume

  t subway construction

  S active source
1984 EW subway construction

- Depression of groundwater table $\geq 2$ m
- $> 2000 \, \mu g/L \, \Sigma$ CHC

**NW extension of plume**

- t subway construction
- S pump & treat at source
1992 EW subway construction

- Depression of groundwater table ≥ 2 m
- > 2000 μg/L Σ CHC

NW extension of plume

t subway construction

w water abstraction

S pump & treat at source
Immobile metabolite-plume (cDCE) in aquifer

To explain the observed immobility of the metabolite plume \( (v_a \approx 100 \text{ m/a}) \), hypotheses were proposed and tested:

1. unknown sources?
2. erosion channel as source?
3. heterogenous flow?
4. high sorption?
Improving network of observation wells

testing, validating, building

20 new well groups:
- a. shallow
- b. medium deep
- c. deep well

old observation wells 2'' – 5'', screen ≥ 2 m
new observation wells 2'', screen 2 m

3D-representation required!
Fe monitoring
$E_H$ monitoring
(operational ORP, SHE)
VC monitoring

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cDCE monitoring

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Estimating dissolved inventory of metabolites

1. Interpolation of monitoring data (cDCE, VC & TCE) into voxelgrid using Open-Source GIS GRASS
2. 3D-Grid evaluation
3. Inventory of dissolved metabolites
4. Output of initial conditions for model

Decrease of metabolite mass observed between 2003/04 – 2006 (≤ 118 wells).
Mass Σ CHC (previous monitoring, << wells, diff. accounting method). TCE minor
The aquifer

Medium - coarse grained sands: glacio-fluviatile, Upper Terrace

$\kappa_f: 1 \times 10^{-4} - 1 \times 10^{-5} \text{ m/s (model)}$

Fine - coarse gravel, stones: glacio-fluviatile, Lower Terrace

$\kappa_f: \text{approx. } 2 \times 10^{-3} \text{ m/s (model)}$

Lower Cretaceous marine mudstone

Fe(III)oxihydroxide crusts

Phreatic surface

Clay lenses, ice wedges (not shown)

5 cm
From drill database to 3D model

- 20 observation wells
- 16 direct push holes
- 130 database records (validated)
- 10 vertical layers, 250 000 knots,
- 3.5 x 3 km, finite difference, phreatic, code FeFlow
Hypothesis erosion channel as source

channel as 2\textsuperscript{nd} source

mudstone, lower cretaceous
Erosion channel as source? **No!**

**Hypothesis:**
DNAPL gravity flow into erosion channel (subglacial) → now a secondary source for dissolution of CHC?

**Methods:**
S-wave seismic transects + DP-logs (EC-profile, VAP) to verify gravel/clay boundary + 60 DP GW-samples

**Results:**
VC and ethene found in channel, but no TCE or PCE
S-wave seismics is a good tool for subsurface investigation in densely populated areas.
Hypothesis high sorption (... on coal & lithic particles)

TOC = 0.075 wt.%

TOC has up to $\times 100$ higher sorption capacity if incoaled.
$\leq$ anthracite in sand fraction

- hysteresis (sorption - desorption)
- kinetic control

Hartog et al. 2004: GCA
Ran et al. 2005: ES&T.
Sorption parameters should be site specific

Session "Processes" at 17:30: Dethlefsen et al. in more detail

"Henry"-approach not suitable

Two-Site-Non-Equilibrium-Sorption (van Genuchten) is required to fit experimental data with $^{14}$C cDCE and aquifer sediment columns (3) + lignite blank column (1)

Sorption parameters should be site specific

Session ''Processes'' at 17:30: Dethlefsen et al. in more detail
Inventories measured and estimated

CHC, sorbed\(^1\)

CHC\(^2\), dissolved

products of reductive and oxidative dechlorination of TCE, cDCE and VC:

\[
\text{C}_2\text{H}_4, \text{C}_2\text{H}_6 \rightarrow \text{CO}_2
\]

6 - 16 t

2 t

? t

\(^1\) result of inverse modeling

\(^2\) results from monitoring
Conceptual reactive transport model

TCE$_{s1}$, TCE$_{s2}$, cDCE$_{s1}$, cDCE$_{s2}$, VC$_{s1}$, VC$_{s2}$

K_d, K_d,rate

TCE$_{sol}$, cDCE$_{sol}$, VC$_{sol}$

rate, cDCE$_{sol}$, VC$_{sol}$

CO$_2$ + H$_2$O

rate (high)

Oxidizing reaction zone II

GW-flow direction

Ethene

Red. reaction zone I

rate

Conceptual reactive transport model

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Initial distribution of VC and cDCE
Prediction results

council monitoring

project

Beginner Prognoserechnung

Legende

Summe LHKW

cDCE

VC

TCE

Fit der Modellergebnisse

Prognose über Alldaten

Prediction

Funktion 1. Ordnung
Modeling cDCE attenuation
## Results of reactive transport modeling

<table>
<thead>
<tr>
<th></th>
<th>TCE</th>
<th>cDCE</th>
<th>VC</th>
<th>Σ CHC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CHC dissolved 2005</strong></td>
<td>0.1 t</td>
<td>1.2 t</td>
<td>0.8 t</td>
<td>2.1 t</td>
</tr>
<tr>
<td><strong>CHC sorbed 2005</strong></td>
<td>0.6 – 1.7 t</td>
<td>3.1 – 8.0 t</td>
<td>2.3 – 6.3 t</td>
<td>6 – 16 t</td>
</tr>
<tr>
<td><strong>Inventory CHC 2005</strong></td>
<td>0.7 – 1.8 t</td>
<td>5.3 – 9.2 t</td>
<td>3.1 – 7.1 t</td>
<td>8 – 18 t</td>
</tr>
<tr>
<td><strong>Two-site retardation model</strong> (R changes with $K_{oc}$)</td>
<td>$R_s=3$, $R_R=3$</td>
<td>$R_s=2$, $R_R=2$</td>
<td>$R_s=1.9$, $R_R=1.9$</td>
<td>--</td>
</tr>
<tr>
<td>Reaction rate $K$ in 1/s</td>
<td>$1 \times 10^{-8} - 5 \times 10^{-8}$</td>
<td>$1 \times 10^{-8} - 5 \times 10^{-8}$</td>
<td>$2 \times 10^{-8} - 1 \times 10^{-7}$</td>
<td>--</td>
</tr>
<tr>
<td>Mass turnover rate</td>
<td>0.025 t/a</td>
<td>0.3 t/a</td>
<td>0.3 t/a</td>
<td>--</td>
</tr>
<tr>
<td><strong>Compliance with threshold value for MNA</strong></td>
<td>20 – 35 a to &lt; 100 µg/l Σ CHC</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NA: feasible and finite in this case

1. Source is secured. 2. Plume is receding. 3. Key degradation processes were identified by evaluation of monitoring. 4. They were implemented into the 3D reactive transport model (10 species). 5. Model prediction says: 20 – 35 years will pass before regulatory level (100 µg/L CHC) will be met.
Conclusions: transfer and decision making

- Hypothesis Unknown sources --- not likely
- Hypothesis **channel** as secondary source --- No!
- Hypothesis heterogenous flow domains --- possibly: ice wedges
- Hypotheses **kinetic sorption** on kerogens --- Yes!
  - aquifer sediment contains kerogens in sand fraction
  - site specific sorption isotherms were obtained from column experiments, kerogens displayed slow desorption properties
- The plume has loaded the aquifer, it is a source now itself
- transfer of parameters to 1D, 3D reactive transport code
- Immobile plume behaviour is satisfactorily explained
- Natural degradation of CHC down to regulatory level (100 µg/L Σ CHC) has been predicted for a timespan of **up to 35 years**
- A secured source, a site specific model based on **quality controlled monitoring** (aimed at 3D representation of processes) are mandatory prerequisites.
- MNA: "Smart" monitoring and assessment of prediction have to continue
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