Time-integrated monitoring of PAHs in ground water using the Ceramic Dosimeter passive sampling device

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Sampling over time

Discontinuous

Continuous

Time-integrated monitoring of PAHs

May 19 to Nov 19
Passive Sampling Device

- No pumps required
- Undisturbed water sampling

The basics of passive sampling
Passive Sampling Devices

- Undisturbed water sampling

The basics of passive sampling
## Devices used in groundwater

<table>
<thead>
<tr>
<th>Sampler</th>
<th>Substanzen</th>
<th>Typ</th>
<th>Sampling times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passive-Diffusion-Bag-Samplers (PDBS)</td>
<td>BTEX, chlorinated hydrocarbons; metals, trace elements</td>
<td>Equilibrium, quantitative</td>
<td>1 – 2 weeks</td>
</tr>
<tr>
<td>Diffusions-Multi-Layer-Sampler (DMLS)</td>
<td>BTEX, metals, sulfate, nitrate, chloride</td>
<td>Equilibrium, quantitative</td>
<td>2 – 4 weeks</td>
</tr>
<tr>
<td>Solid-Phase-Micro-Extraction (SPME)</td>
<td>BTEX, PAHs, PCBs, VOCs, Pesticides</td>
<td>Equilibrium, quantitative</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Gore®-Sorber</td>
<td>BTEX, MTBE, PAK, VOCs, SVOC</td>
<td>Equilibrium, semi-quantitative</td>
<td>2 weeks</td>
</tr>
<tr>
<td>Gaiasafe-Sampler</td>
<td>organic substances, metals, sulfate, phosphate</td>
<td>Non-equilibrium [Time-integrating] semi-quantitative</td>
<td>2 days – 2 months</td>
</tr>
<tr>
<td>Semi-Permeable-Membrane-Device (SPMD)</td>
<td>PCBs, chloro-Pesticides, BTEX</td>
<td>Non-equilibrium [Time-integrating] potentially quantitative</td>
<td>about 4 weeks</td>
</tr>
<tr>
<td>Ceramic-membrane based devices</td>
<td>PAK, BTEX, chlorinated hydrocarbons</td>
<td>Non-equilibrium [Time-integrating] quantitative</td>
<td>several months</td>
</tr>
</tbody>
</table>

Ceramic membrane-based devices

Original idea and design: P. Grathwohl – University of Tübingen

[Ceramic Dosimeter: German Patent DE 198 30 413 A1, 1999]

- 5 cm long
- 1 cm in diameter
- pore size: 5 nm
- thickness: 1.5 mm

Ceramic tube with sorbent

Microbes cannot enter

Robust diffusion barrier

The Ceramic Dosimeter
Calculation of average water concentrations

\[ M = D_e \frac{\Delta C}{\Delta x} \cdot A \cdot t \]

- \( M \) = accumulated mass
- \( D_e \) = effective diffusion coefficient
- \( \Delta C \) = \( C_{\text{water}} - C_{\text{Dosi}} = C_{\text{water}} - 0 = C_{\text{water}} \)
- \( \Delta x \) = thickness of the ceramic tube
- \( A \) = surface area of the ceramic tube
- \( t \) = sampling time

\[ D_e = D_w \cdot \varepsilon^m \]

Archie's law (for diffusion in porous media)

- \( D_e \) = effective diffusion coefficient
- \( D_w \) = diffusion coefficient in water
- \( \varepsilon \) = tube porosity
- \( m \) = Archie's law exponent

The Ceramic Dosimeter
Previous applications

1. H. Martin et al.: CSIRO (Australia)/University of Tübingen (Germany)

using *Dowex Optipore* as a sorbent material

[Previous applications graph showing water concentration over time for conventional water samples and dosimeter average.]

[Martin H. et al. 2003, ES&T 37, 1360]
Previous applications

2. H. Martin (Ph.D. Thesis),
   M. Piepenbrink (Diploma Thesis)
   University of Tübingen (Germany)

**Amberlite IRA-743** for sampling of PAHs
- good wettability
- high affinity for PAHs
- long-term stability
Study design

- Tubes filled with sorbent (~ 1.5 g) and saturated with distilled water
- Former gas works site in Germany
- 3 Boreholes (named 1 to 3)
- Ceramic Dosimeters fixed on strings
- Positioned in screened portion of each bore hole in 6-8 m depth

Time-integrated monitoring of PAHs
Sampling scheme for each bore hole

- Ceramic Dosimeters:
  - 12 months

- Snap-shot samples (taken in duplicate):
  - every second week for first 6 months
  - once after 12 months

Time-integrated monitoring of PAHs
Chemical analysis

- Ceramic Dosimeters:
  - In aceton
  - + Internal standard

- Snap-shot samples:
  - 700 mL water to
  - 10 ml of cyclohexan and
  - 10 µL internal deuterated standard

Time-integrated monitoring of PAHs
Appearance after field application

Bore hole 1 (3)
No visible changes throughout sampling

Bore hole 2
Brownish-black discoloration due to unexpected tar oil phase

Time-integrated monitoring of PAHs
Determination of aqueous concentrations:
- Snap-shot & Dosimeter-derived -

Time (months)

aqueous concentration [µg/L]

0 5 10 80 85 90

Nap

Snap-shot (raw data)

Time-averaged PAH conc. derived from snap-shot

Dosimeter-derived concentrations

Time-integrated monitoring of PAHs
Comparison of aqueous concentrations:

Time-integrated monitoring of PAHs
Direct comparison: Dosimeter-derived vs. time-averaged snap-shot samples

Borehole 1

Borehole 2

Borehole 3

Time-integrated monitoring of PAHs
2 x 6 months versus 1 x 12 months:

Time-integrated monitoring of PAHs
Summary: Field evaluation

1. Determination of aqueous concentration
   Ceramic Dosimeter ≅ time-averaged snap-shot samples

2. Additional information required
   Temperature

3. Time frame
   Suitable for long-term monitoring

Time-integrated monitoring of PAHs
Summary: Advantages & Limitations

**Advantage:**

→ Stability and thickness of ceramic membrane

**Limitation:**

→ Low sampling rates
  
  (1.5 to 2.5 mL per day at 14°C)

→ Ceramic dosimeter detection limits:
  
  for 1 µg/L of PAH = 15 days
  
  for 0.1 µg/L of PAH = 150 days

Time-integrated monitoring of PAHs
Conclusion

Ceramic Dosimeter filled with Amberlite IRA-743

→ Proven suitability for the cost- and labor-efficient long-term monitoring of PAHs in groundwater

→ Ready to be widely applied!

→ More information now available:
   Bopp et al., 2005, J. Chromatography A, 1072, 137-147

Time-integrated monitoring of PAHs
Further developments

**Toximeter**

- based on ceramic membrane
- designed to combine chemical analysis and toxicological endpoints

[Bopp, Dissertation, 2004]
Many thanks for:

Helpful discussions
• Peter Grathwohl
• Holger Martin
• Matthias Piepenbrink

Fantastic technical help
• Thomas Wendel
• Annegret Walz

Financial support
German Federal Ministry of Education and Research
[Project RETZINA, 02WT0041]