Fractionation and chemical analysis of watercourse SPMD extracts

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Content:

• Introduction
• Pre-treatment of SPMD extracts
• Fractionation plan
• Substance classes and single compounds
• Example of physico-chemical calculations
• Summary and outlook
**Introduction** - Semipermeable Membrane Devices (SPMDs)

- SPMDs are passive in situ partitioning systems
- SPMDs can monitor truly dissolved organic contaminants (air/water/sediment)
- SPMDs mimic bioconcentration processes and allow detection of trace chemicals
SPMD Design

Polyethylene Membrane
(75-90 µm thick)

Pore Size <10 Å

Lipid (Triolein)

Contaminant Molecule

Water

Interior

SPMD
Fractionation plan

Biofouling removal

Sealed in can

Transport

SPMD exposure

Dialytic recovery of sequestered contaminants

Organic solvent

Dialysate

Discard

Size exclusion chromatography + Flash-Chromatography

Chromatographic analysis of contaminants in 4 fractions
SPMD deployment sites

- in the highly polluted area of Bitterfeld/Wolfen
- chemical production plants from 1960-1991
- 3000 t DDT; 7600 t HCH; other residues
SPMD Sampling site - Spittelwasser Creek
Pre-treatment and fractionation of SPMD extracts

- Dialytic recovery of analytes with hexane
  - for solvent exchange (trioleine with hexane)
- Size exclusion chromatography (SEC)
  - for separating trioleine (and sulfur) from the main hexane fraction
- Flash-Chromatography
  - modified silica-column chromatography (*Gogou et al. 1998*)
  - elution of substances with different polar solvents
  - separation of extract into 4 fractions (from unpolar to polar compounds)
Fractionation of SPMD extracts with flash-chromatography

F1 : chlorobenzenes, PCBs, n-alkanes
F2 : branched alkanes, PAHs, alkyl-PAHs, HCHs
F3 : chloronitrobenzenes, DDTs, DDDs
F4 : oxy-PAHs, phthalates, phenoles
Fractions and compound classes

• Often analyzed substance classes: PAHs, HCHs, PCBs, Dioxines, herbicides

• Analysis of whole extract:
  Fraction 1: polychlorinated benzenes, PCNs, PCBs, alkanes; tetrabutyltin
  Fraction 2: branched alkanes, PAHs, alkyl-PAHs, DDTs, DDDs, DDEs,
               alkyl benzenes; diphenylether
  Fraction 3: chloronitrobenzenes, alkylated nitrophenoles, HCHs, acridines,
               oxy-PAHs; benzophenone
  Fraction 4: phthalates, chlorophenoles, alkylphenoles, dyestuffs, musk ketones

• logK_{OW} range of detected substances: 1,1 - 7,4
Selected chemicals sampled by SPMDs

High amounts of **2-(methylthio)benzothiazole** (MTBT) in SPMD extracts

- also found in german bight of the north sea (*Bester et.al. 1997*)
- Pathway: biotransformation of fungicide TCMTB (Busan) (*Brownlee 1992*) or metabolite from rubber production processes

![Chemical structures](image)

TCMTB → MBT → MTBT

$logK_{OW} : 3,15$
Selected chemicals sampled by SPMDs

• High amounts of **Nitrofen** (TOK) in SMPDs
• used as weed killer/fungicide
• carcinogen and suspected endocrine disruptor
• forbidden in USA since 1983

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M      : 284 g/mol
logK\text{OW} : 4.64
S      : 1 mg/L
Selected chemicals sampled by SPMDs

- **Prometryn** (s-triazine compound)
- wide used herbicide
- produced in Bitterfeld from 1960 to 1990
- found in sediment in the area of Bitterfeld and confirmed as a chemical causing significant toxicity to algae (scenedesmus) (*Brack et al. 1999*)

\[
\begin{align*}
\text{M} & : 241 \text{ g/mol} \\
\log K_{\text{OW}} & : 3.51 \\
S & : 33 \text{ mg/L}
\end{align*}
\]
Brief summary

- SPMDs sample a large range of weak hydrophobic to hydrophobic substances.
- SPMDs simulate a „worst case scenario“ in terms of the number of accumulated chemicals.
- SPMDs sample only truly dissolved substances.

Main approaches:

- application of fractionation techniques for the determination of trace levels of contaminants → toxicity identification evaluation (TIE)
- calculation of distribution patterns for known toxicants
Example of physico-chemical calculations

- fugacity quotients -
Calculation of water concentrations

- linear model (for linear uptake kinetics)
- used for hydrophobic substances

The ambient "truly dissolved" water concentration \( C_w \) can be estimated based on the concentration in the SPMD \( C_{\text{SPMD}} \), the volume of the SPMD \( V_{\text{SPMD}} \), the effective sampling rate \( R_s \), and the time of deployment \( t \):

\[
C_w = C_{\text{SPMD}} \times V_{\text{SPMD}} / (R_s \times t)
\]

- equilibrium model (assuming SPMD has reached saturation for an analyte)
- used for less hydrophobic substances

\[
C_w = C_{\text{SPMD}} \times K_{\text{LW}}
\]
Fugacity quotients

- fugacity quotients give potential flux directions (if water or sediment are potential sources of contaminants)
- important for understanding the partitioning of substances between different compartments (global partitioning, seasonal trends)

\[
\begin{align*}
  f_w &= \frac{C_w}{Z_w} & Z_w &= \frac{1}{H} \\
  f_S &= \frac{C_S}{Z_S} & Z_S &= \frac{(f_{OC} \rho K_{OC})}{H} \\
  \text{fugacity quotient:} & \quad \frac{f_w}{f_S}
\end{align*}
\]

- \( f = \text{fugacity} \)
- \( Z = \text{fugacity capacity} \)
- \( H = \text{Henry’s law const} \)
- \( C = \text{concentration} \)
Fugacity quotients

\[ \frac{f_w}{f_s} \]

- Indeno[1,2,3]pyrene
- Benzo[g,h,i]perylene
- Benzo[a]pyrene
- Benzo[k]fluoranthene
- Benzo[b]fluoranthene
- Chrysene
- Benzo[a]anthracene
- Pyrene
- Fluoranthene
- Anthracene
- Phenanthrene

\[ 1 \times 10^{-4} \quad 1 \times 10^{-3} \quad 0.01 \quad 0.1 \quad 1 \quad 10 \]

Equilibrium

- Flux from sediment to water
- Flux from water to sediment
Summary and Outlook

SPMDs sample a broad spectrum of hydrophilic and lipophilic substances.

A fast non target screening of SPMD extracts with the presented analytical methods is a good basis for a decision-making of further steps in SPMD research, including:

- determining physico-chemical properties for selected contaminants
- choosing suitable biotests for SPMD extracts
- powerful basis for toxicity identification evaluations (TIE)
Thank you!
Summary and Outlook

SPMDs sample a broad spectrum of truly dissolved hydrophilic and lipophilic substances.

The fractionation and analytical determination of SPMD extracts with the methods presented here, are a solid basis for further steps in SPMD research, including:

• determining physico-chemical properties for selected contaminants
• choosing suitable biotests for SPMD extracts
• powerful basis for toxicity identification evaluations (TIE)
AMDIS

Automated Mass spectral Deconvolution & Identification System (NIST)

AMDIS automatically extracts pure (background free) component mass spectra from highly complex GC-MS data files and uses these purified spectra for a search in a mass spectral library.

Analysis steps:

• noise analysis
• component perception
• spectrum deconvolution
• compound identification