Fractionation and chemical analysis of watercourse SPMD extracts

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- Pre-treatment of SPMD extracts
- Fractionation plan
- Substance classes and single compounds
- Example of physico-chemical calculations
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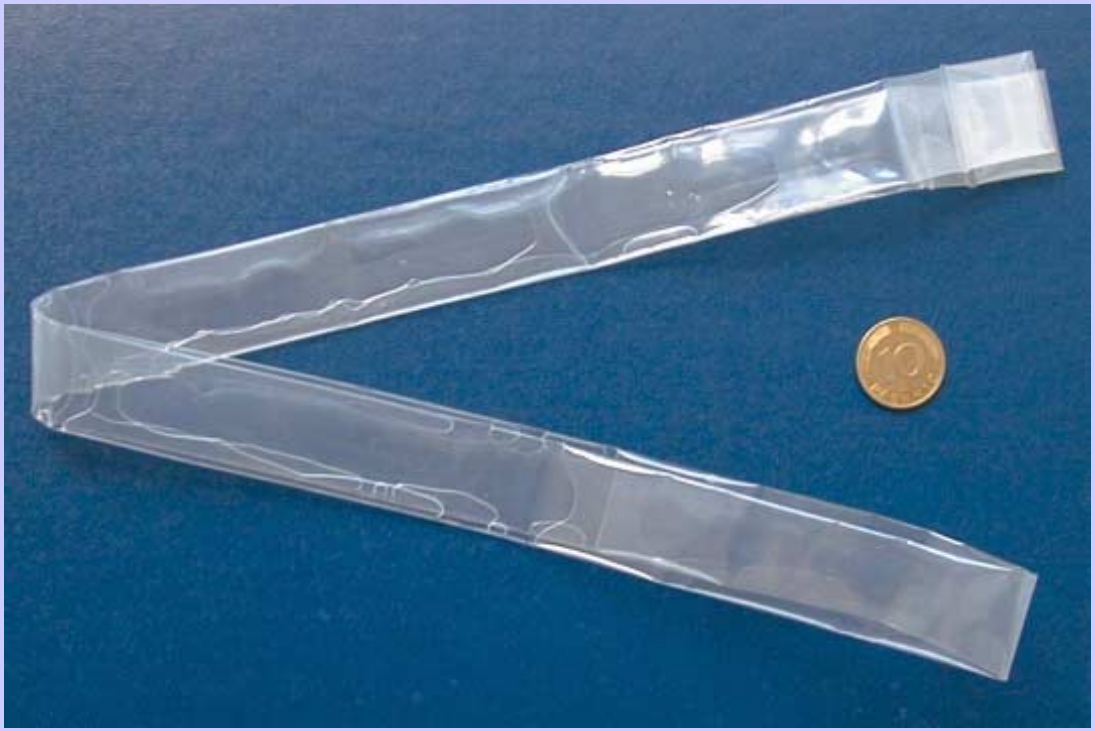
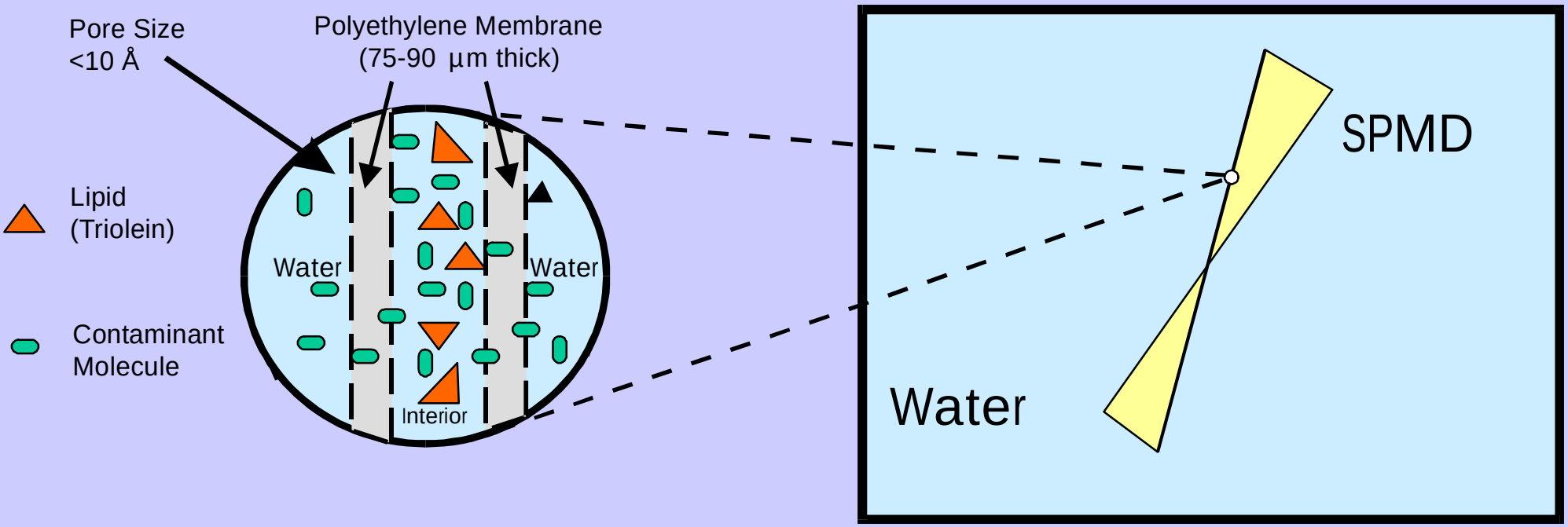
Introduction - **S**emi**p**ermeable **M**embrane **D**evices (SPMDs)

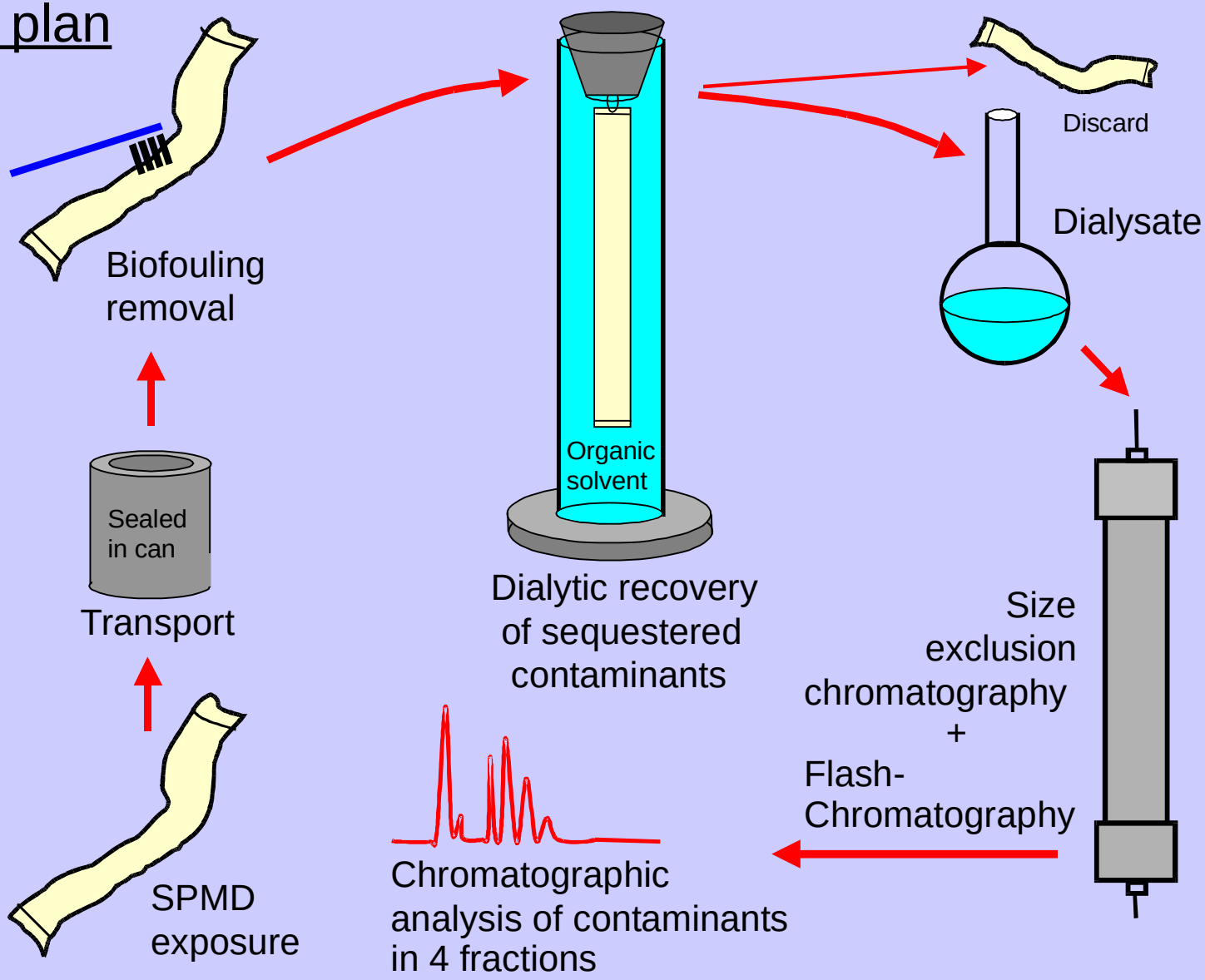
- SPMDs are passive in situ partitioning systems
- SPMDs can monitor truly dissolved organic contaminants (air/water/sediment)
- SPMDs mimic bioconcentration processes and allow detection of trace chemicals



SPMD Design

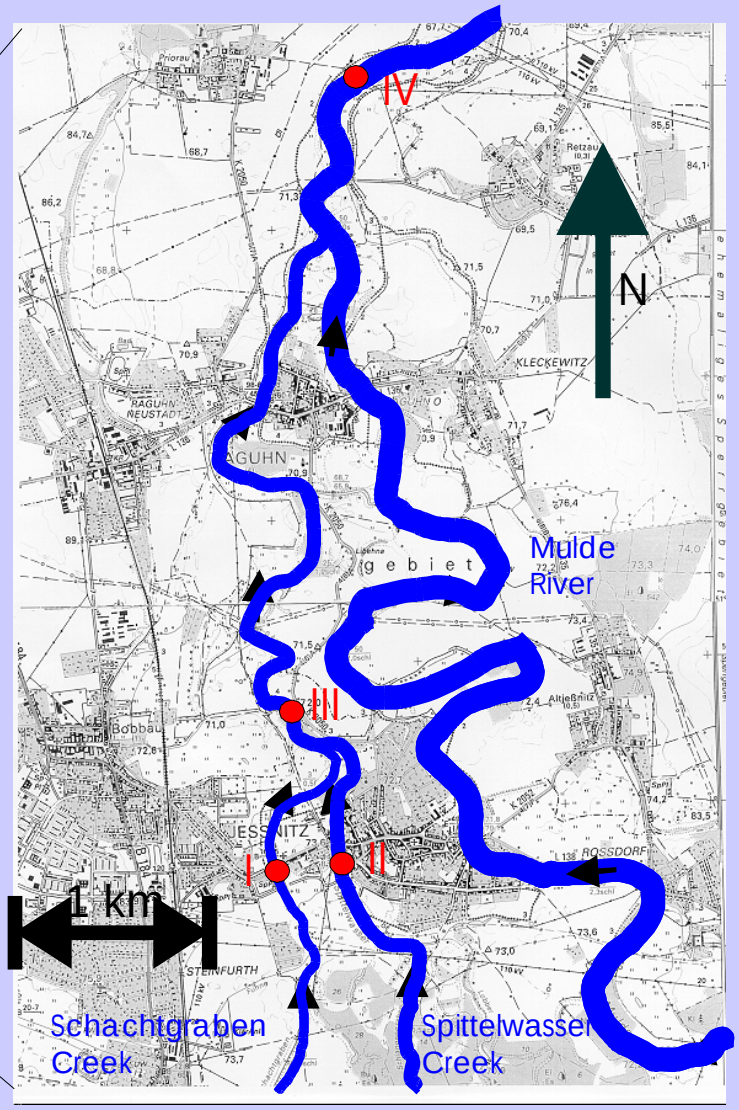

Pore Size
<10 Å
Polyethylene Membrane
(75-90 µm thick)
Lipid
(Triolein)
Contaminant
Molecule
Water
Water
Interior
SPMD
Water

Fractionation plan



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

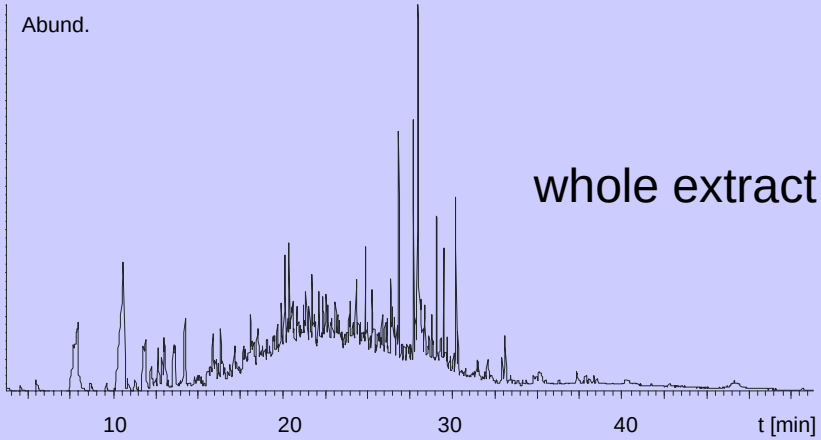


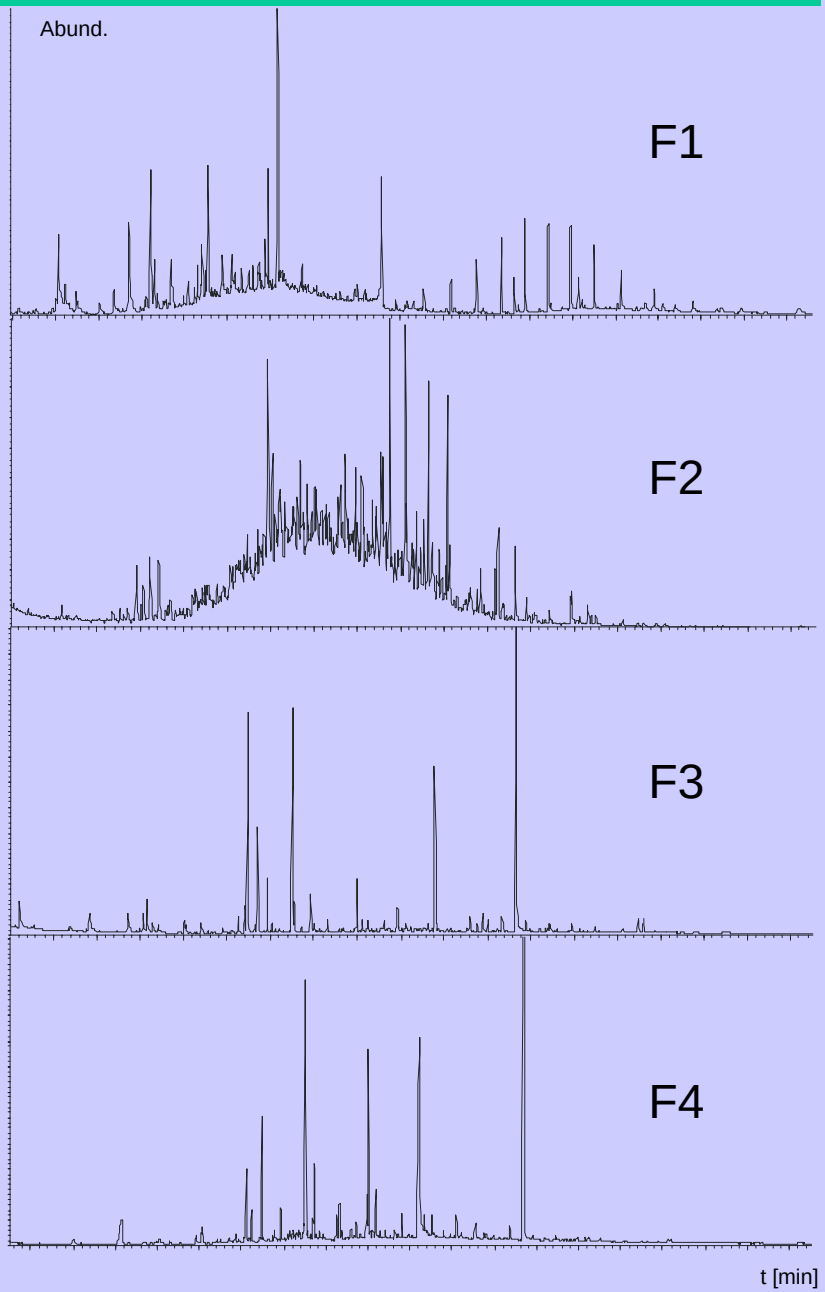
SPMD Sampling site - Spittelwasser Creek

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

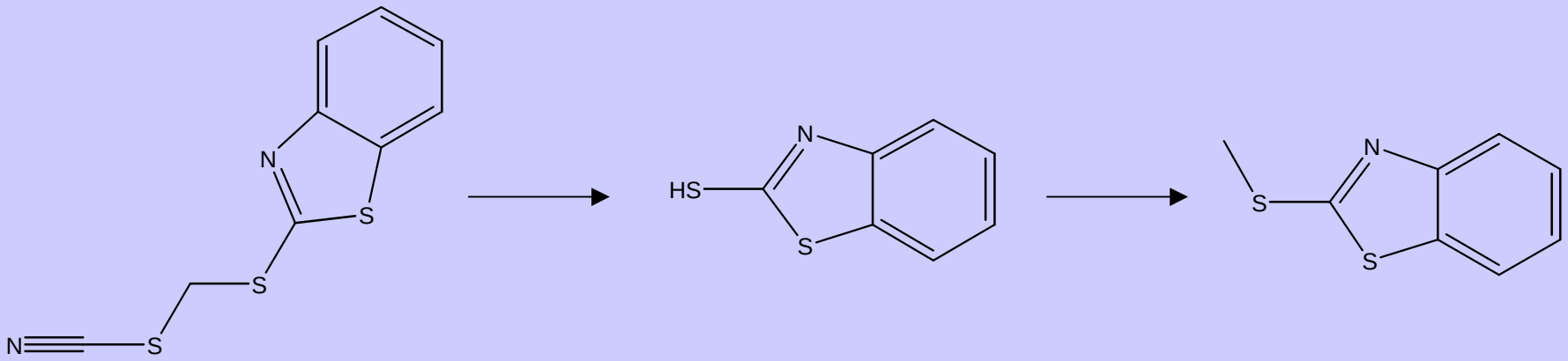
  Fraction 4: phthalates, chlorophenoles, alkylphenoles, dyestuffs, musk ketones

- $\log K_{OW}$ 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

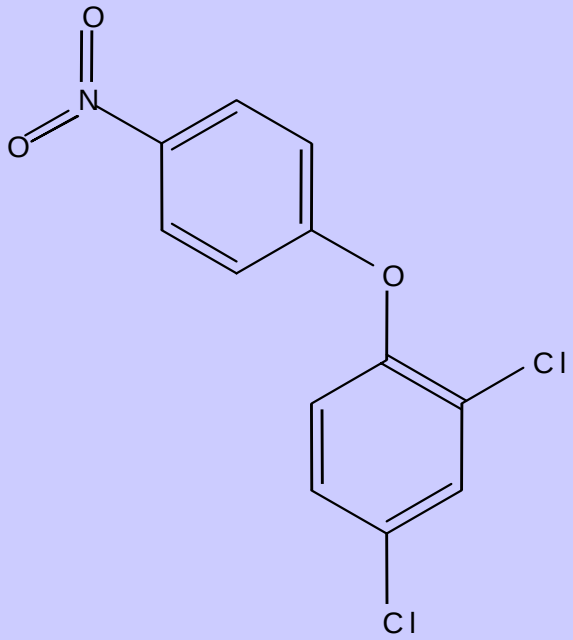


TCMTB MBT MTBT

$\log K_{OW}$: 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



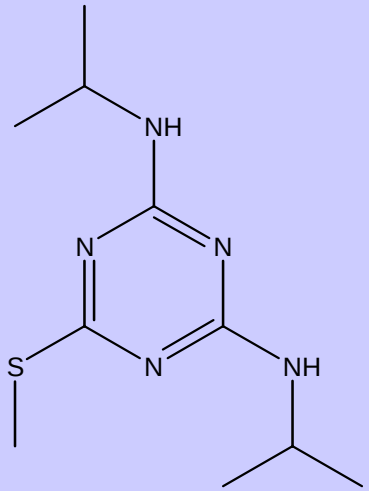
M : 284 g/mol

$\log K_{OW}$: 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)*



M : 241 g/mol

$\log K_{OW}$: 3,51

S : 33 mg/L

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 know 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_{SPMD}), the volume of the SPMD (V_{SPMD}), the effective sampling rate (R_s), and the time of deployment (t):

$$C_w = C_{SPMD} * V_{SPMD} / (R_s * t)$$

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

$$C_w = C_{SPMD} * K_{LW}$$

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 compartiments (global partitioning, seasonal trends)

$f_w = C_w/Z_w$ $\quad Z_w = 1/H$

$f_S = C_S/Z_S$ $\quad Z_S = (f_{OC}\, \rho\, K_{OC})/H$

fugacity quotient: $\mathbf{f_w / f_S}$

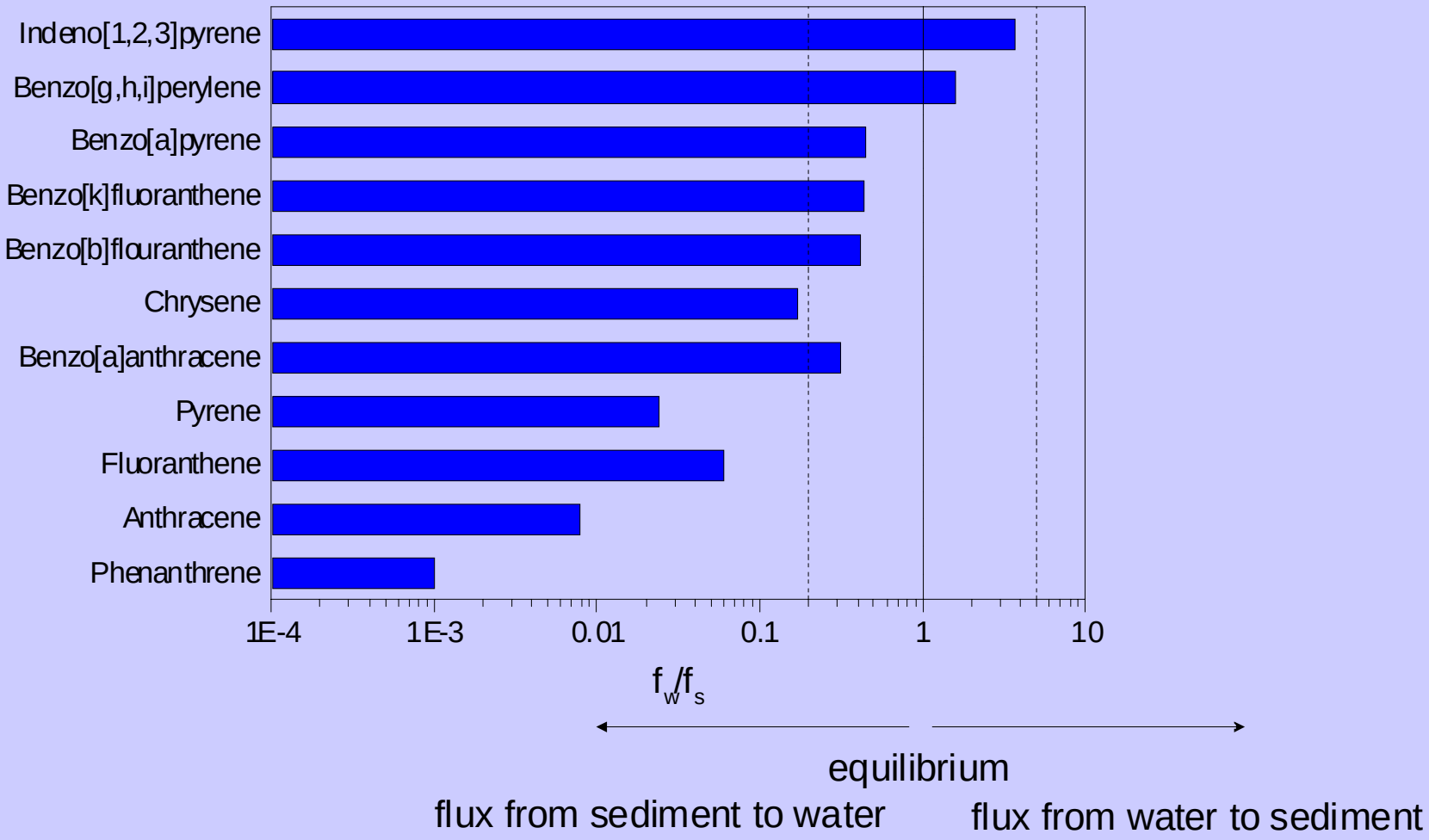
f = fugacity

Z = fugacity capacity

H = Henry´s law const

C = concentration

Fugacity quotients



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:

- determing physico-chemical properties for selected contaminants
- choosing suitable biotests for SPMD extracts
- powerfull 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:

- determing physico-chemical properties for selected contaminants
- choosing suitable biotests for SPMD extracts
- powerfull basis for toxicity identification evaluations (TIE)

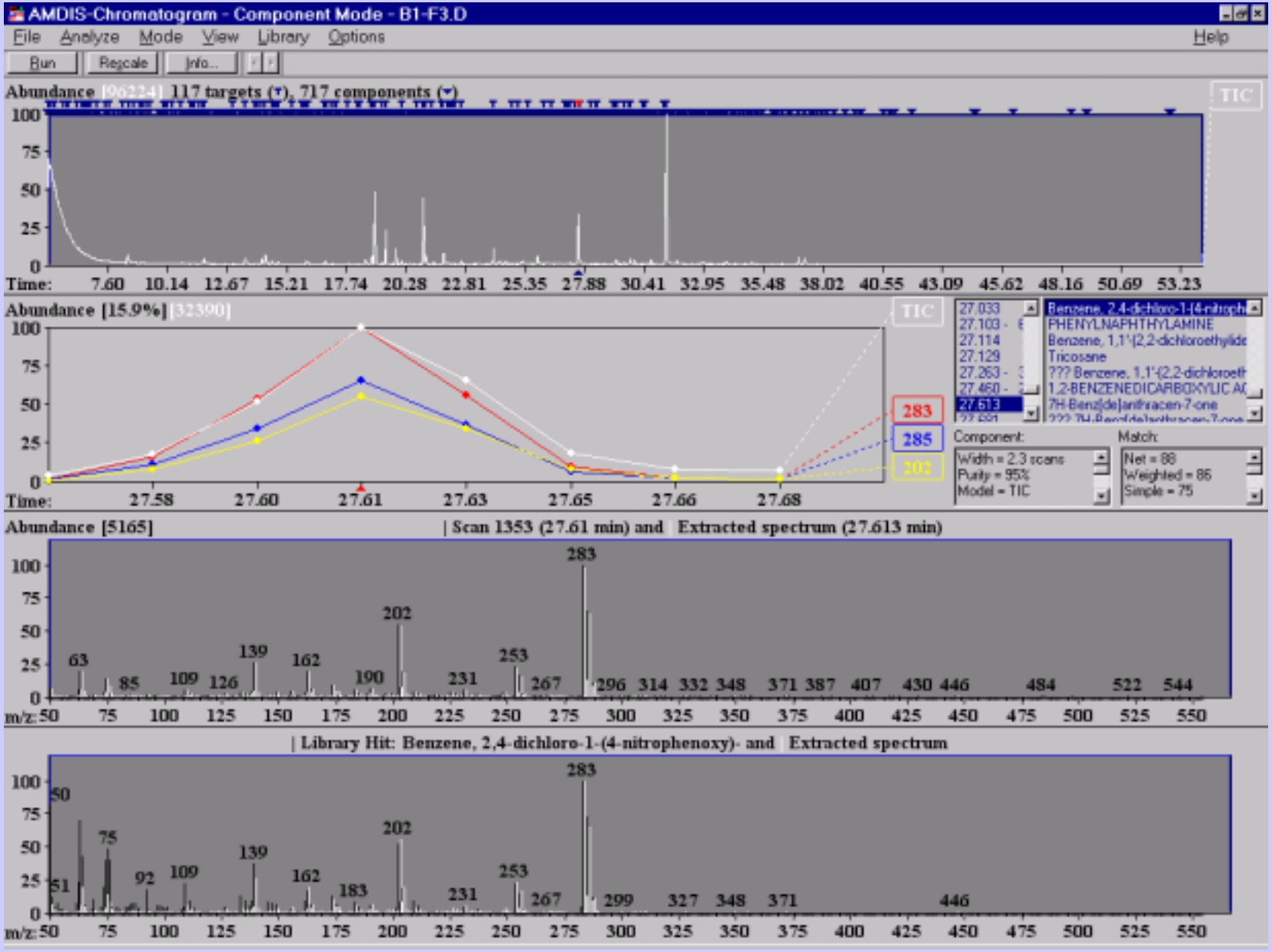
AMDIS

Automated **M**ass spectral **D**econvolution & **I**dentification **S**ystem (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


AMDIS-Chromatogram - Component Mode - B1-F3.D
File Analyze Mode View Library Options Help
Run Rescale Info...
Abundance [96224] 117 targets (▾), 717 components (▾)
TIC
Time: 7.60 10.14 12.67 15.21 17.74 20.28 22.81 25.35 27.88 30.41 32.95 35.48 38.02 40.55 43.09 45.62 48.16 50.69 53.23
Abundance [15.9%] [32390]
TIC
283
285
202
Time: 27.58 27.60 27.61 27.63 27.65 27.66 27.68
27.033
27.103 - 6
27.114
27.129
27.263 - 3
27.460 - 2
27.613
Benzene, 2,4-dichloro-1-(4-nitroph
PHENYLNAPHTHYLAMINE
Benzene, 1,1'-(2,2-dichloroethylide
Tricosane
??? Benzene, 1,1'-(2,2-dichloroeth
1,2-BENZENEDICARBOXYLIC AC
7H-Benz[de]anthracen-7-one
Component:
Width = 2.3 scans
Purity = 95%
Model = TIC
Match:
Net = 88
Weighted = 86
Simple = 75
Abundance [5165] | Scan 1353 (27.61 min) and Extracted spectrum (27.613 min)
283 202 139 162 253 63 85 109 126 190 231 267 296 314 332 348 371 387 407 430 446 484 522 544
m/z: 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550
| Library Hit: Benzene, 2,4-dichloro-1-(4-nitrophenoxy)- and Extracted spectrum
283 202 139 162 253 50 75 92 109 51 183 231 267 299 327 348 371 446
m/z: 50 75 100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550