



# **Fractionation and chemical analysis of watercourse SPMD extracts**

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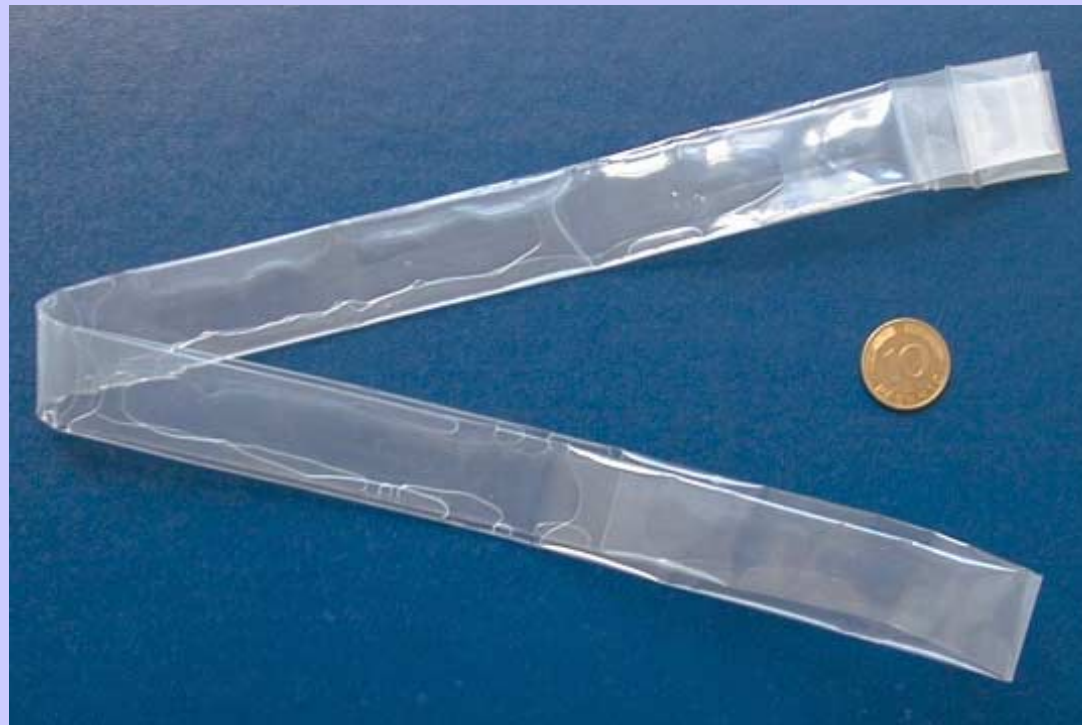


## Content:

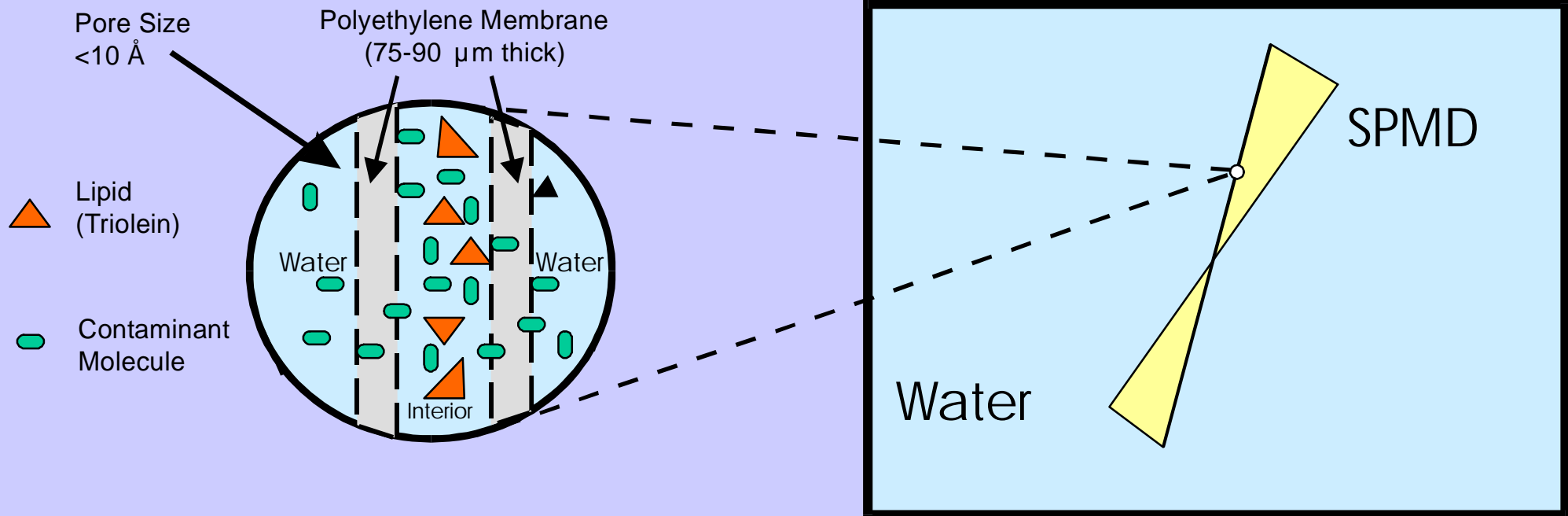
- Introduction
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## Introduction - **Semipermeable Membrane Devices (SPMDs)**

- 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

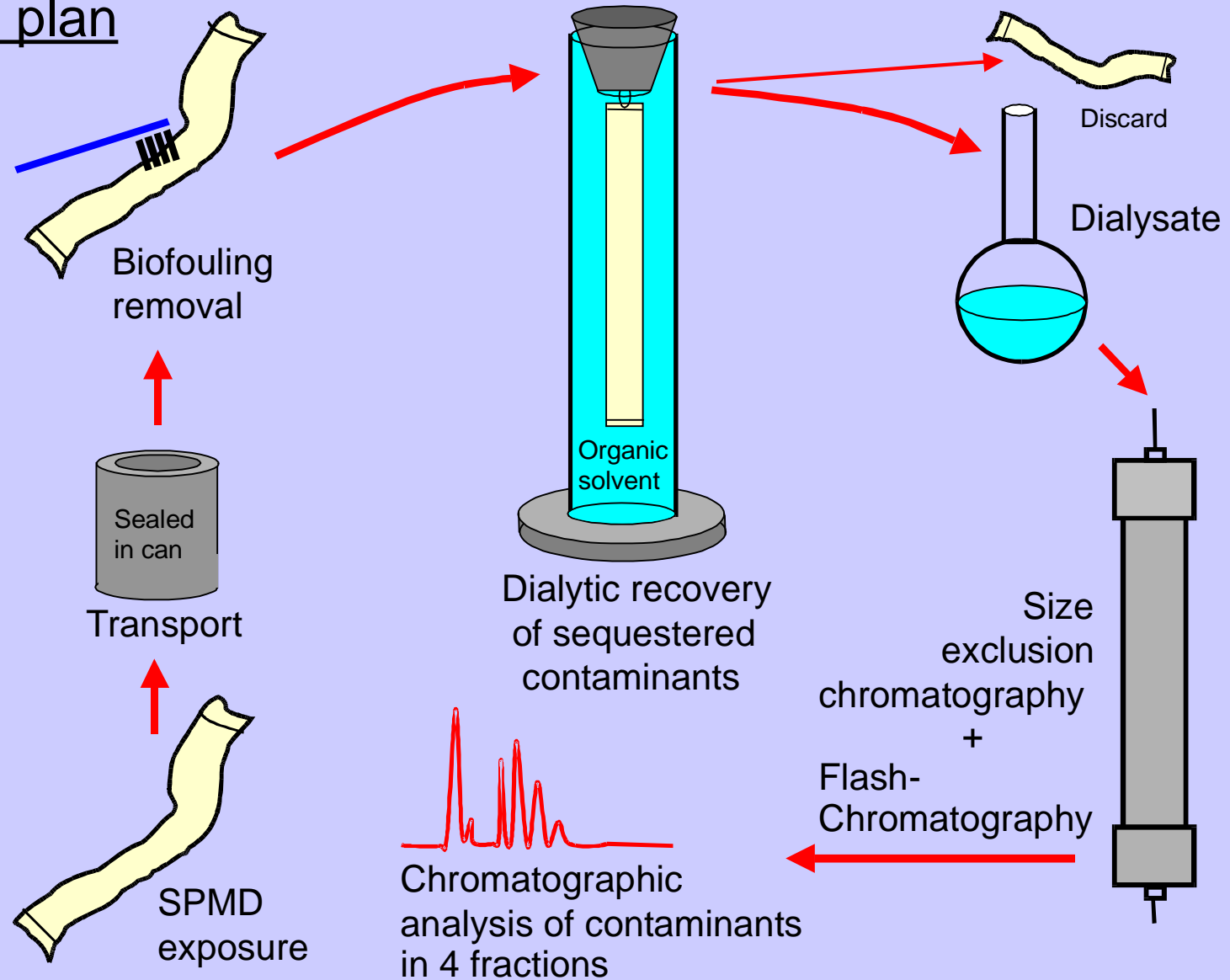


# SPMD Design





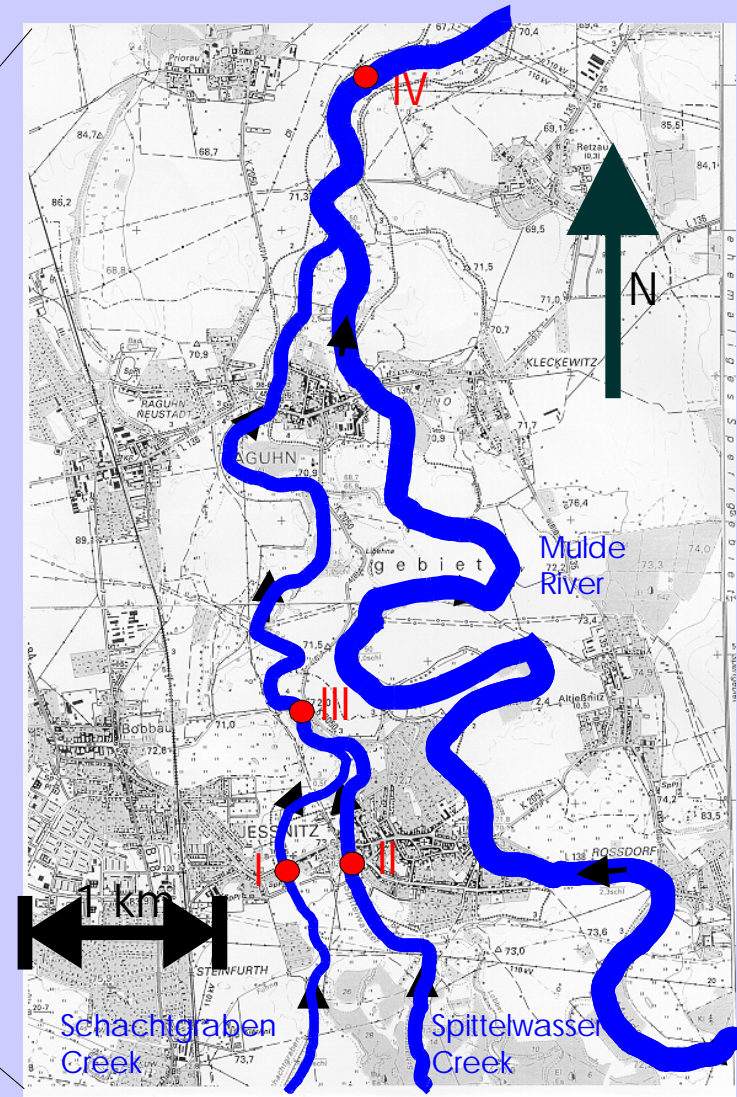
# Fractionation plan





## 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

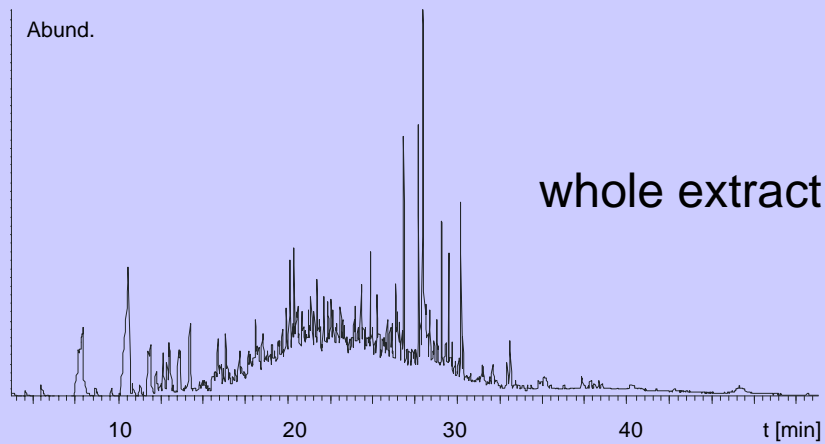




## Pre-treatment and fractionation of SPMD extracts

- 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

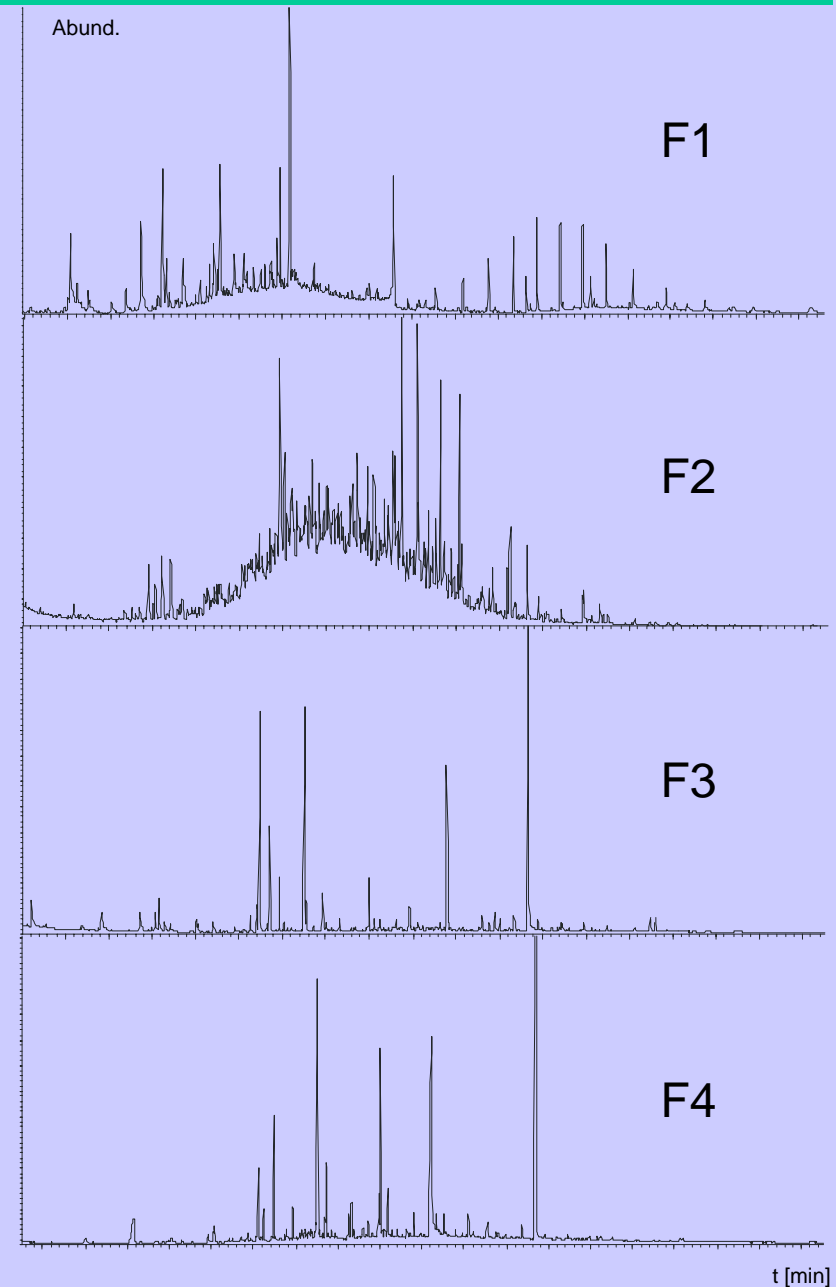


F1 : chlorobenzenes, PCBs, n-alkanes

F2 : branched alkanes, PAHs, alkyl-PAHs, HCHs

F3 : chloronitrobenzenes, DDTs, DDDs

F4 : oxy-PAHs, phthalates, phenoles



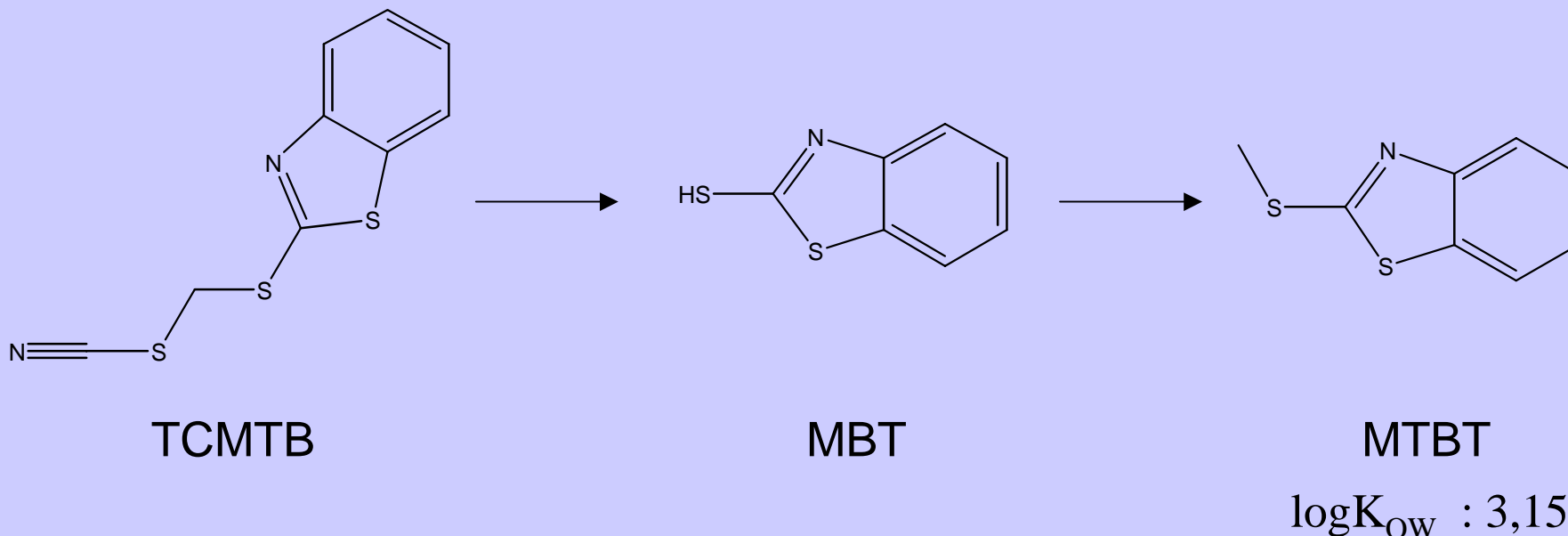
## Fractions and compound classes

- 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

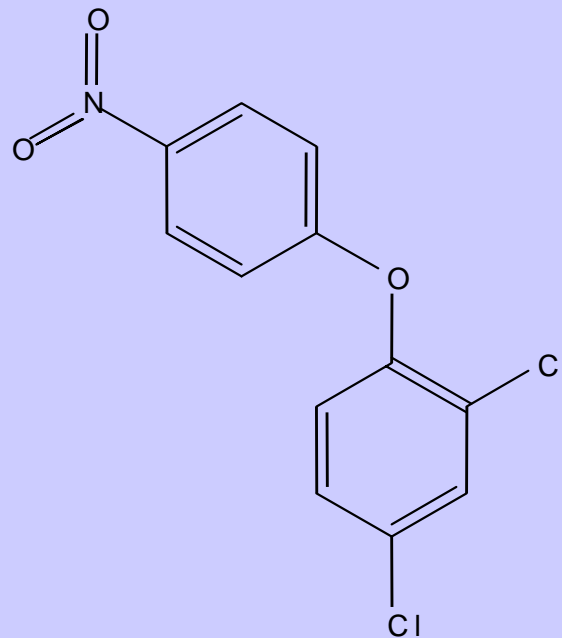
High amounts of **2-(methylthio)benzothiazole** (MTBT) in SPMD extracts

- 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



## 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

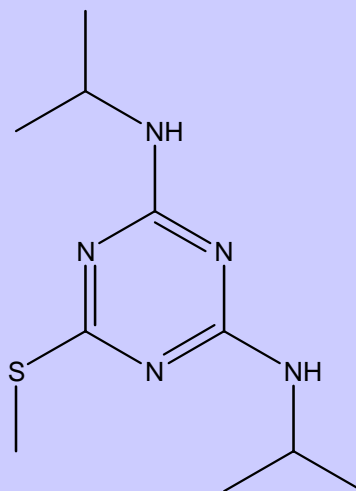
logK<sub>OW</sub> : 4,64

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

logK<sub>OW</sub> : 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 compartments (global partitioning, seasonal trends)

$$f_w = C_w / Z_w$$

$$Z_w = 1/H$$

f = fugacity

$$f_s = C_s / Z_s$$

$$Z_s = (f_{oc} \rho K_{oc}) / H$$

Z = fugacity capacity

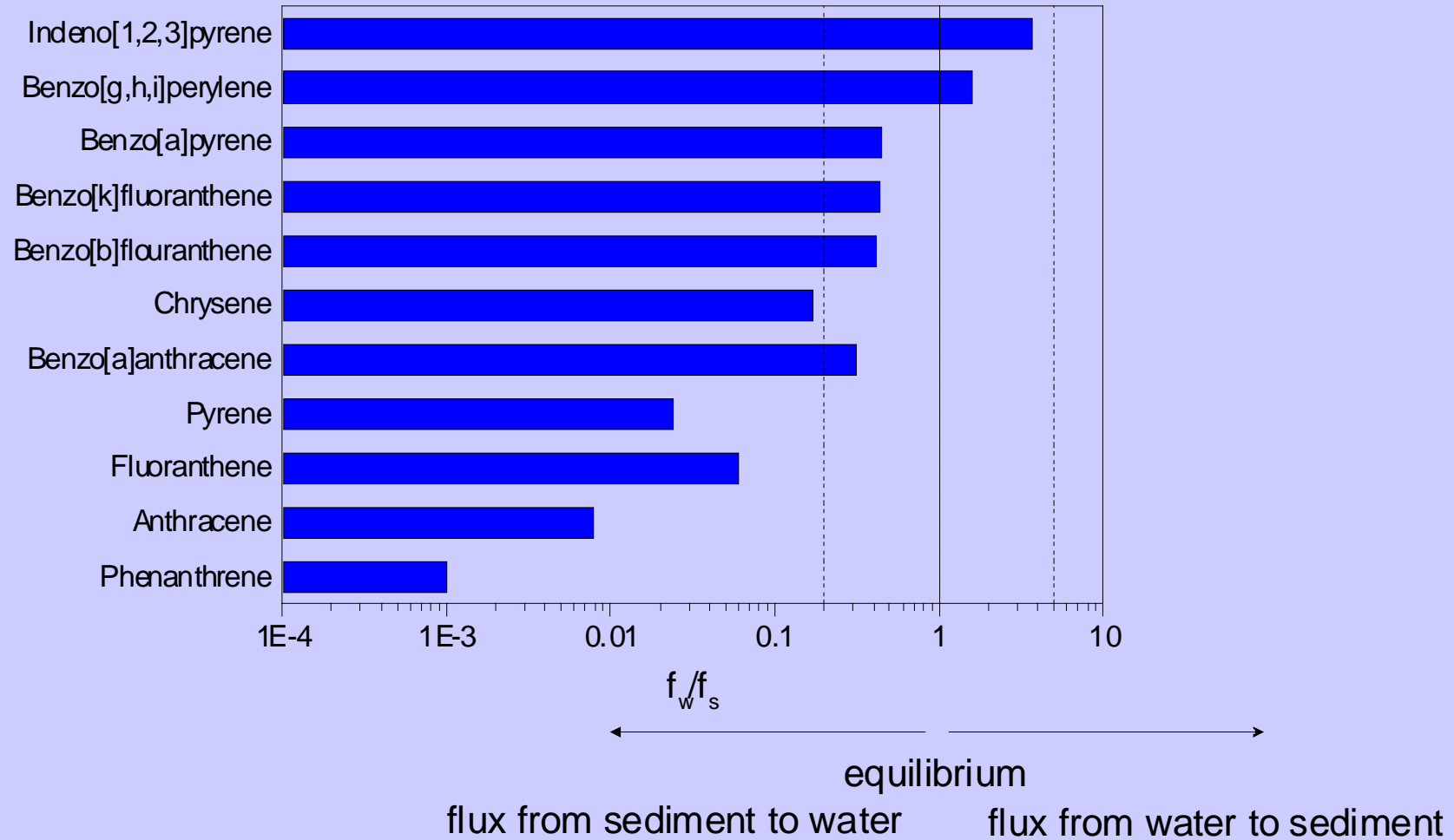
H = Henry's law const

**fugacity quotient:**  $f_w / f_s$

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:

- 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

**A**utomated **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



