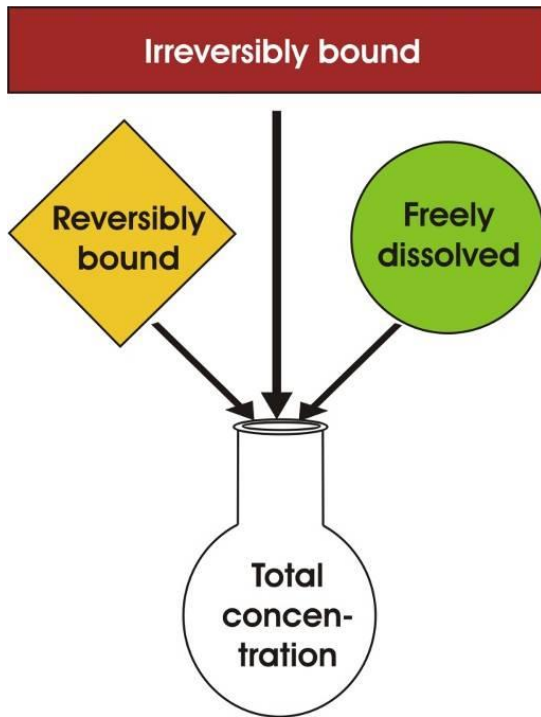


# Equilibrium sampling for a thermodynamic assessment of contaminated sediments

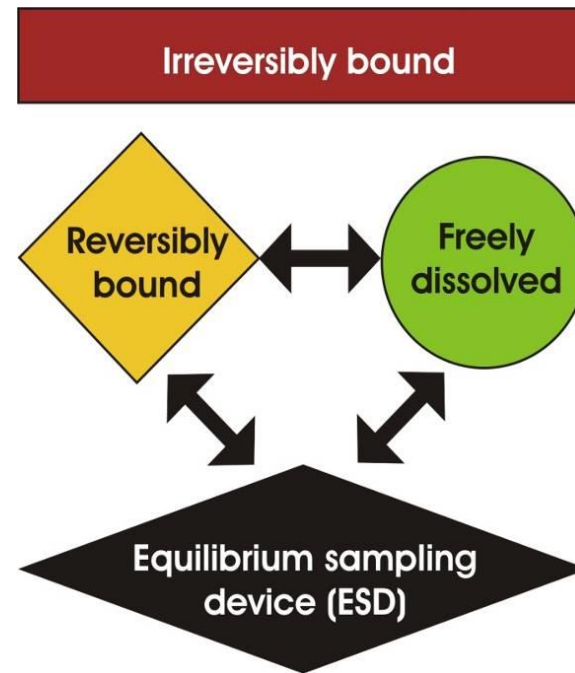
Philipp Mayer<sup>1</sup>, Stine N. Schmidt<sup>1</sup>, Kimmo Mäenpää<sup>2</sup>,  
Gesine Witt<sup>3</sup>, Sabine Schäfer<sup>4</sup>, Phil Gidley<sup>5</sup> & Annika Jahnke<sup>6</sup>

<sup>1</sup>Technical University of Denmark, <sup>2</sup>University of Eastern Finland, <sup>3</sup>Hamburg University of Applied Sciences, Germany, <sup>4</sup>German Federal Institute of Hydrology, <sup>5</sup> USACE-ERDC, USA & <sup>6</sup>Stockholm University, Sweden (now UFZ, Germany)

## Classical extraction



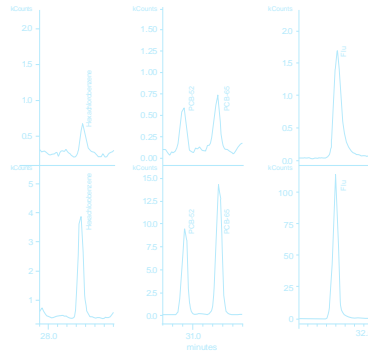
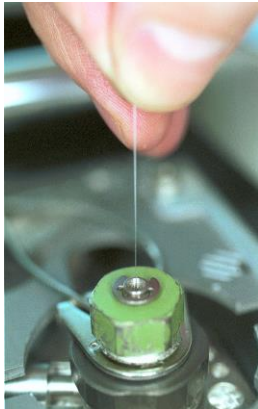
## Equilibrium sampling device (ESD)



# 1) Matrix-SPME with disposable fibers (2000)



1. Equilibrate thin polymer with sample



2. Measure  $C_{PDMS}$

$$3. C_{free} = C_{PDMS} / K_{PDMS,water}$$

Mayer et al, ES&T, 2000, V 34: 5177-5183

Mayer et al., ES&T, 2003, V37: 184A-191A

## 2) Silicone coated vials (2008)

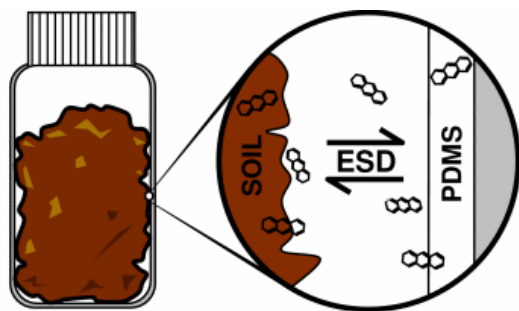
# Chemistry Central Journal

Methodology

### Determining the chemical activity of hydrophobic organic compounds in soil using polymer coated vials

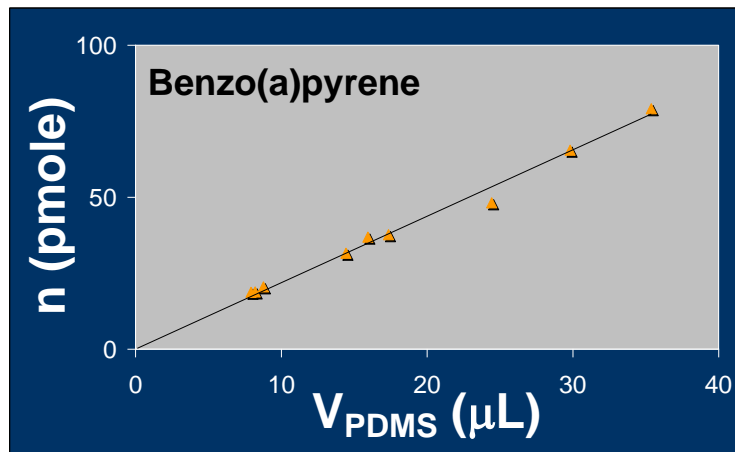
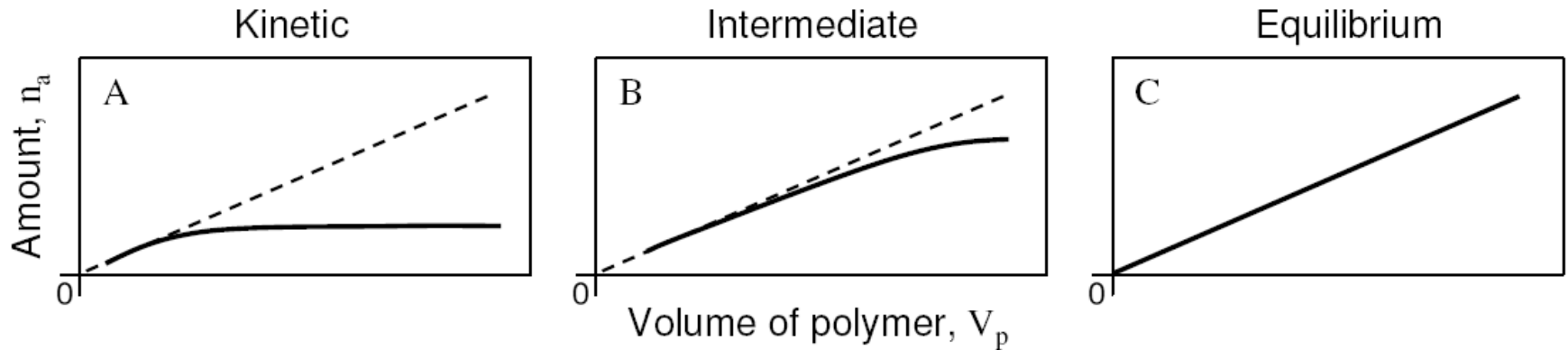
Fredrik Reichenberg<sup>1,2</sup>, Foppe Smedes<sup>3</sup>, Jan-Åke Jönsson<sup>2</sup> and Philipp Mayer\*<sup>1</sup>

Address: <sup>1</sup>Department of Environmental Chemistry and Microbiology, National Environmental Research Institute, University of Aarhus, PO Box 358, 4000 Roskilde, Denmark, <sup>2</sup>Division of Analytical Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden and <sup>3</sup>Ministry of Transport, Public Works and Water management, National Institute for Coastal and Marine Management/RIKZ, PO Box 207, 9750 AE Haren, Netherlands



Drawing of equilibrium sampling device (ESD) for determination of thermodynamic activity by partitioning to micrometer thin polydimethylsiloxane (PDMS).

# Coated vials with multiple coating thickness



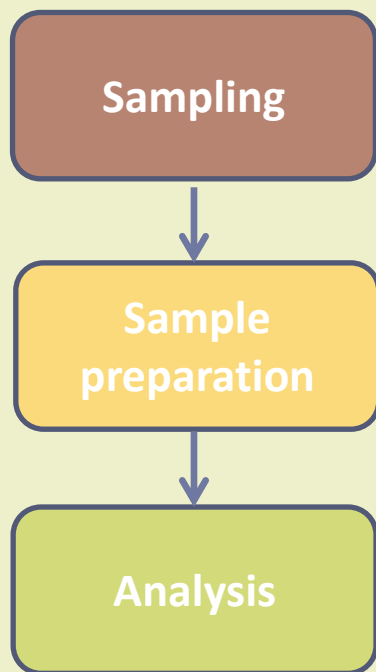
Confirms:

1. equilibrium
2. negligible depletion
3. no surface artefacts/abrasion

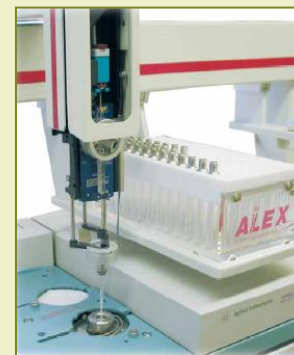
3)

## Passive Equilibrium Sampler for in Situ Measurements of Freely Dissolved Concentrations of Hydrophobic Organic Chemicals in Sediments

Gesine Witt,<sup>\*,†</sup> Susann-Cathrin Lang,<sup>†</sup> Dagny Ullmann,<sup>†</sup> Gotja Schaffrath,<sup>†</sup> Detlef Schulz-Bull,<sup>‡</sup> and Philipp Mayer<sup>§</sup>



- **in-situ deployment of sampler**
- **rinse with water and wipe dry**
- **store fiber in GC injection liner**
  
- **insert fiber with automated injection liner exchange (ALEX)**
- **thermal desorption**
- **MS identification/ quantification**



# Measurement endpoints of Equilibrium Sampling

PCB concentrations in polymer  $C_{\text{polymer} \rightleftharpoons \text{sed}}$  can be converted into:

1) The effective concentration driving diffusion

$$C_{\text{free}} \text{ (g L}^{-1}\text{)} = \frac{C_{\text{polymer} \rightleftharpoons \text{sed}} \text{ (g kg}^{-1}\text{)}}{K_{\text{polymer}:\text{water}} \text{ (L kg}^{-1}\text{)}} \quad (\text{since 2000})$$

2) The chemical activity (energetic state) driving equilibrium partitioning

$$a \text{ (unit less)} \cong \frac{C_{\text{free}} \text{ (g L}^{-1}\text{)}}{S_L \text{ (g L}^{-1}\text{)}} \quad (\text{since 2006})$$

**3) The thermodynamic potential for bioaccumulation**

$$C_{\text{lip} \rightleftharpoons \text{sed}} \text{ (g kg}^{-1}\text{)} = C_{\text{polymer} \rightleftharpoons \text{sed}} \text{ (g kg}^{-1}\text{)} \times K_{\text{lip:pol}} \text{ (kg kg}^{-1}\text{)} \quad (\text{since 2011})$$

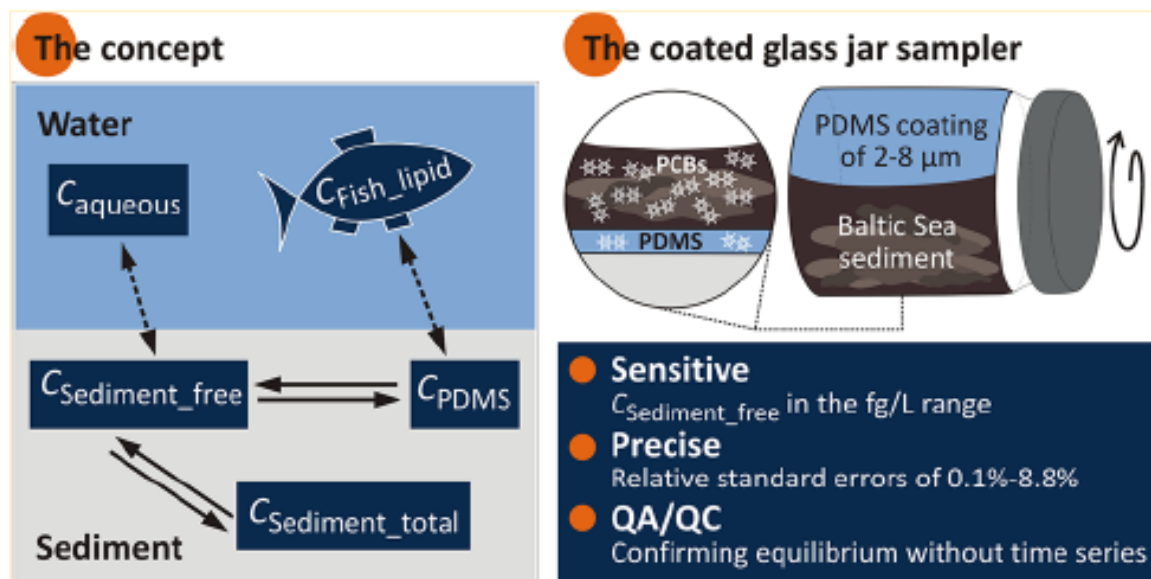
Case Studies focusing on  
PCBs &  $C_{lip \rightleftharpoons sed}$



1)

## Sensitive Equilibrium Sampling To Study Polychlorinated Biphenyl Disposition in Baltic Sea Sediment

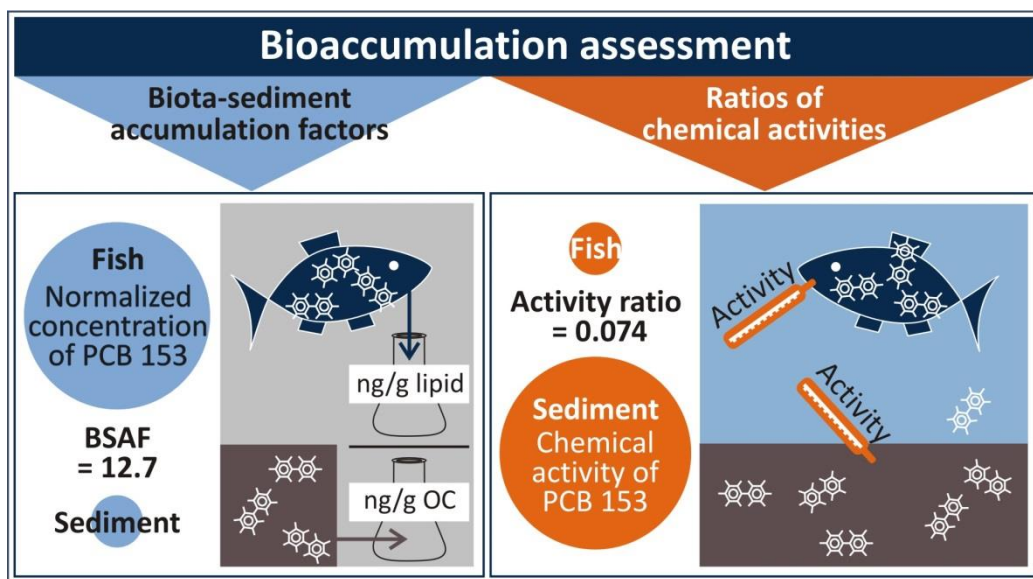
Annika Jahnke,<sup>\*,†</sup> Philipp Mayer,<sup>‡</sup> and Michael S. McLachlan<sup>†</sup>



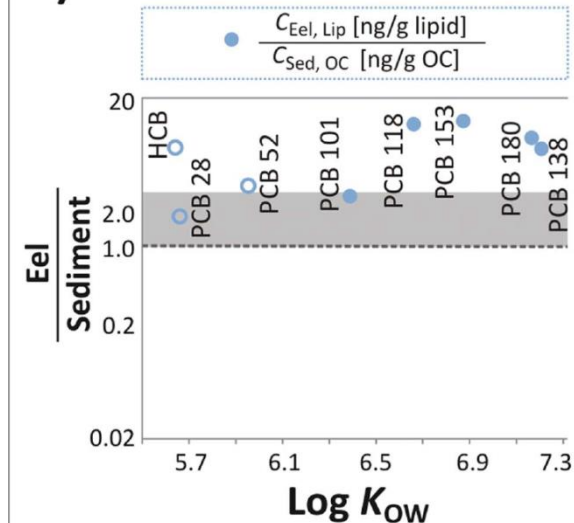
## Silicone passive equilibrium samplers as 'chemometers' in eels and sediments of a Swedish lake†

Cite this: *Environ. Sci.: Processes Impacts*, 2014, 16, 464

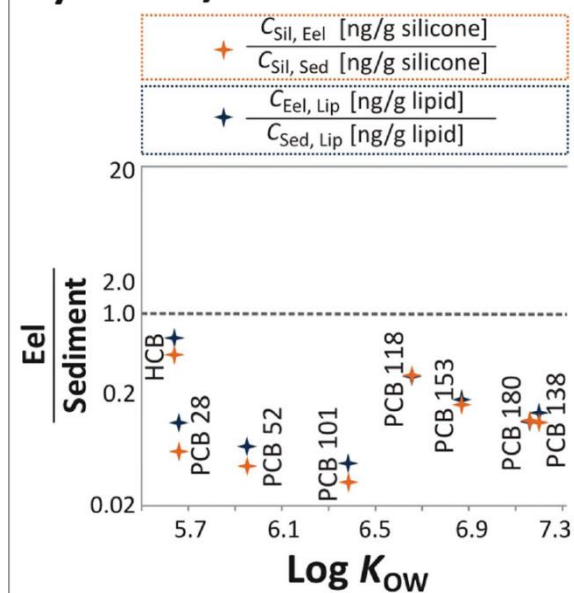
Annika Jahnke,<sup>\*a</sup> Philipp Mayer,<sup>bc</sup> Michael S. McLachlan,<sup>a</sup> Håkan Wickström,<sup>d</sup> Dorothea Gilbert<sup>c</sup> and Matthew MacLeod<sup>a</sup>



### A) BSAFs



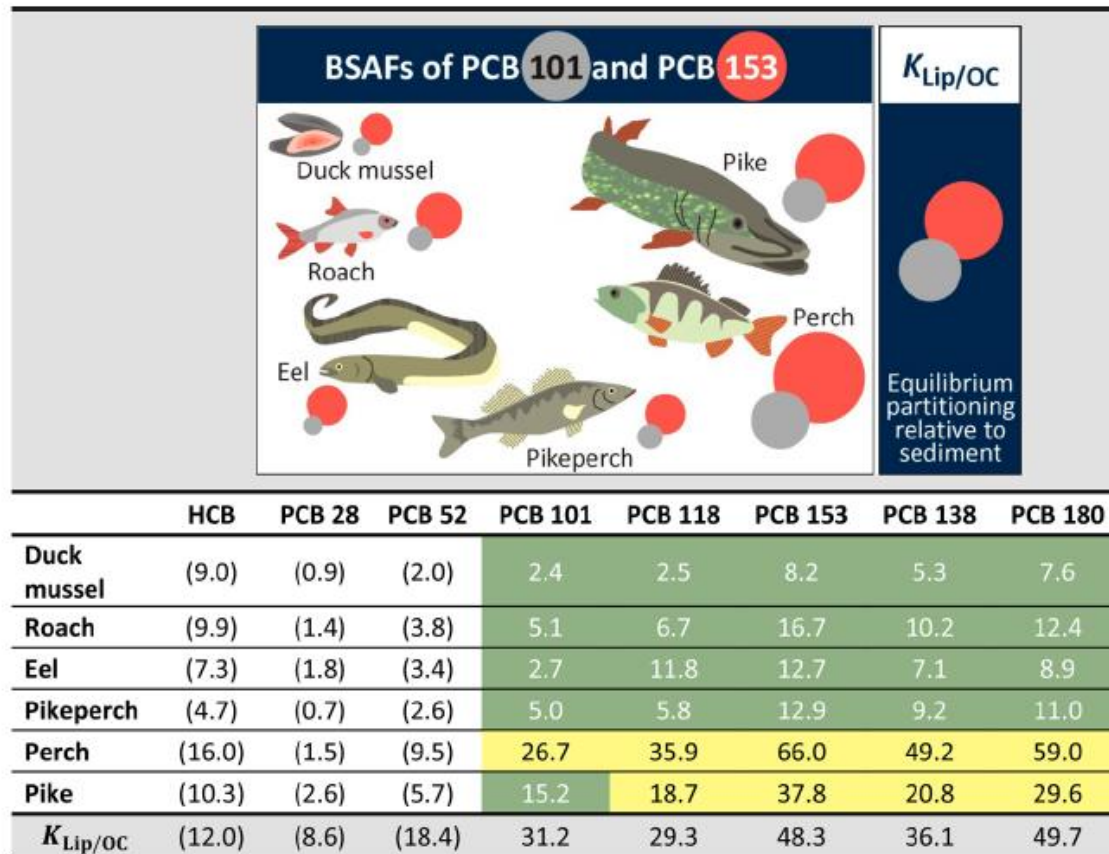
### B) Activity ratios



3)

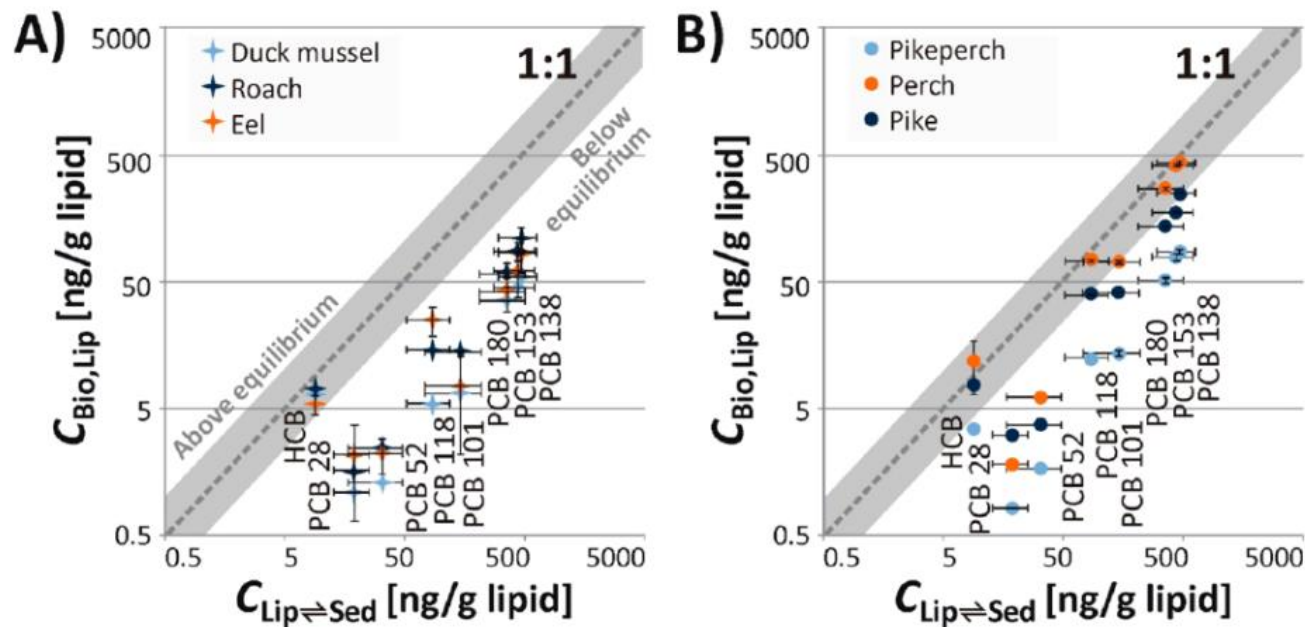
# Equilibrium Sampling to Determine the Thermodynamic Potential for Bioaccumulation of Persistent Organic Pollutants from Sediment

Annika Jahnke,<sup>\*,†</sup> Matthew MacLeod,<sup>†</sup> Håkan Wickström,<sup>‡</sup> and Philipp Mayer<sup>§</sup>



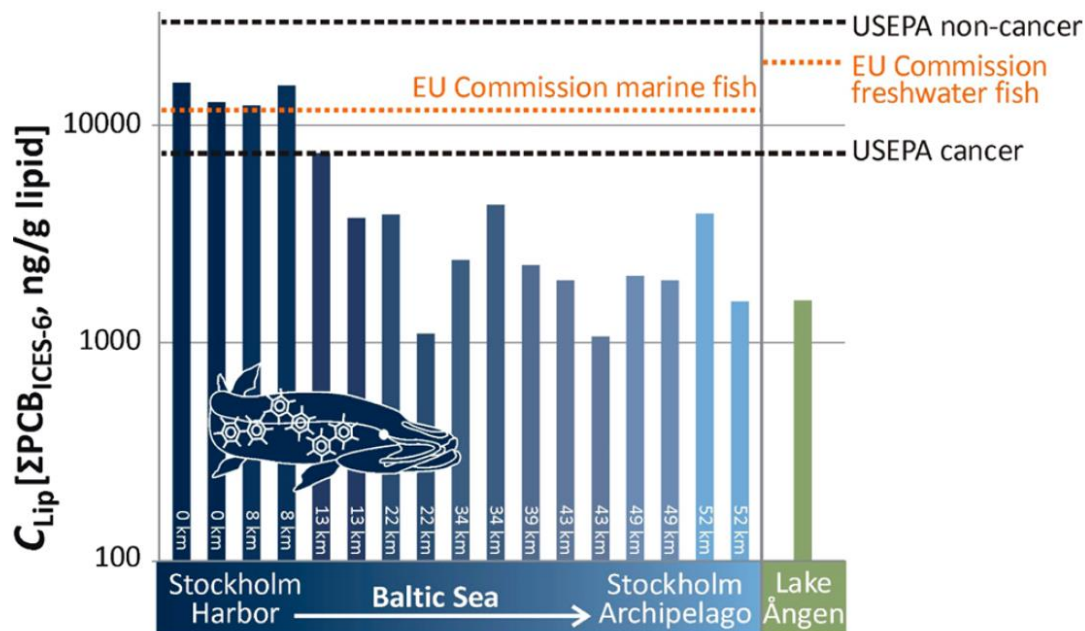
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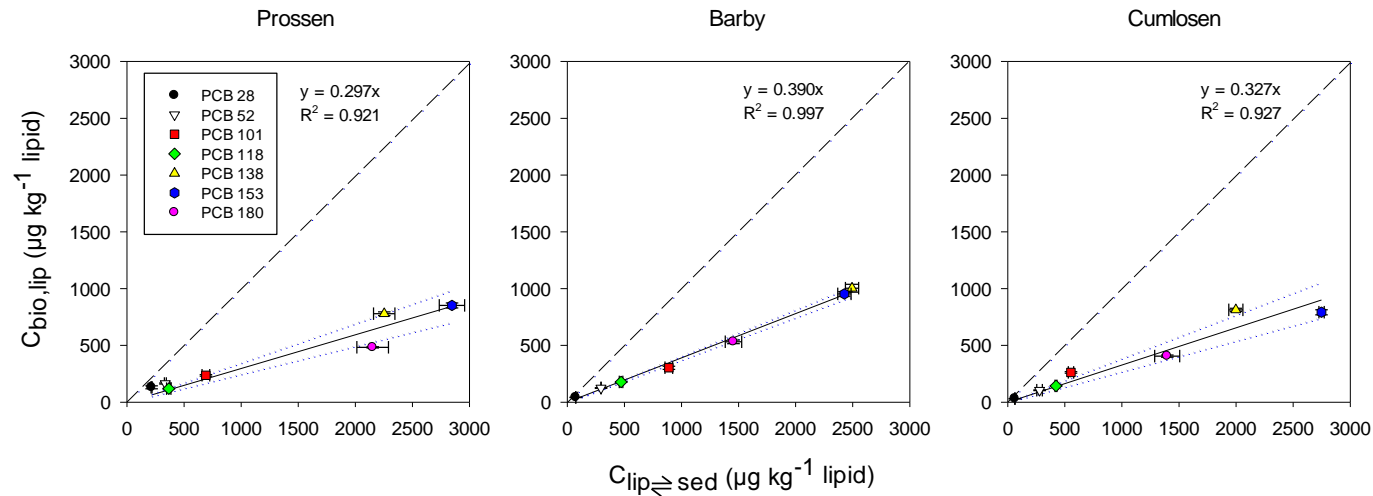


# Equilibrium sampling of polychlorinated biphenyls in River Elbe sediments – Linking bioaccumulation in fish to sediment contamination



Sabine Schäfer<sup>a,\*</sup>, Catherine Antoni<sup>a,1</sup>, Christel Möhlenkamp<sup>a</sup>, Evelyn Claus<sup>a</sup>, Georg Reifferscheid<sup>a</sup>, Peter Heininger<sup>a</sup>, Philipp Mayer<sup>b</sup>

1. ex situ equilibrium sampling of sediment from 10 locations in River Elbe (Germany)
2.  $C_{lipid-normalized}$  in common bream from independent monitoring program



1. Cross validation of two monitoring programs
2. Bioaccumulation in common bream tightly linked to  $C_{lip=sed}$ 
  - $R^2 > 0.9$  (linear scale!) & very similar slopes between sites

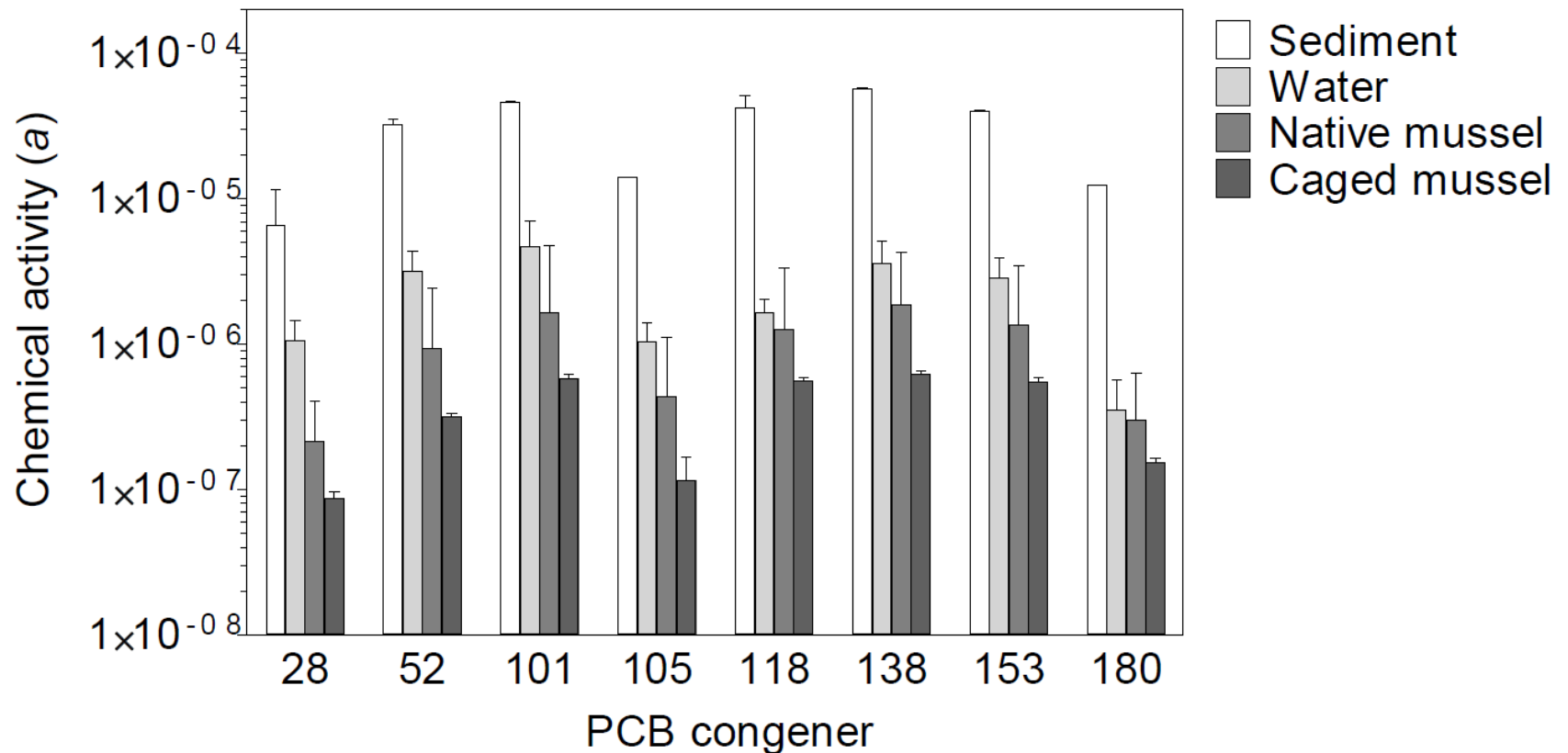


5)

ET&C, 2015, V 34: 2463–2474 (DOI: 10.1002/etc.3099)

## Fate of polychlorinated biphenyls in a contaminated lake ecosystem: Combining equilibrium passive sampling of sediment and water with total concentration measurements of biota

Kimmo Mäenpää, Matti Leppänen, Kaisa Figueiredo, Philipp Mayer, Dorothea Gilbert, Sirpa Herve, Annika Jahnke, Carmen Gil-Allué, Jarkko Akkanen, Inna Nybom, Auli Kostamo



# Quantitative Thermodynamic Exposure Assessment (Q-TEA) Supporting Resilient Contaminated Sediment Site Restoration

**USACE-ERDC** (Lead): Todd S. Bridges, Philip T. Gidley, Guilherme Lotufo, Carlos Ruiz, Alan J. Kennedy,

**DTU**: Philipp Mayer, Stine Nørgaard Schmidt

**Sediment Solutions**: Upal Ghosh

**USA-EPA**: Robert M. Burgess

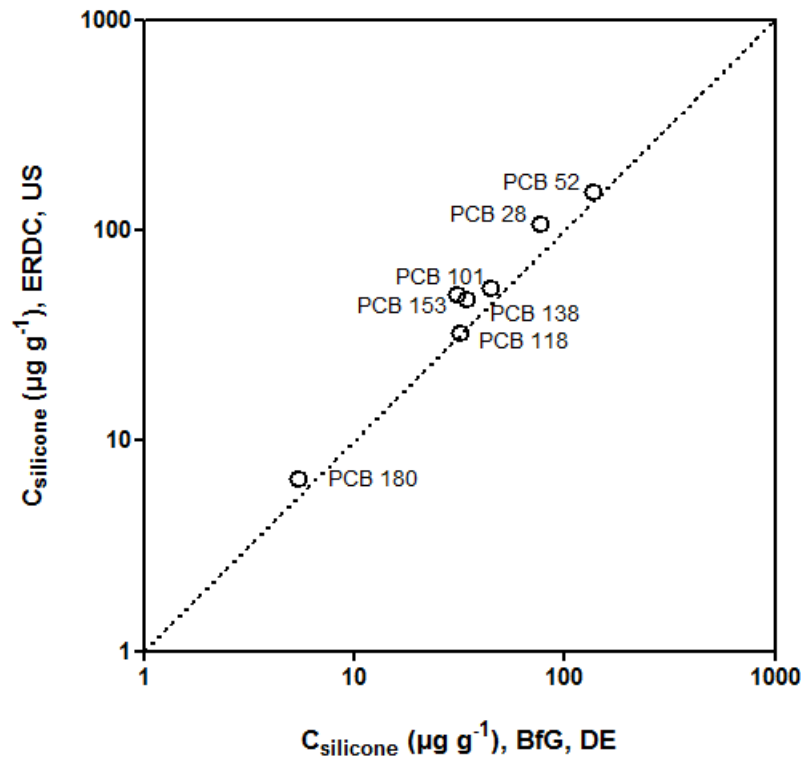
**Northeastern University**: Loretta Fernandez,





# Cross validation of equilibrium sampling

1. Coated jars produced at DTU & BfG
2. Equilibrium sampling of New Bedford sediment at BfG & ERDC
3. Instrumental analysis at BfG & ERDC



# Conclusions and take home messages

## Equilibrium sampling of sediments

- equilibrium sampling feasible even for PCBs
- can yield  $C_{\text{free}}$ , chemical activity &  $C_{\text{lip} \rightleftharpoons \text{sed}}$

## $C_{\text{lip} \rightleftharpoons \text{sed}}$

- in all studies so far  $\geq C_{\text{lipid,normalized}}$
- thermodynamic potential for bioaccumulation

Sediments have high PCB levels, not only in concentration but also thermodynamically!

## **Acknowledgements**

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- Danish Council for Independent Research in Technology and Production Sciences (FTP)
- Swedish Research Council FORMAS
- German Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety
- German Research Council (DFG)
- Academy of Finland
- US Strategic Environmental Research and Development Program (SERDP) (14 ER03-035/ER-2431).