

# A role (or roles) for passive sampling in regulatory monitoring

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# Why would anyone use PS?

- “Complex” calculation of  $C_{TWA}$  and understanding of principle of passive sampling
- Need for ingenuity during sampler deployment
- Never sure samplers will be there upon return!
- Costs due to the need for blanks/control samplers (including PRC data)
- Cannot directly compare passive sampling data with EQS for nonpolar organics

# Why not?

- Cost efficiency when representative data is ~~needed~~ (time integrative nature of the sampling)  
**wanted**
- Dissolved concentrations – A better measure of surface water quality
- Limits of detection
- Variability of passive sampling data

# Monitoring tasks

- Testing for compliance (with EQS)
- Monitoring long-term trends
- Measurement of riverine fluxes
- Source tracking and assessment of spatial distribution
- Linking exposure and effects
- Contaminant speciation

# This presentation

1. Improving representativeness
  - Combining bottle sampling and passive sampling
2. Measurement of riverine fluxes (e.g. OSPAR)
  - Total/dissolved fluxes of trace nonpolar organics
3. Long-term trends
  - Surface water concentrations of polycyclic aromatic hydrocarbons (PAHs)
4. Testing for compliance (e.g. WFD)
  - Contaminant concentrations at low yet relevant concentrations

# 1. Sampling representativeness

Characteristic: Time-integrative sampling

- Reduce monitoring burden
- Support spot sampling with passive sampling
- Use of the Chemcatcher and DGT samplers for monitoring trace metals
- Fieldwork in the River Meuse (NL)

## 1. Sampling representativeness

# Passive sampling for metals

- Reduce monitoring burden
- Support spot sampling with passive sampling
- Develop knowledge of water body specific contaminant speciation and partitioning data
- Use of the Chemcatcher and DGT samplers for metals
- Measurement of a labile fraction of metals and total/filtered fractions by two procedures

# 1. Sampling representativeness

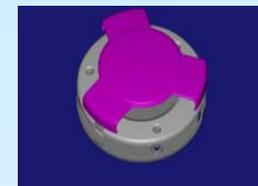
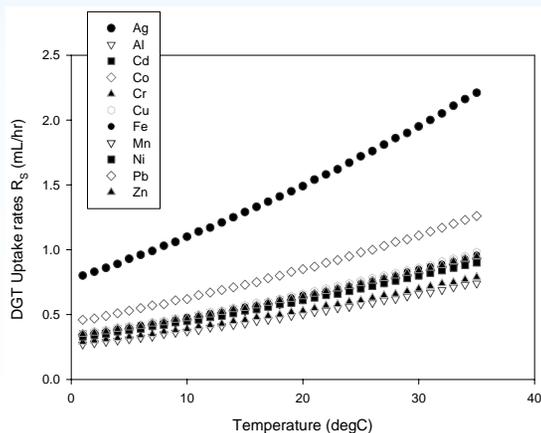
## Time-weighted average concentrations



### The DGT:

- Polyacrylamide diffusive gel layer and a chelex resin for accumulation of metals
- Elution with 1M HNO<sub>3</sub> and analysed by ICP-MS

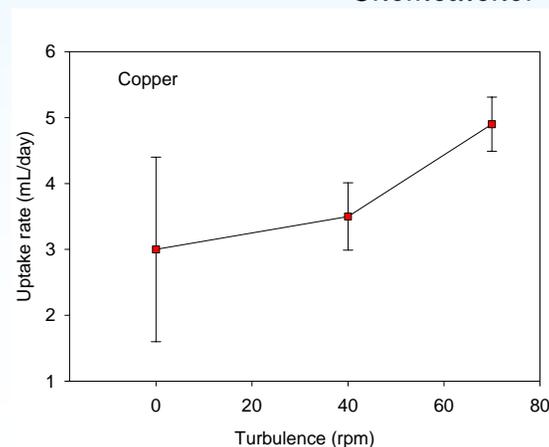
$$C_{DGT} = \frac{M_{DGT} \Delta g}{DtA}$$



### The Chemcatcher:

- Cellulose diffusion-limiting membrane and chelating disk as a receiving phase
- Elution with HNO<sub>3</sub> and extract is analysed by ICP-MS

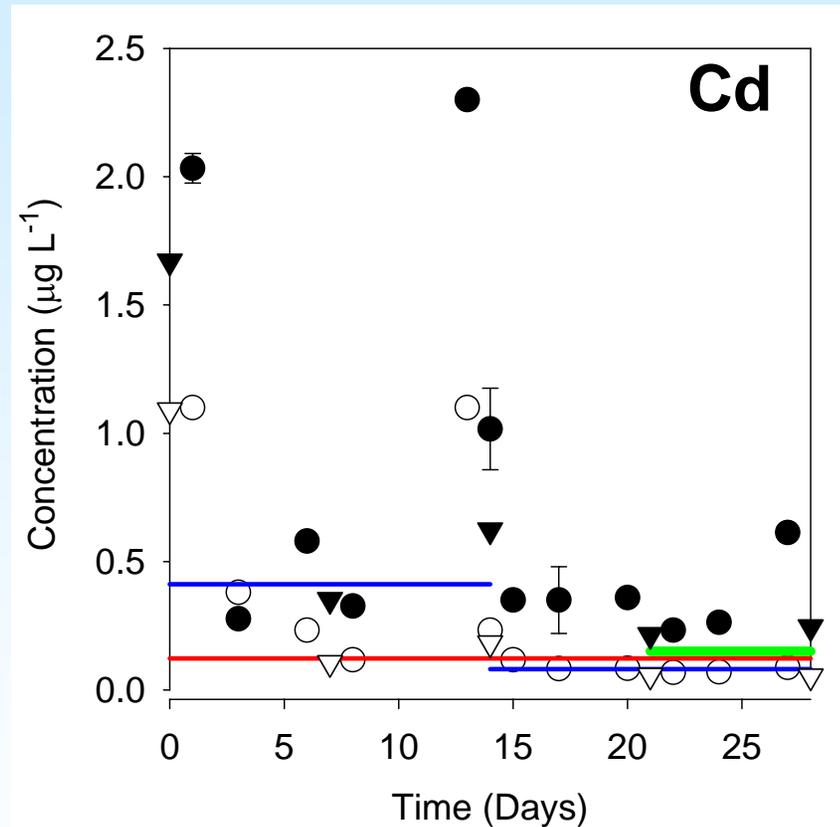
$$C_{Chemcatcher} = \frac{M_{Chemcatcher}}{R_s t}$$



## 1. Sampling representativeness

# Passive sampling for metals

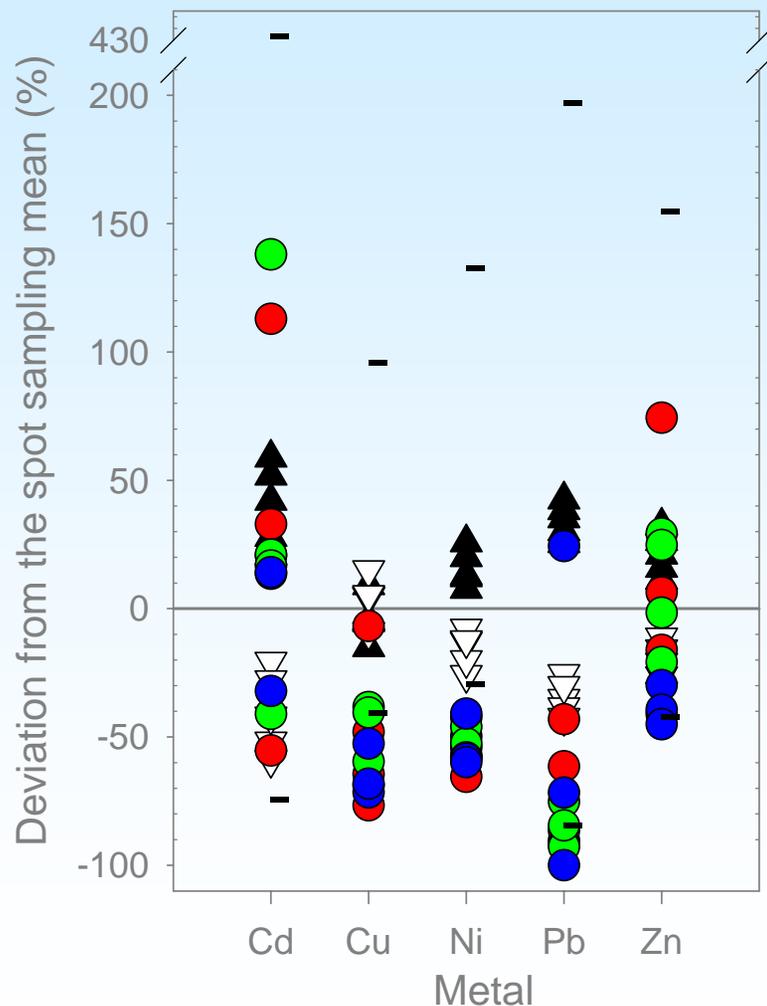
River Meuse  
Eijsden (NL)  
In 2005



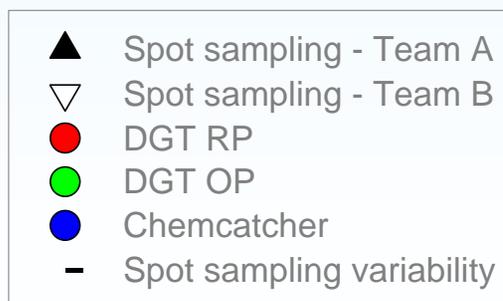
- Total C<sub>Team A</sub>
- ▼ Total C<sub>Team B</sub>
- Filtered C<sub>Team A</sub>
- ▽ Filtered C<sub>Team B</sub>

## 1. Sampling representativeness

# Passive sampling for metals



- Comparison of passive sampling data (7, 14, 21 and 28 day exposures) with mean filtered concentrations by spot sampling (reference value)



## 2. Riverine fluxes

Characteristic: LODs & time-integrative sampling

- Monitoring of direct inputs and discharges from rivers (e.g. for OSPAR region)
- Contaminant present:
  - Dissolved (and complexed for metals)
  - Sorbed to SPM, dissolved organic matter & colloids
- Can we estimate all of these from one single measurement? And with what confidence?

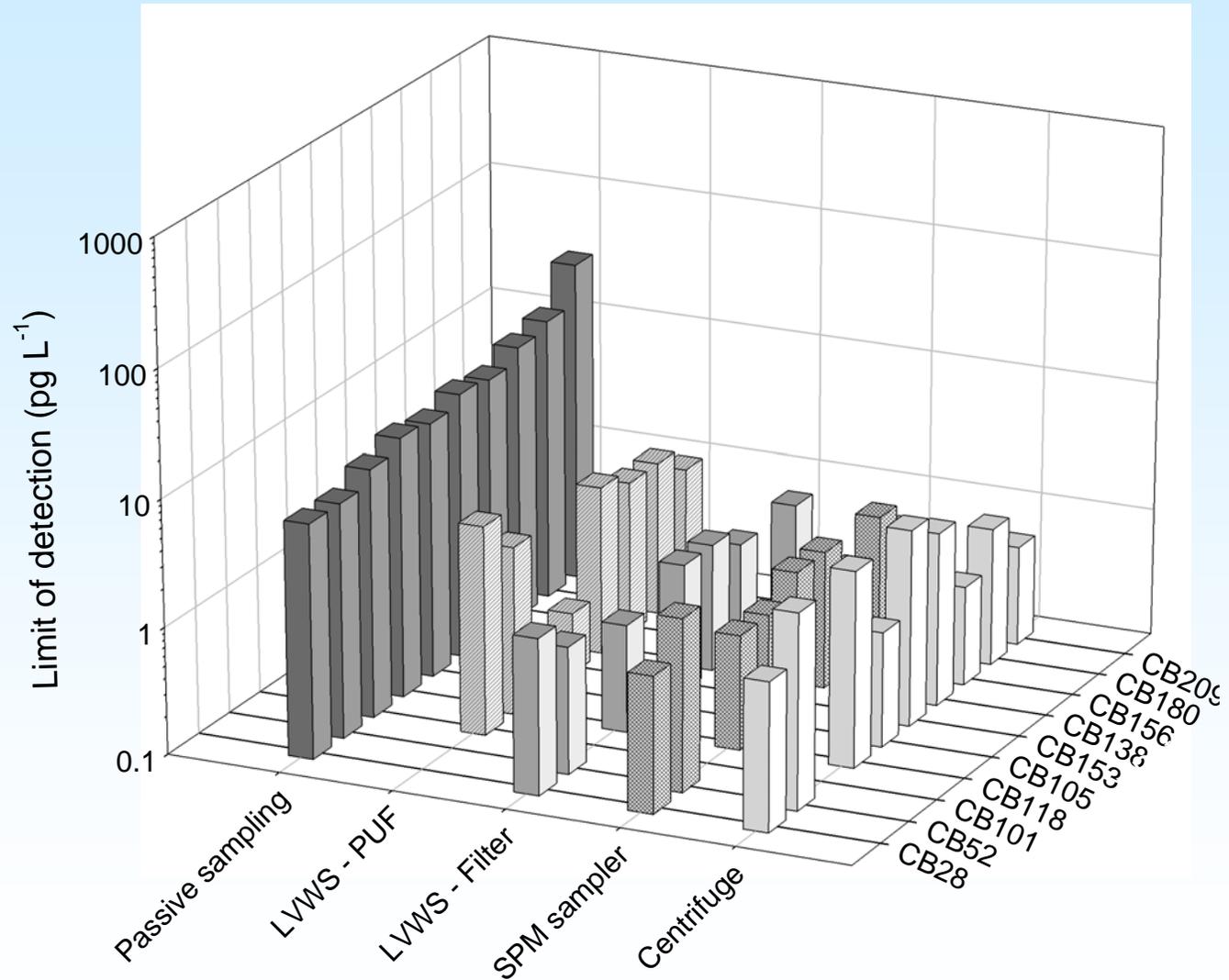
## 2. Riverine fluxes

# PCBs in the Drammenselva River (Norway)

- Measurement of dissolved and particulate matter-associated contaminants
- Passive sampling with SPMDs
- Monitoring of SPM with continuous-flow centrifugation/large volume water sampling

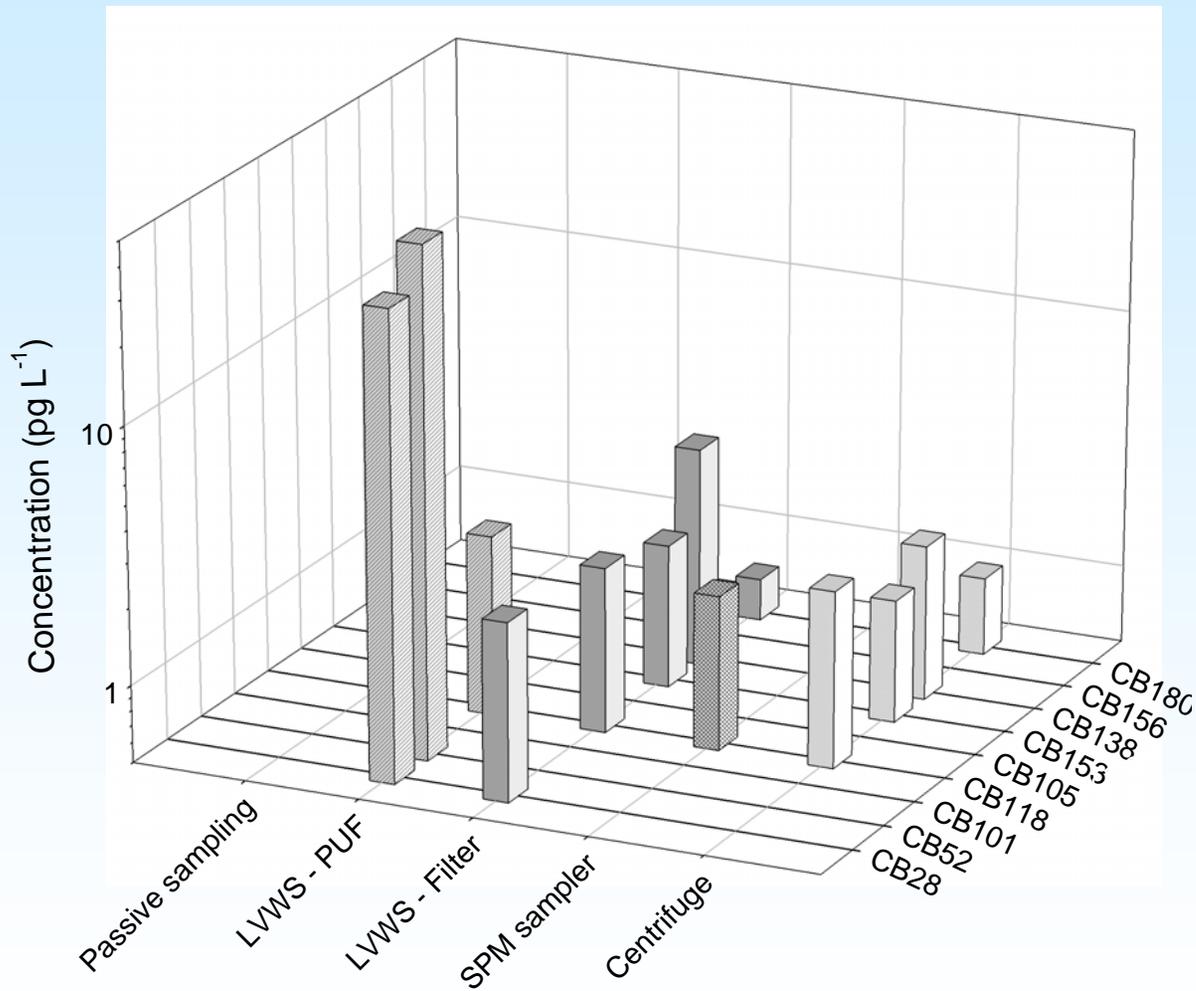
## 2. Riverine fluxes

# Limits of detection for PCBs



## 2. Riverine fluxes

# Contaminant concentrations



Estimation  
of  
distribution  
between  
phases  
(e.g.  $K_{\text{POC}}$ )

## 2. Riverine fluxes

# Contaminant fluxes Drammenselva River

- How does  $C_{TWA}$  vary with  $C_{total}$ ?
- LODs for bottle sampling for PCBs  $\sim 1 \text{ ng L}^{-1}$  (0.1 for HR-GC)
- Riverine flux: 10 kg/year to 10 g/year estimates
- Put into perspective:
  - Uncertainties on flow & SPM/POC measurements
  - Variability of SPM levels with depth and along river sections or transects

# 3. Long term trends

Characteristics: LODs, method with low variability

- As part of many legislative texts
- Do they need to be based on  $C_{total}$ ?
- Or are dissolved phase concentrations sufficient?
- Knowledge of contaminant partitioning

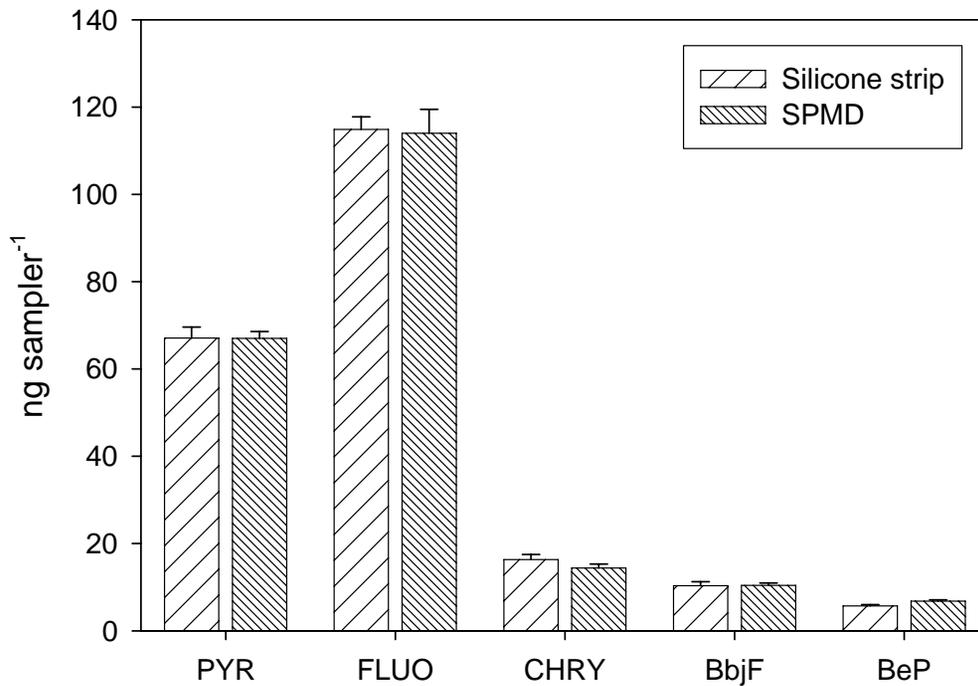
### 3. Long term trends

# Sampling with LDPE/silicone

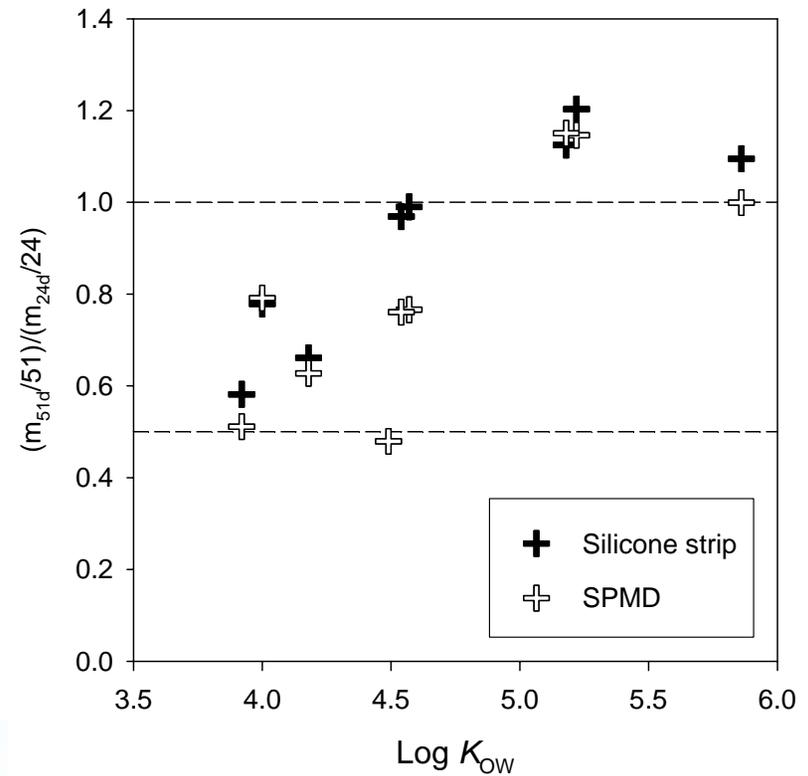
- Reproducibility of sampler production
- Variability of masses absorbed (24 & 51 days)
- Further long-term data

### 3. Long term trends

# PAH Masses accumulated



51 day exposure



### 3. Long term trends

## Trend monitoring with passive samplers

- Reproducibility of sampler production:
  - PRC spike RSD < 10 %
- Variability in masses absorbed
  - RSD ~ 5 % with identical sampler surface area and deployment
- Similar data quality for 24 and 51 d exposures
- Do we need to know about changes in contaminant distribution between phases with changes in total concentrations?

# 4. Testing for compliance

- Issues with LODs for standard bottles sampling for non-polar organics ... (e.g. WFD)
- Are EQS for bottom sediments an acceptable replacement? What are the challenges?
- Setting “dissolved phase” EQS?
- What about measuring dissolved concentrations and estimated  $C_{total}$  empirically?

# Conclusions

- Passive samplers offer possibilities for improvements in data quality for regulatory monitoring tasks
- In most cases, a knowledge and understanding of contaminant speciation and partitioning (specific to each water body) is a prerequisite
- Apparent equilibrium partitioning and/or safety factors?

# Acknowledgements

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