

ICCE 2017

Monitoring water quality using passive sampling in kinetic mode:

A new calibration approach using the concentration ratio of passive samplers with different thicknesses

Hanna Fuchte

Hanna.Fuchte@bio5.rwth-aachen.de

Institute of Environmental Research, RWTH Aachen University

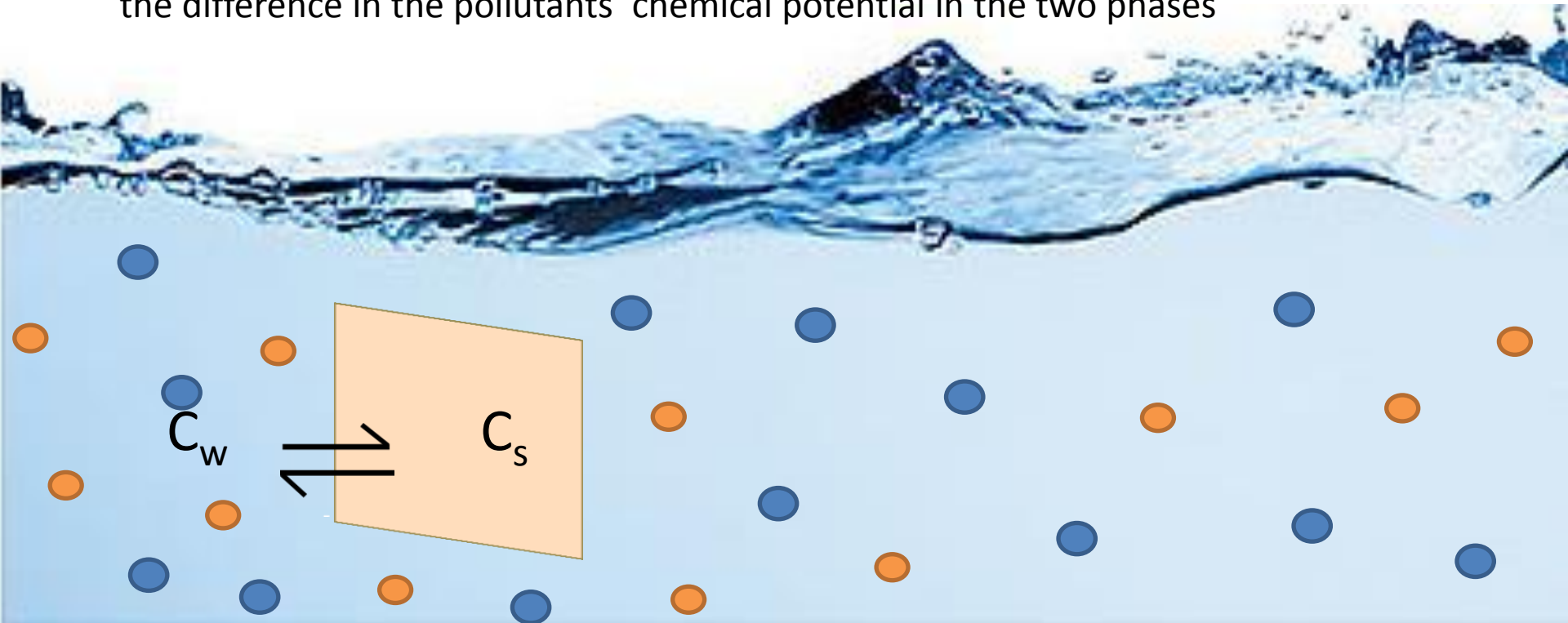
Andreas Schäffer, Kees Booij, Kilian Smith

Introduction

Monitoring pollutants in natural and waste water is essential to protect ecosystems and human health.

Passive sampling: Promising tool to measure freely dissolved concentrations of a broad range of pollutants.

How it works: pollutants distribute between water and sampler phases driven by the difference in the pollutants' chemical potential in the two phases

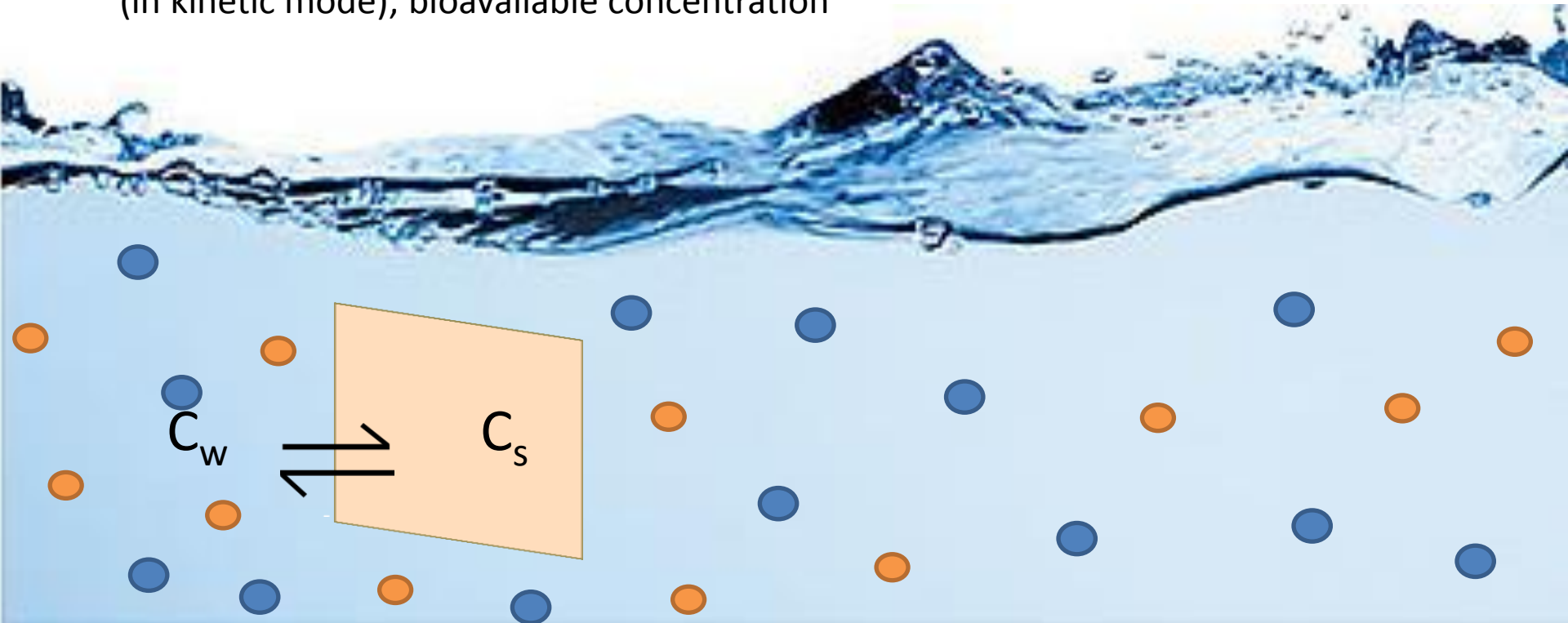


Introduction

Monitoring pollutants in natural and waste water is essential to protect ecosystems and human health.

Passive sampling: Promising tool to measure freely dissolved concentrations of a broad range of pollutants.

Advantages: clean samples with upconcentrated analytes; time weighted average (in kinetic mode); bioavailable concentration

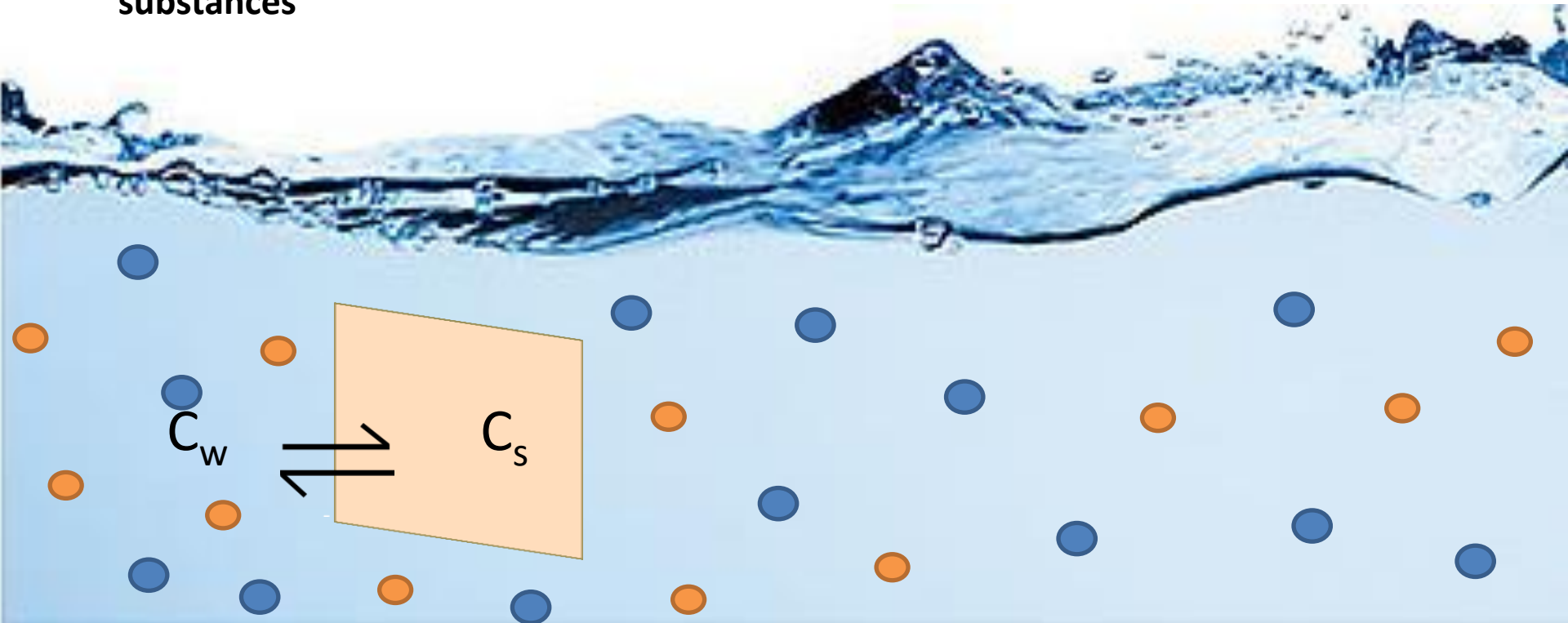


Introduction

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Passive sampling: Promising tool to measure freely dissolved concentrations of a broad range of pollutants.

This approach was tested using **silicone passive samplers** for **non - polar substances**



Introduction

Kinetic region

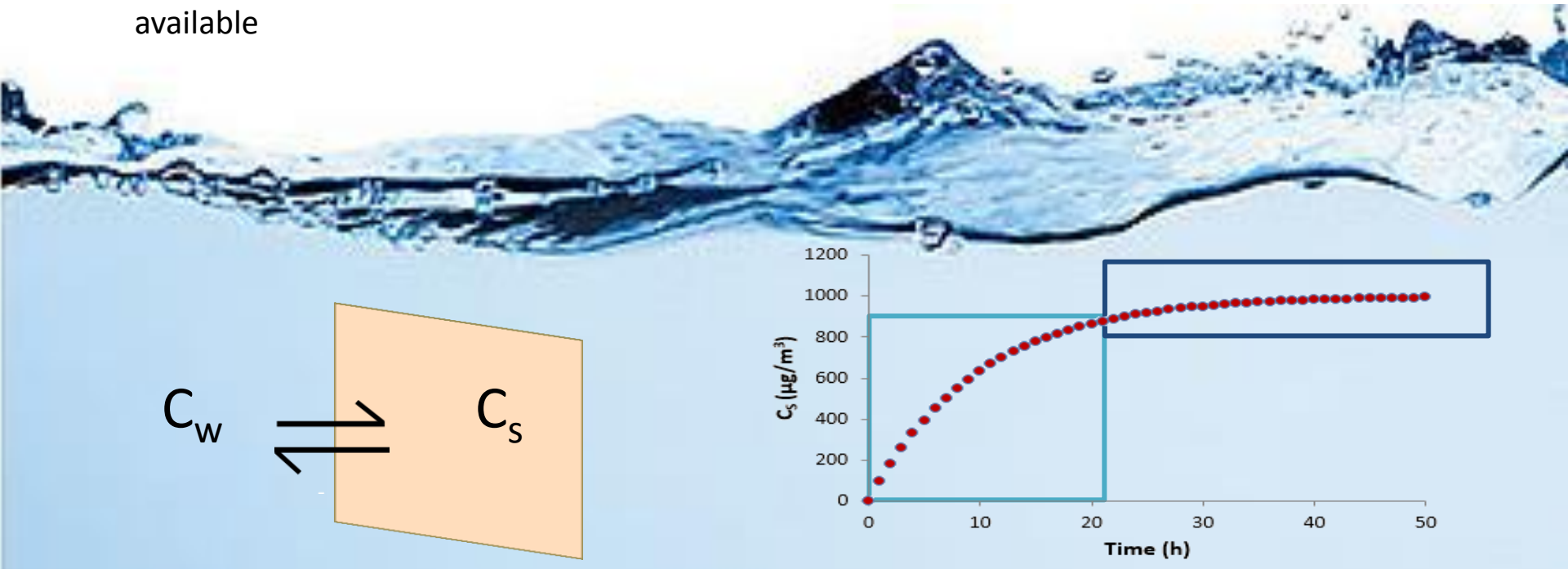
$$C_S = C_W \cdot K_{SW} \cdot (1 - \exp^{-k_e \cdot t})$$

Uptake kinetics have to be known →
Performance Reference Compounds:
Sometimes expensive and not always
available

Equilibrium

$$C_S = C_W \cdot K_{SW}$$


For very hydrophobic substances
equilibrium attainment can take month



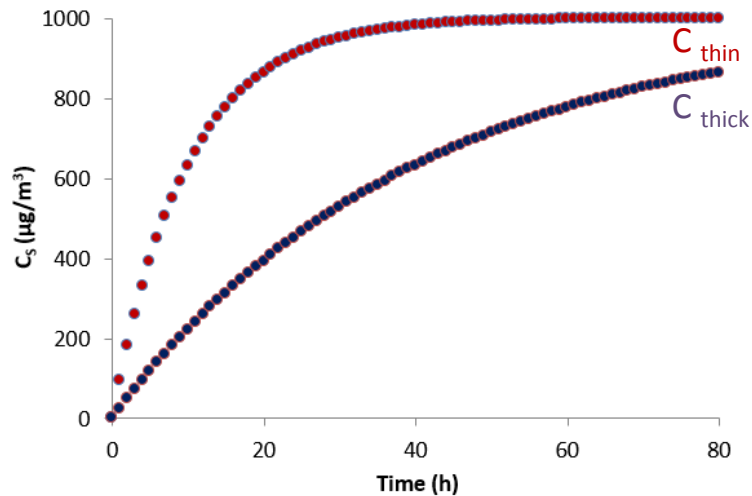
C_S = passive sampler conc. (ng/ml), C_W = dissolved concentration (ng/ml), K_{SW} = equilibrium sampler to water partitioning coefficient,
 k_e = uptake rate constant (1/h), t = time (h)

Passive Sampling with two samplers of different thicknesses

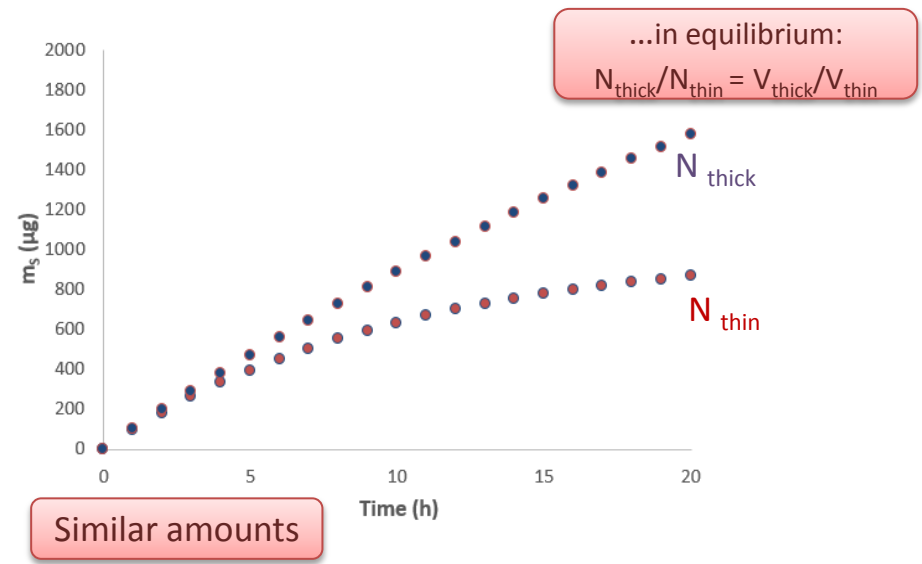
- ✓ same architecture
- ✓ same hydrodynamic regime

- ✓ same surface area 
- ✓ different volumes (V_{thick} and V_{thin})

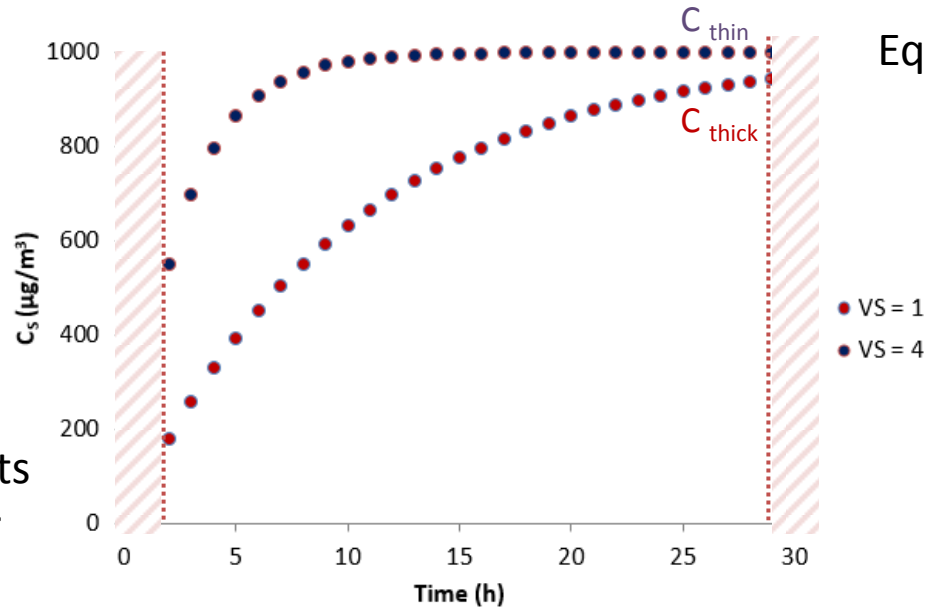
Temporal evolution of concentrations (C_{thick} and C_{thin}):



Temporal evolution of accumulated amounts (N_{thick} and N_{thin}):



Concentration Ratio Approach for Determining Dissolved Environmental Concentrations



Equilibrium sampling:
 $C_S = C_W \cdot K_{SW}$

differences in amounts
 \approx measurement error

Hypothesis: When two samplers made of the same silicone material and with the same surface area but different volumes are deployed in parallel in the same hydrodynamic regime, measuring the ratio of their concentrations at a single point during the kinetic uptake phase allows the dissolved concentration in the surrounding medium to be determined.

$C_S =$ passive sampler conc. (ng/ml), $C_W =$ dissolved concentration (ng/ml), $K_{SW} =$ equilibrium sampler to water partitioning coefficient

Considerations and Calculations

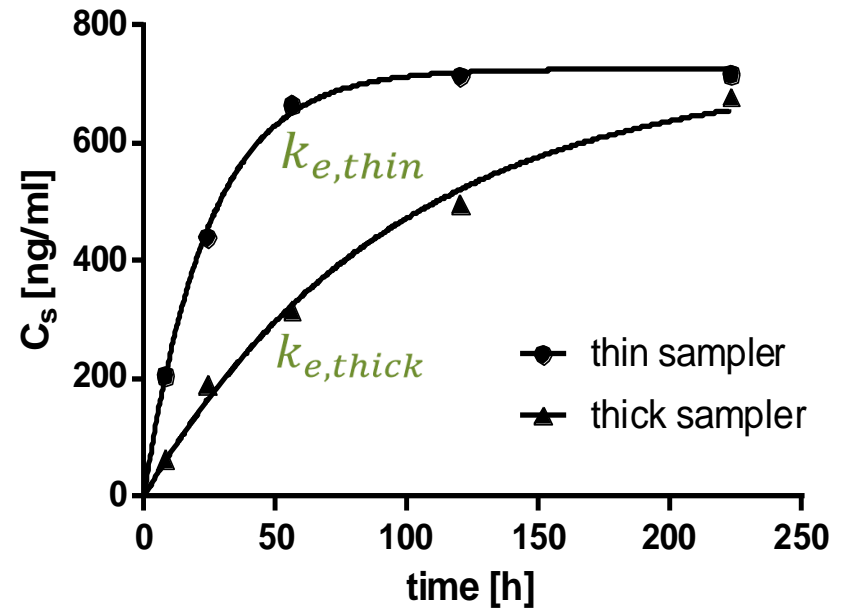
$k_{e,thin}$ and $k_{e,thick}$ can be derived from **measurements** but also from **theory**:

From kinetic measurements:

$$C_S = C_W \cdot K_{SW} \cdot (1 - \exp^{-k_e \cdot t})$$

$$-k_{e,thin} = \frac{\ln\left(1 - \frac{C_{S,thin}}{C_W \cdot K_{SW,thin}}\right)}{t}$$

$$-k_{e,thick} = \frac{\ln\left(1 - \frac{C_{S,thick}}{C_W \cdot K_{SW,thick}}\right)}{t}$$



C_S = passive sampler conc. (ng/ml), C_W = dissolved concentration (ng/ml), K_{SW} = equilibrium sampler to water partitioning coefficient, k_e = uptake rate constant (1/h), t = time (h)

Considerations and Calculations

From theory: $k_e = \frac{k_O \cdot A}{K_{SW} \cdot V_S}$

When samplers are deployed in parallel:

$$\frac{k_{e,thin}}{k_{e,thick}} = \frac{\frac{\cancel{k_{O,thin}} \cdot \cancel{A_{thin}}}{\cancel{K_{SW,thin}} \cdot V_{S,thin}}}{\frac{\cancel{k_{O,thick}} \cdot \cancel{A_{thick}}}{\cancel{K_{SW,thick}} \cdot V_{S,thick}}}$$

Same k_O , same A and same K_{SW} :

$$k_{e,thin} = \frac{V_{S,thick}}{V_{S,thin}} \cdot k_{e,thick}$$

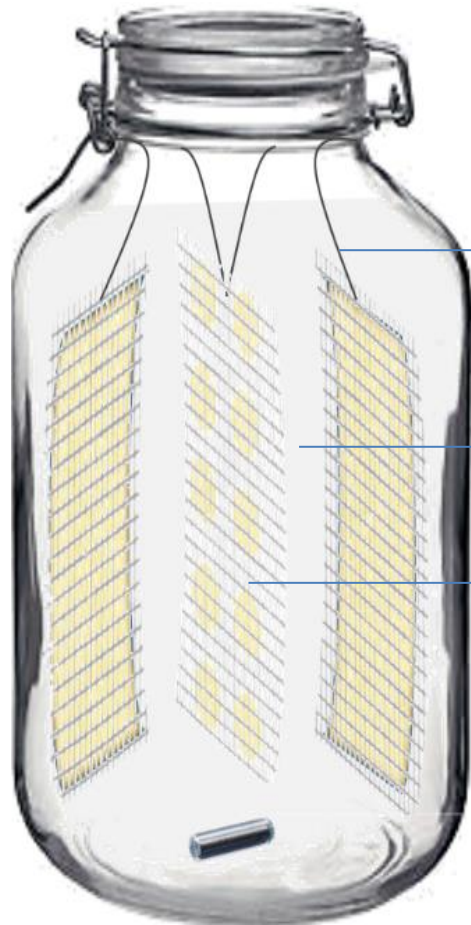
$$\left(1 - \frac{C_{S,thin}}{C_W \cdot K_{SW,thin}}\right)^{V_{S,thin}} - \left(1 - \frac{C_{S,thick}}{C_W \cdot K_{SW,thick}}\right)^{V_{S,thick}} = 0$$

Concentration Ratio Approach - equation

C_S = passive sampler conc. (ng/ml), C_W = dissolved concentration (ng/ml), K_{SW} = partitioning coefficient, k_e = uptake rate constant (1/h), t = time (h), k_O = mass-transfer coefficient (cm/h), A = sampler surface area (cm²), V_S = volume of the sampler (cm³)

Experimental setup

Stirred and unstirred system



→ **Constant dissolved concentrations** via passive dosing sheets loaded with polycyclic aromatic hydrocarbons (PAHs) at ca. 0.1 ng/ml

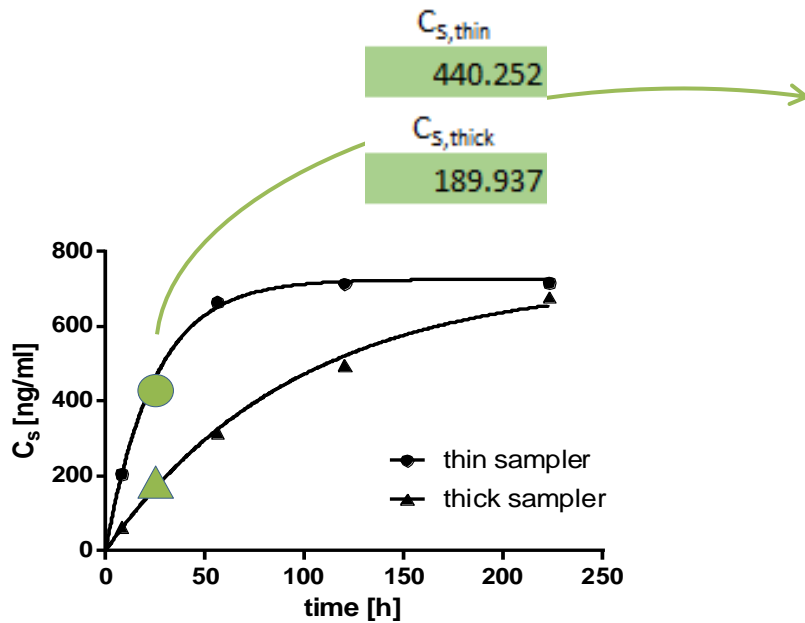
→ **Water samples** taken at start and end for extraction and analysis

→ **Passive samples** – thick and thin PDMS discs (n=5 each)

- $A=1.57 \text{ cm}^2$; $V= 0.016$ and 0.064 cm^3 ; $\varnothing=1\text{cm}$
- taken out at $t = 8, 24, 56, 120$ and 223 hours
- extracted and analysed via GC-MS



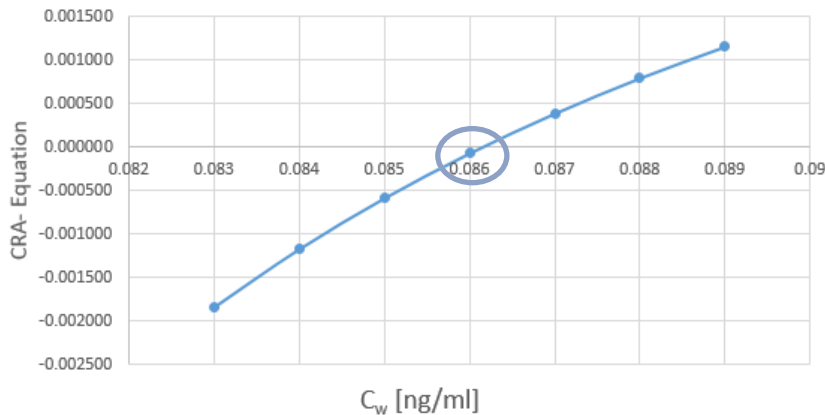
Calculation example – Phenanthrene stirred 24 h



$$\left(1 - \frac{C_{S,thin}}{C_W \cdot K_{SW,thin}}\right)^{VS,thin} - \left(1 - \frac{C_{S,thick}}{C_W \cdot K_{SW,thick}}\right)^{VS,thick} = 0$$

Artificially vary C_W

C_W	CRA - Equation
0.083	-0.001850
0.084	-0.001179
0.085	-0.000591
0.086	-0.000073
0.087	0.000386
0.088	0.000793
0.089	0.001157

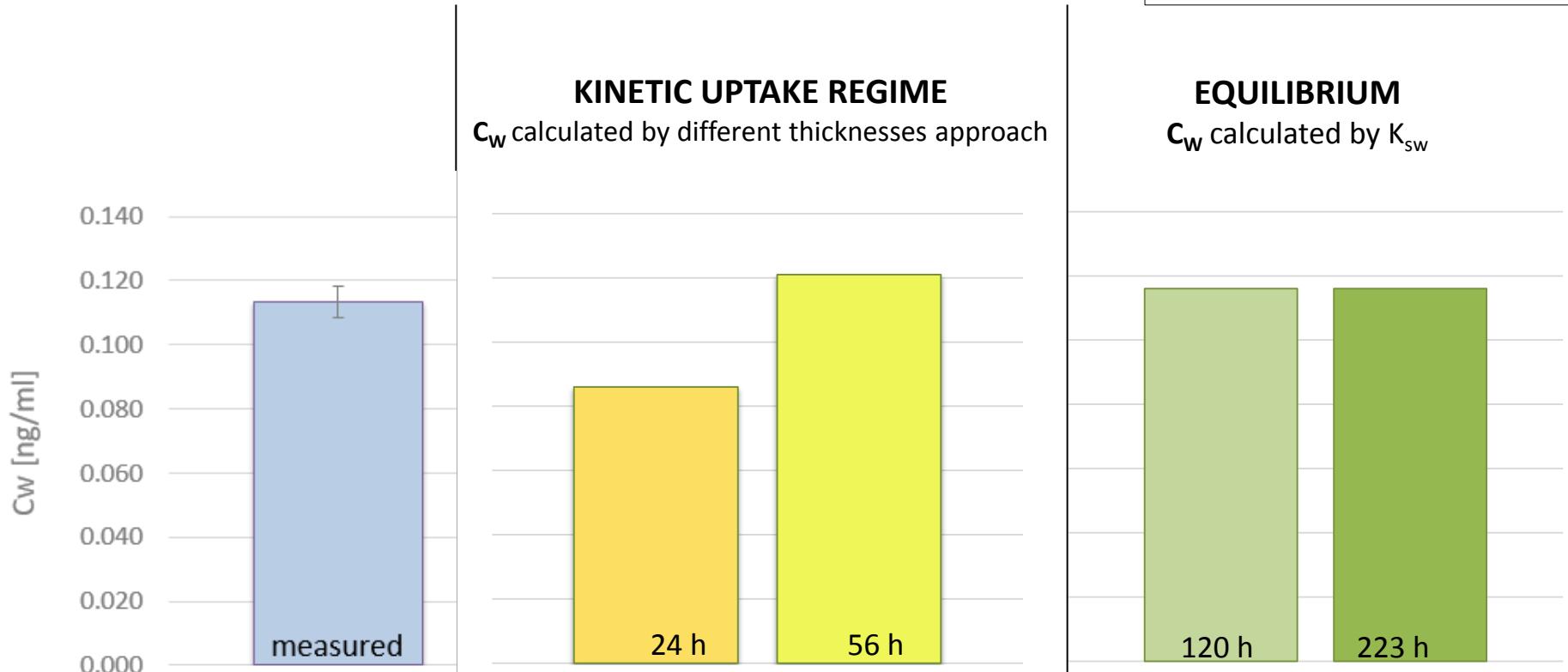
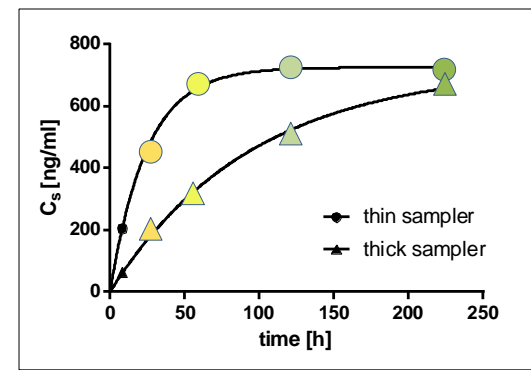


Look where equation approaches **zero**
 (= where graph **crosses the x axis**)

C_S = passive sampler conc. (ng/ml), C_W = dissolved concentration (ng/ml), K_{SW} = equilibrium sampler to water partitioning coefficient

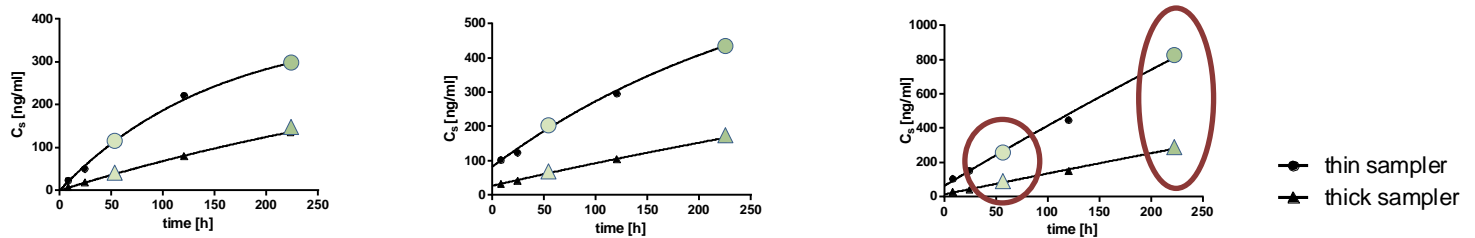
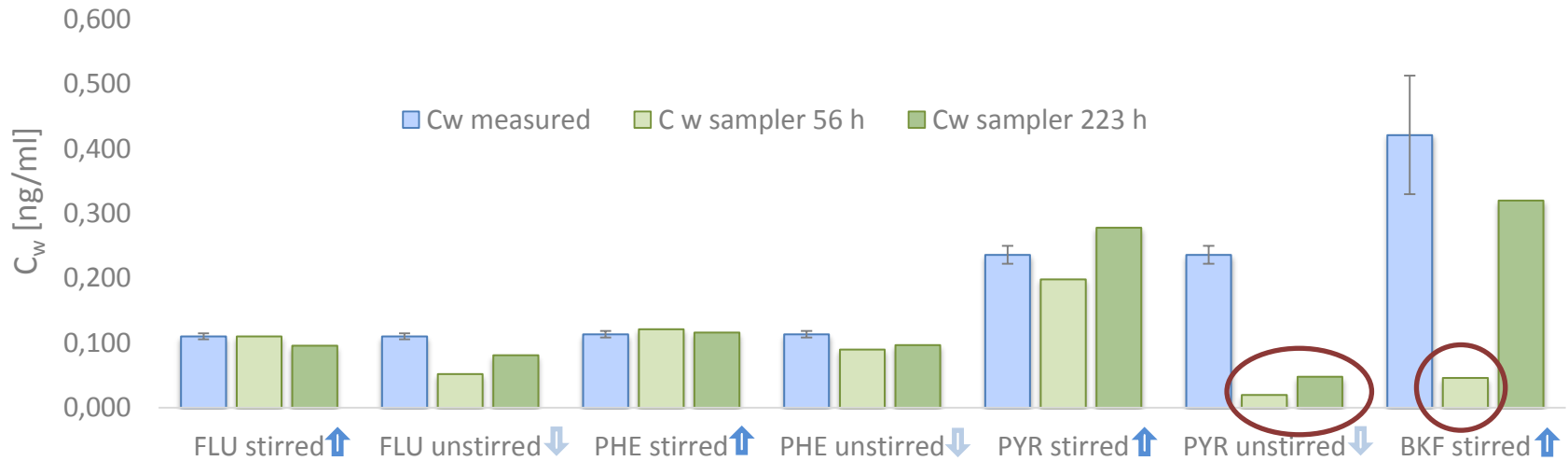
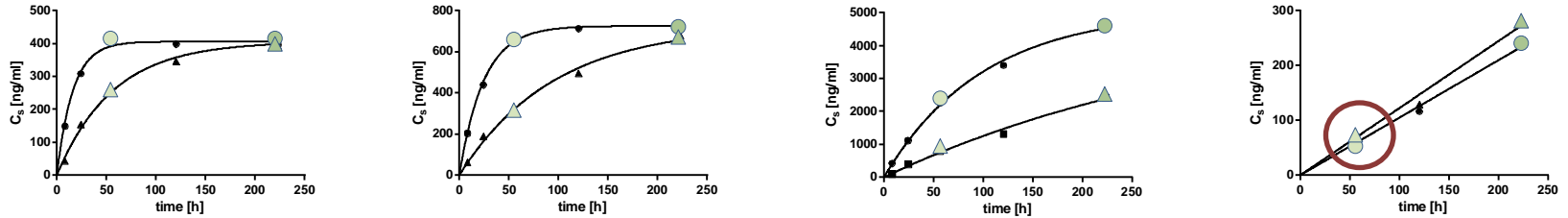
Results - all timepoints

Example: Phenanthrene stirred



C_s = passive sampler conc. (ng/ml), C_w = dissolved concentration (ng/ml), K_{sw} = equilibrium sampler to water partitioning coefficient

Results – early and late timepoint different substances – stirred and unstirred



C_s = passive sampler conc. (ng/ml), C_w = dissolved concentration (ng/ml)

Outlook

Practical application:

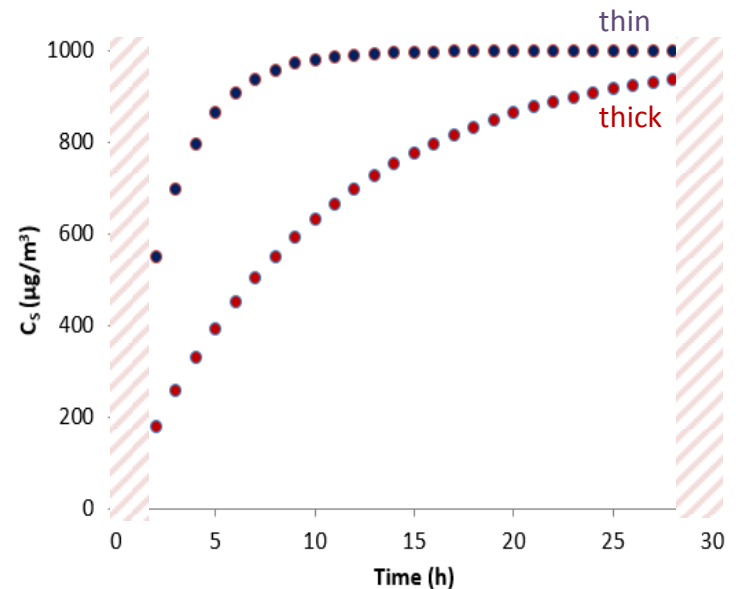
When an appreciable degree of equilibrium is at least the thin sampler is attained

→ efficient possibility of determining environmental dissolved concentrations during kinetic sampling

Limitations of approach:

In those cases where sampling in the early stage of kinetic uptake is needed (e.g. highly hydrophobic substances)

→ Method needs further optimization



Thank you for your attention!

Acknowledgements:

This research was funded by the Ministry of Innovation, Higher Education and Research of North Rhine-Westphalia

Ministerium für Innovation,
Wissenschaft und Forschung
des Landes Nordrhein-Westfalen

