



Royal Netherlands Institute for Sea Research

Passive sampling of nonpolar compounds in sediments

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SERDP/ESTCP Passive sampling session
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14. ABSTRACT Passive sampling is a powerful tool for determining the concentrations of truly dissolved contaminants in pore waters as well as for measuring the size of the exchangeable contaminant fraction in the sediment phase. Application of passive sampling of nonpolar contaminants in sediments is technically easy, but conceptually difficult, compared with traditional batch water sampling. The sorption capacity of the samplers and the (equivalent) water sampling rate are the two parameters that are needed to conceptualize the sampling process. These parameters also determine the value of the detection limits and the rate at which passive samplers equilibrate with their environment. After discussing contaminant uptake by passive samplers in an infinite water volume, their behavior in sediments will be dealt with using two practical examples. Exposure to stagnant sediments will be contrasted with exposure to sediment slurries. Passive sampler exposure to sediment slurries at low sampler/sediment phase ratios allows concentrations of dissolved contaminants in the pore water to be estimated. Exposure at high sampler/sediment phase ratios yields information on the size of the contaminant fraction in the sediment that is easily exchangeable with the pore water. Guidelines for designing passive sampler exposures to contaminated sediments will be discussed, and sources of uncertainties in the results will be highlighted.					
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PASSIVE SAMPLING OF NONPOLAR COMPOUNDS IN SEDIMENTS

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Nonpolar samplers for analytes with $\log K_{ow} > 4$

Technically simple

Conceptually difficult (initially)





Outline

■ Theory

- working principles
- concepts & link to batch sampling
 - sampling rates and sorption capacity
 - equilibration times and detection limits
- sampling rate calibration
- finite water volumes and sediment slurries

■ Practice

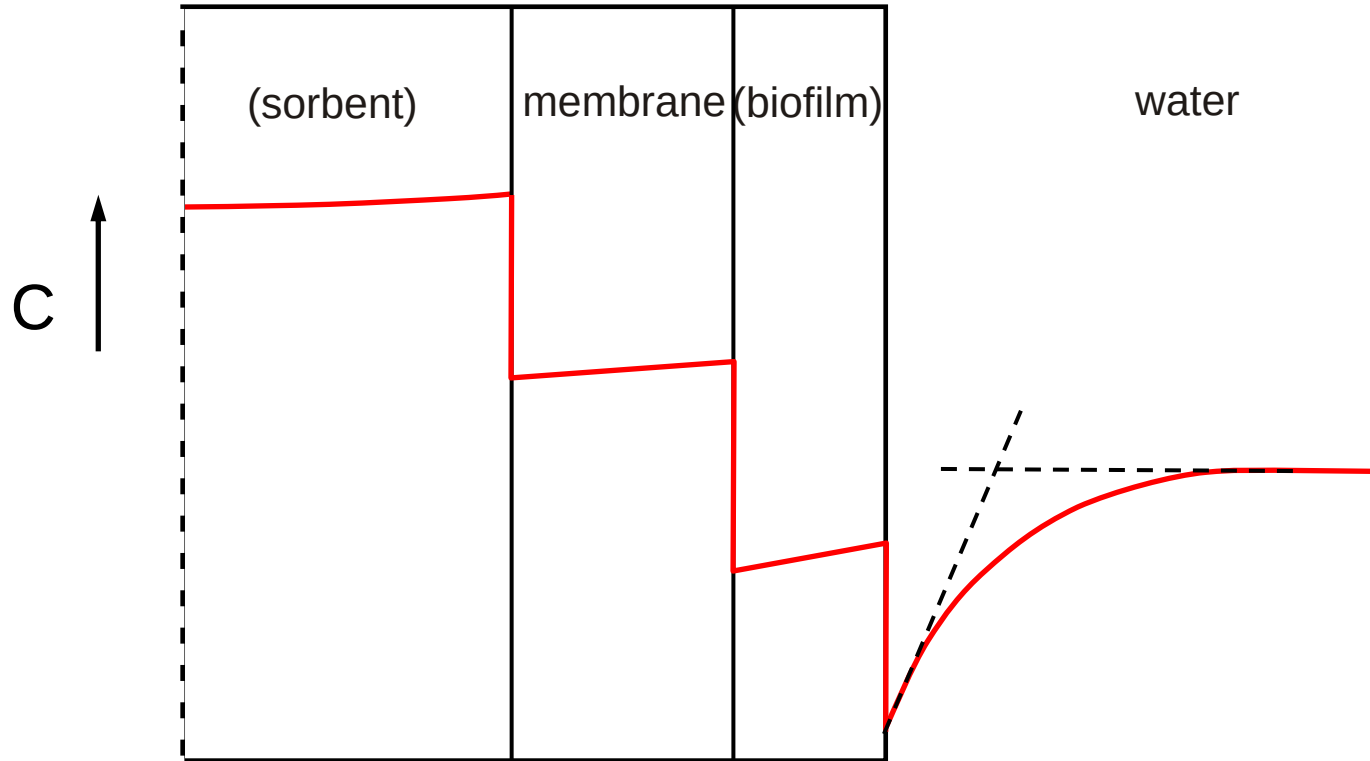
- pore water extraction (measuring C_w)
- sediment extraction (measuring accessible fractions)

■ Achievements & caveats



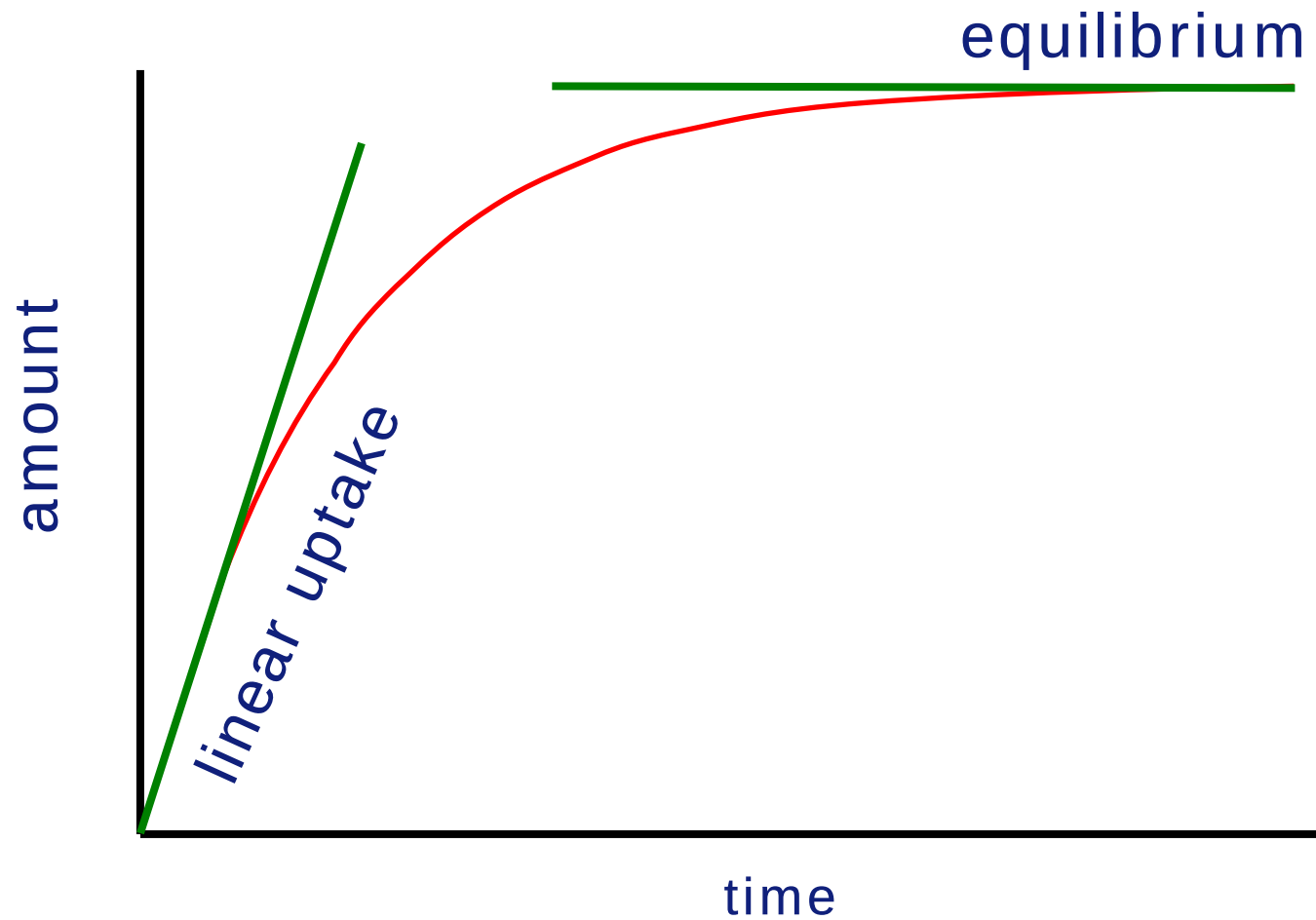
PSDs in water (infinite volume)

Workingprinciple





Uptake kinetics





Linear uptake stage

$$N = R_s C_w t$$

amount

$$\frac{N}{C_w} = \text{effectively extracted water volume} = R_s t$$

$$N = R_s t C_w$$

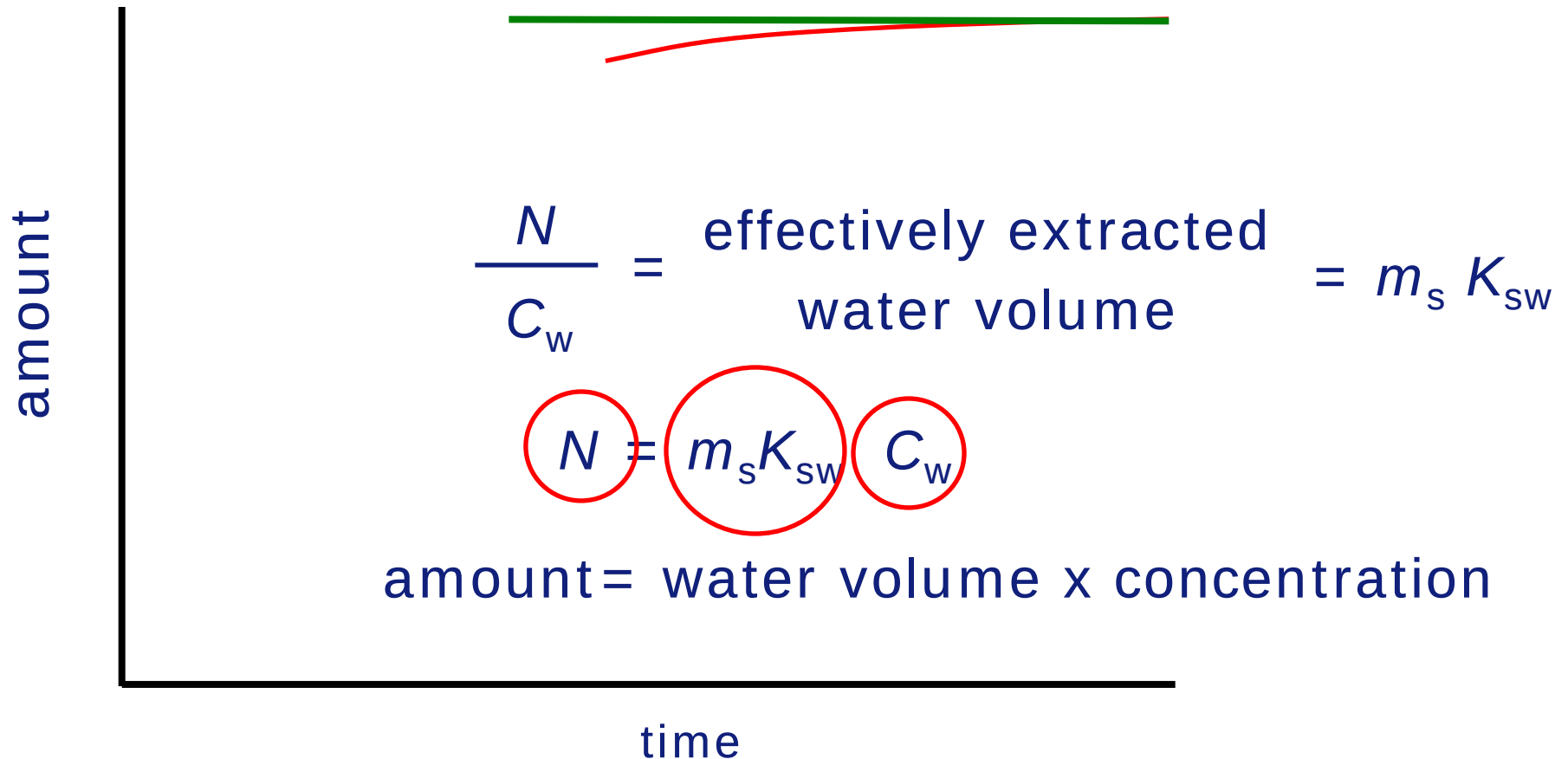
amount = water volume x concentration

time



Equilibrium stage

$$\frac{N}{m_s} = K_{sw} C_w$$





Uptake model (infinite water volume)

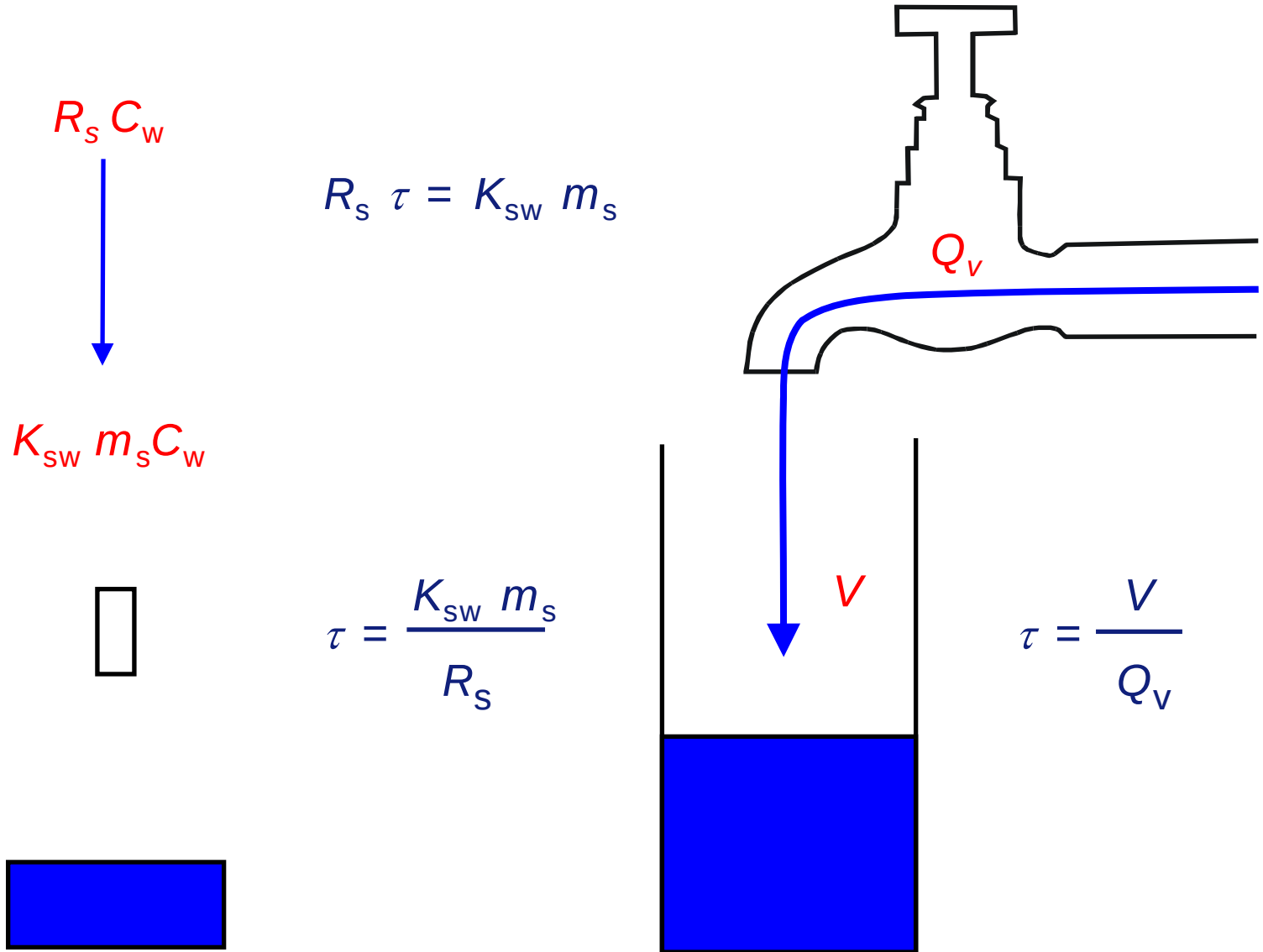
$$N = C_w \underbrace{K_{sw} m_s \left[1 - \exp \left(- \frac{R_s t}{K_{sw} m_s} \right) \right]}_{\text{water volume}}$$

Amount = concentration x

water volume



Equilibration time (TWA window)





Detection limits

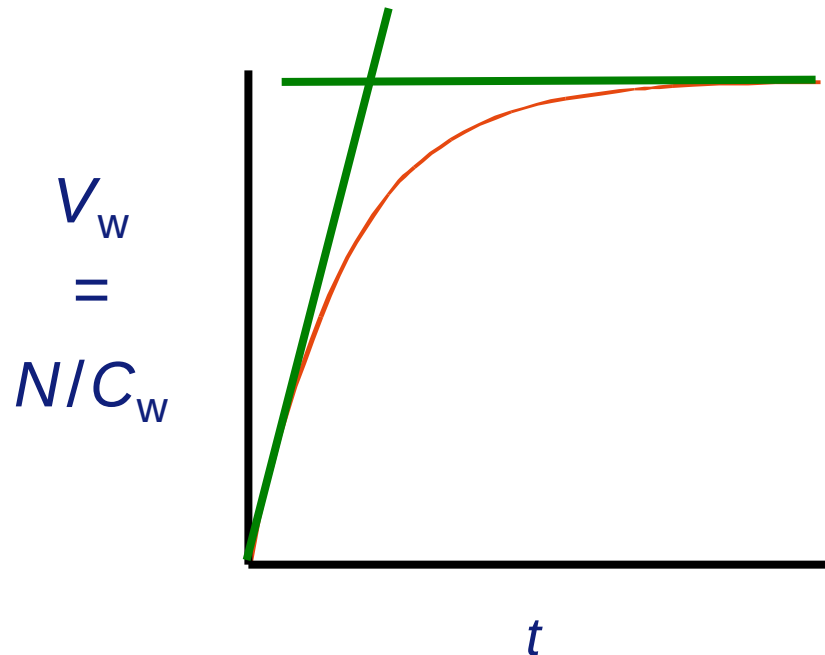
Linear uptake stage

$$V_{wLUS} = R_s t$$

Equilibrium stage

$$V_{wEqS} = m_s K_{sw}$$

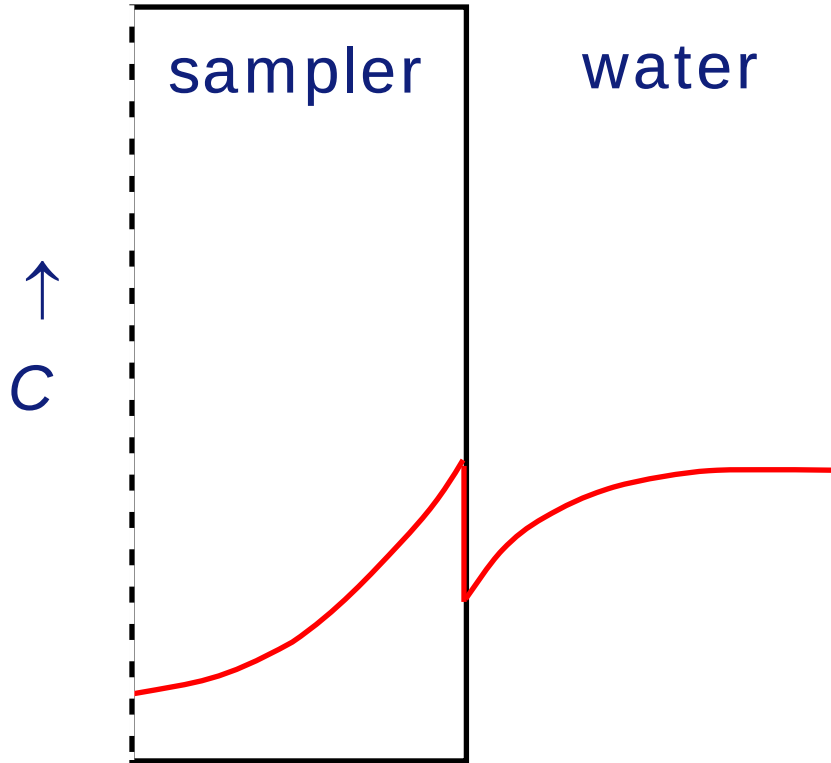
take the lowest
of these



$$DL_{Cw} = \frac{DL_N}{V_w}$$

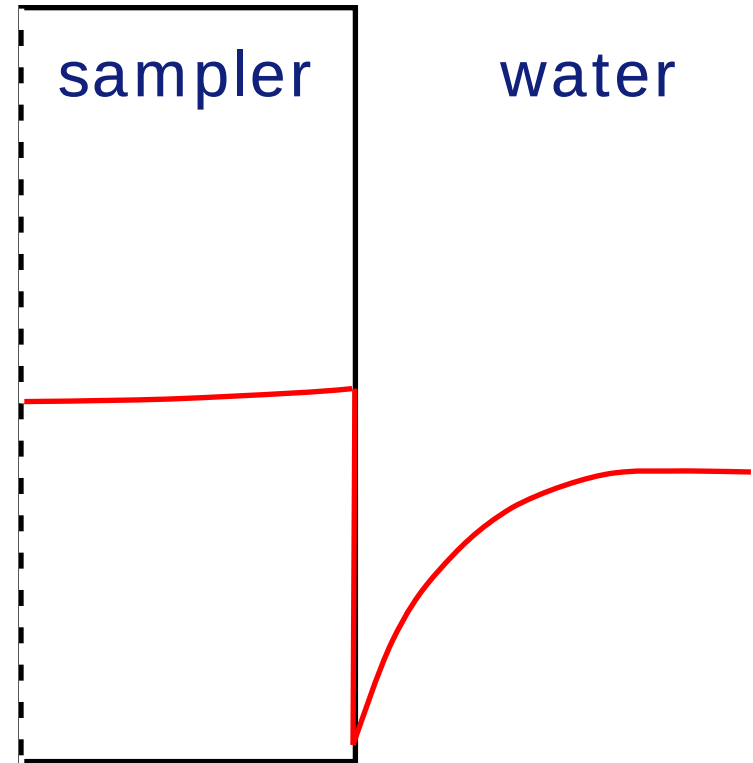


Uptake rate control



membrane-control

$$R_s \sim K_{sw} D_m$$



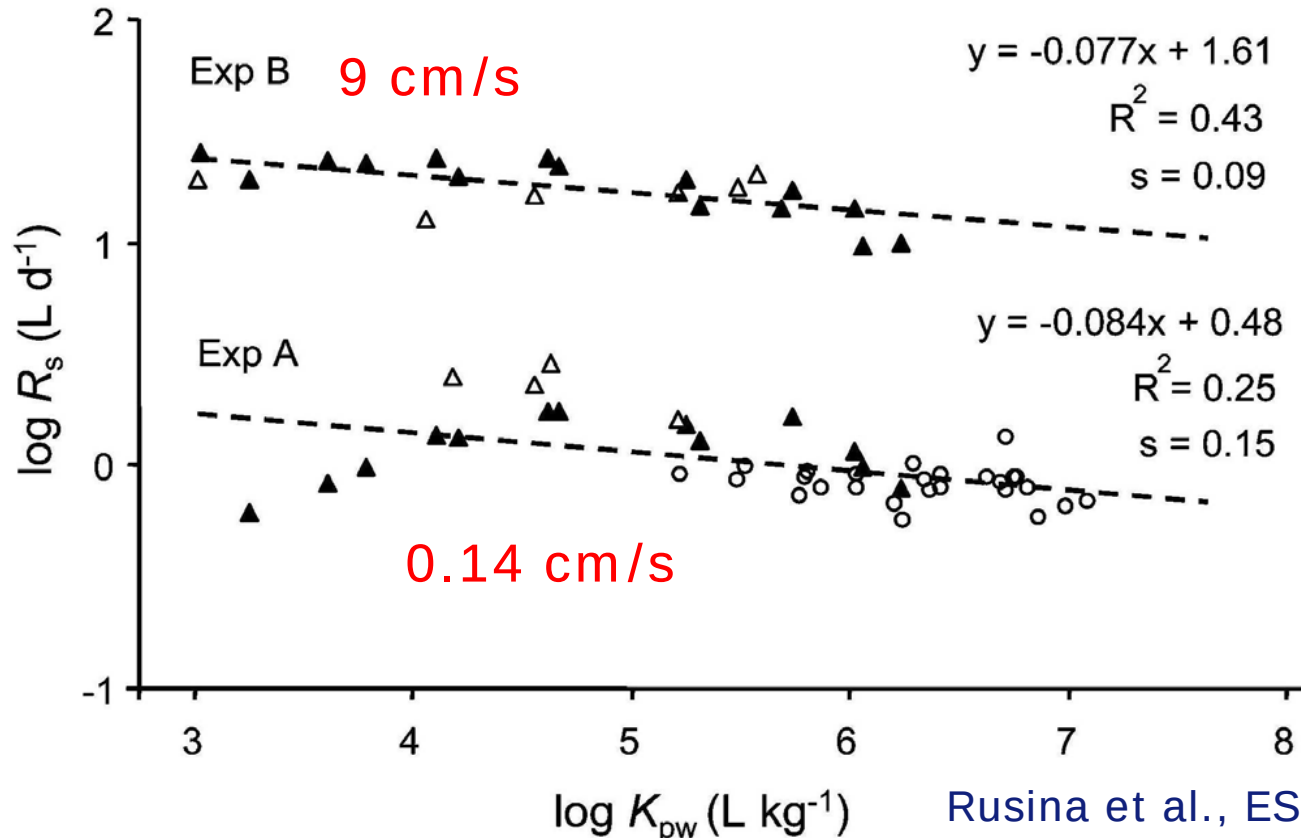
WBL-control

$$R_s \sim D_w^{2/3}$$

Sampling rates (R_s)

compound properties (diffusion coefficient, hydrophobicity)

- temperature
- flow rate
- suspended solids concentration





Calibration of uptake kinetics

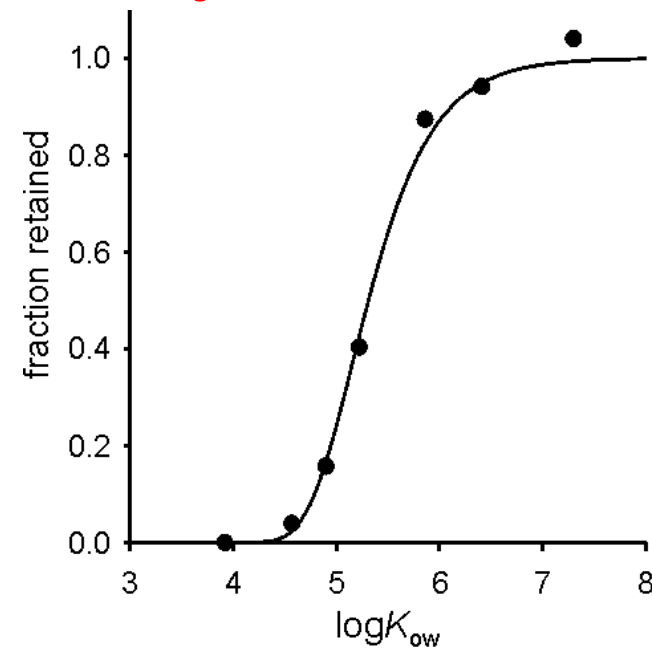
Performance reference compounds

- not occurring in the water
- spiked into PSD before exposure

- dissipation follows: $\frac{N_s}{N_0} = \exp\left(-\frac{R_s t}{K_{sw} V_s}\right)$

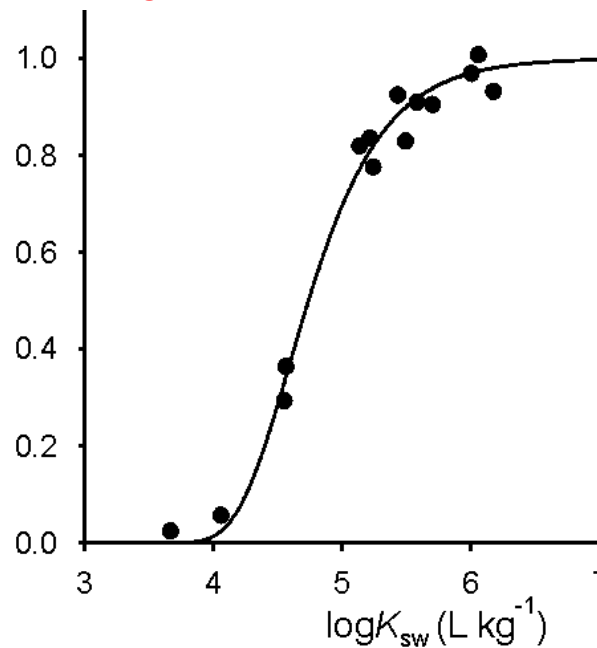
SPMD in water

$$R_s = 5.1 \pm 0.3 \text{ L d}^{-1}$$



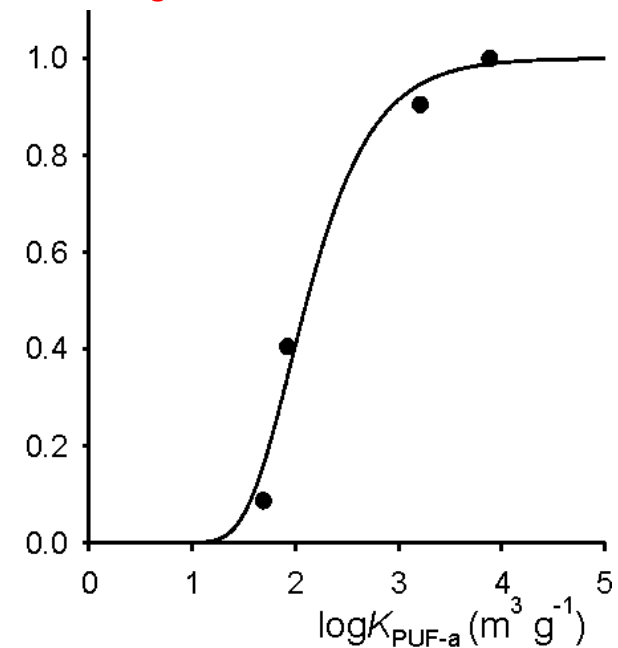
silicone in water

$$R_s = 11.6 \pm 0.7 \text{ L d}^{-1}$$



PUF in air

$$R_s = 5.6 \pm 0.6 \text{ m}^3 \text{ d}^{-1}$$

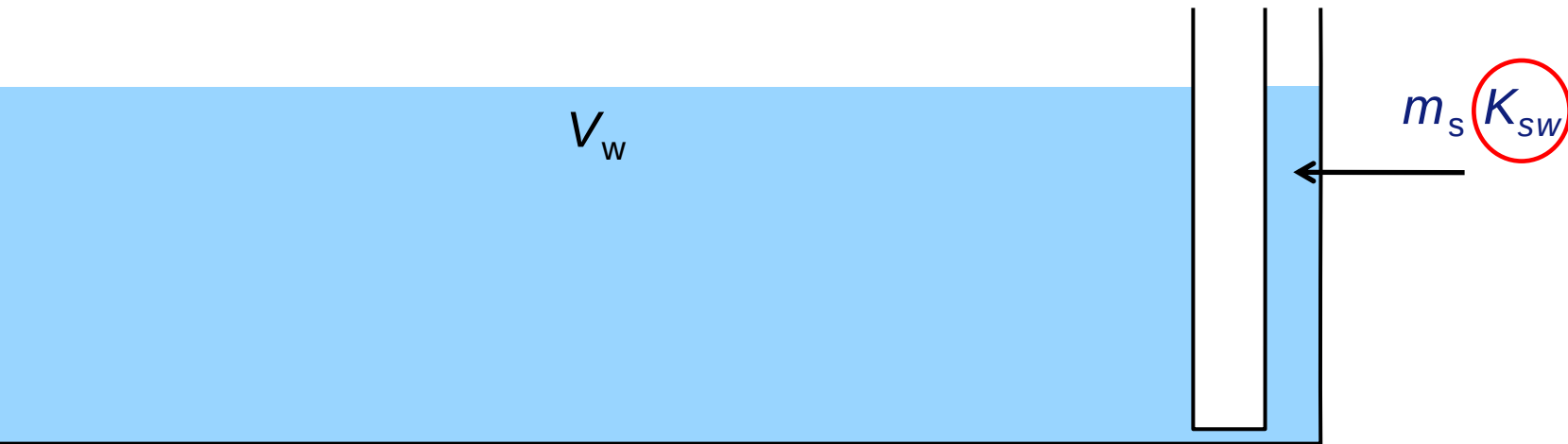




PSDs in water (finite volume)



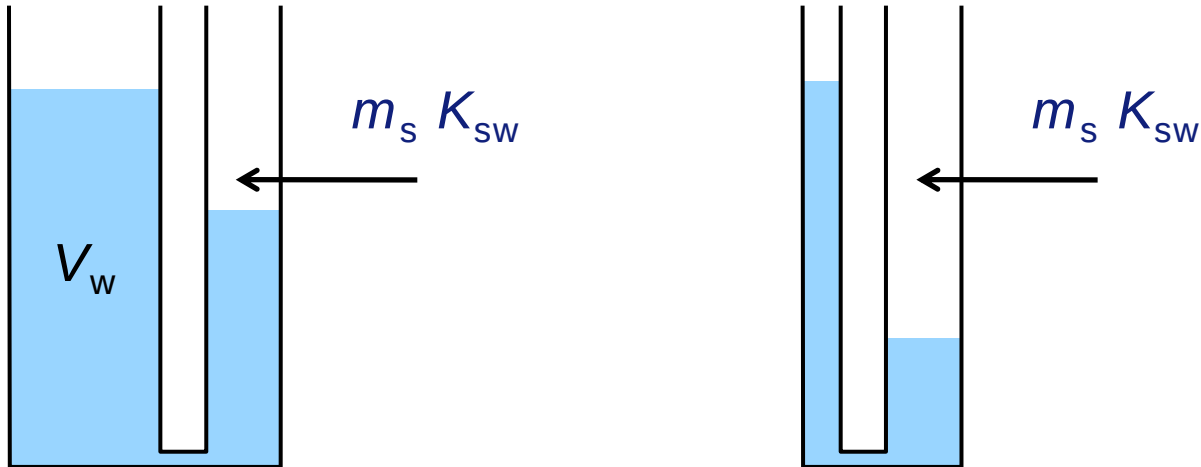
Infinite water volume



“infinite” means: $V_w \gg m_s K_{sw}$



Finite water volume



“finite” means: $V_w \cong m_s K_{sw}$

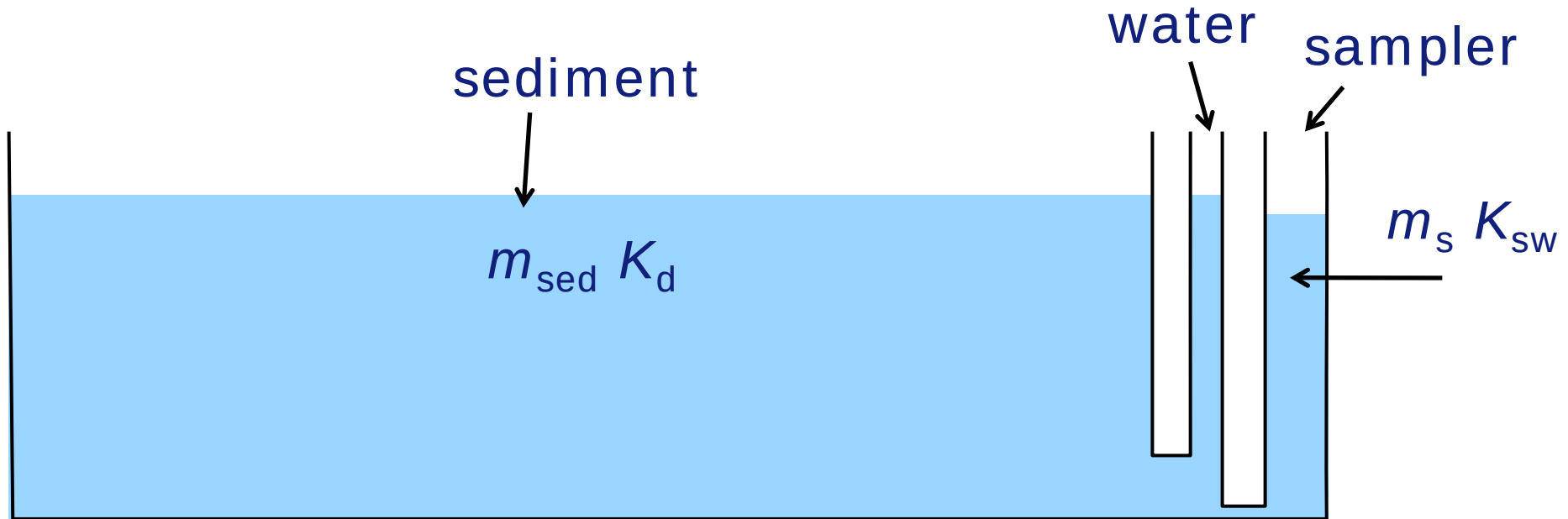
phenanthrene in 10 L water 1 g silicone

$$m_s K_{sw} = 13 \text{ L}$$

faster equilibrium

- at a lower level
- because of depletion

Sampling in sediment slurries



Pore water sniffing: $m_{\text{sed}} K_d + V_w \gg m_s K_{\text{sw}}$

$$C_w(t) \cong C_{w,0}$$



Example 1: pore water sniffing

PAHs/PCBs/HCB in harbor sediments

ES&T 37: 4213-4220,2003



LDPE strips in sediment slurries and stagnant sediments

~160 g sediment (1-4% oc)

~120 mL water

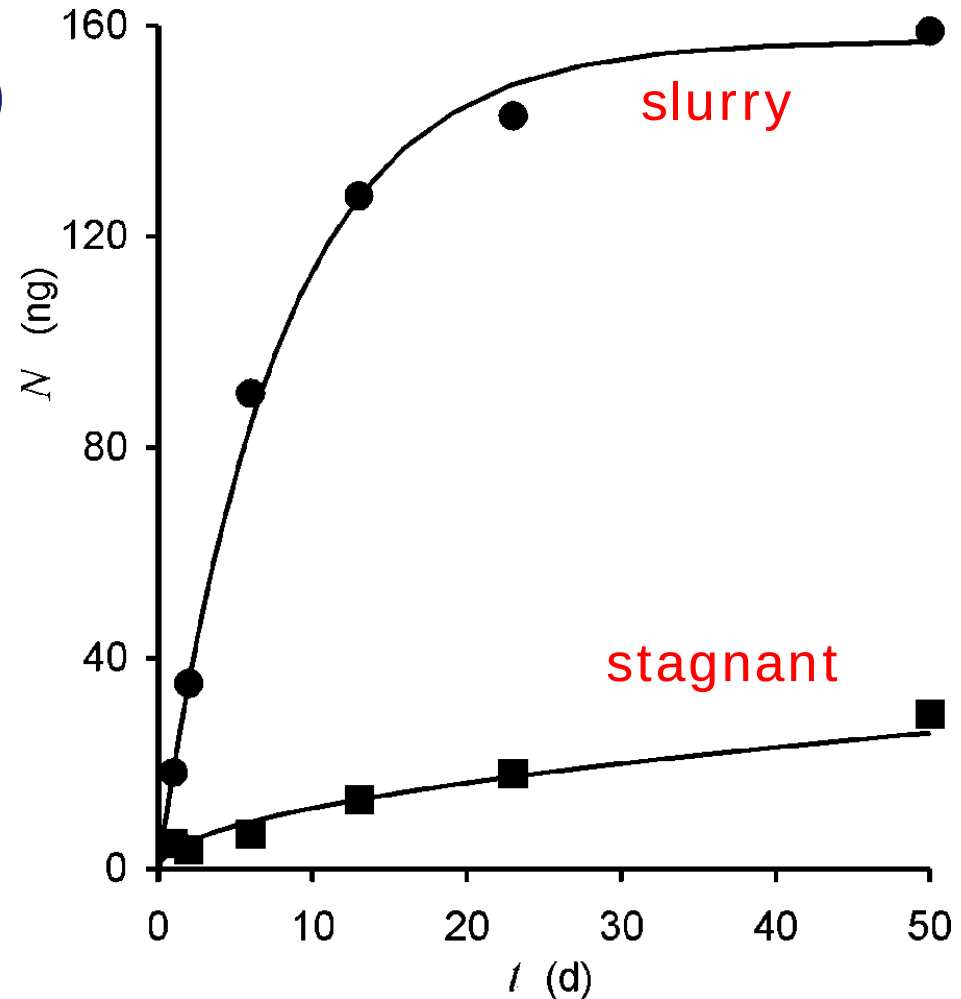
0.5 g LDPE (30x2.5 cm)

50 d exposure

chrysene

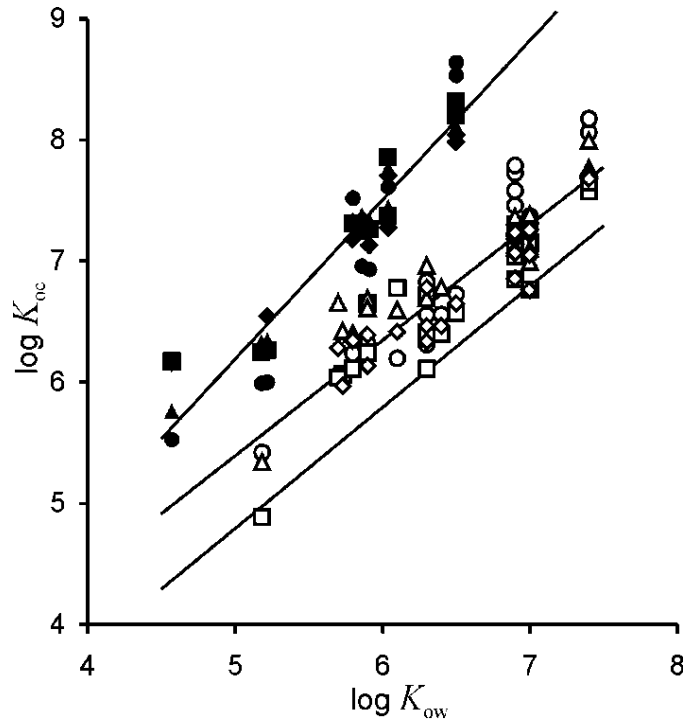
$m_{\text{sed}} K_d \approx 1000 \text{ L}$

$m_s K_{\text{sw}} \approx 300 \text{ L} (\text{☹ or } \text{☹})$

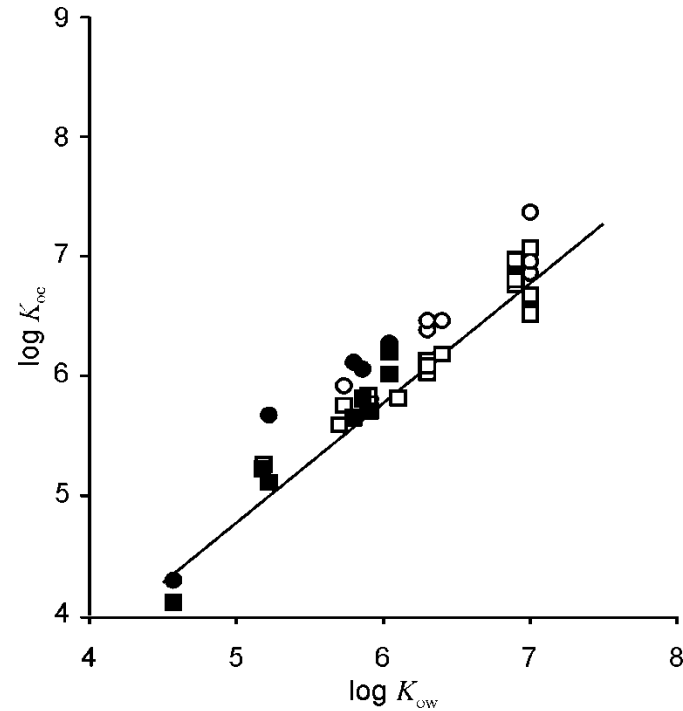




K_{oc}



from C_{sed}/C_w



from uptake rates
in stagnant sediments

$$N \sim A C_w \sqrt{K_d} \sqrt{t}$$



Example 2: nondepletive and depletive extraction

PAHs/PCBs/HCB in estuarine sediments

Smedes, unpublished results



Scaling the experiment

~20 g sediment (2.5% oc)

~200 mL water

0.2, 2, 20 g silicone sheet

48d exposure

$$\frac{m_{\text{sed}} K_d}{m_s K_{\text{sw}}} \approx 120 \text{ L}$$
$$\frac{m_{\text{sed}} K_d}{m_s K_{\text{sw}}} \approx 10, 100, 1000 \text{ L} \quad (\text{☺})$$

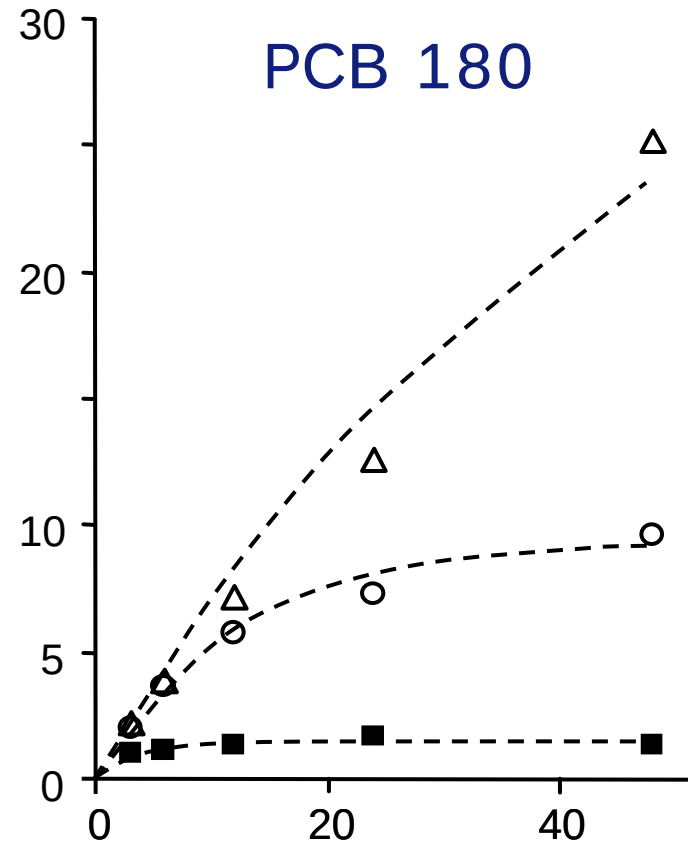
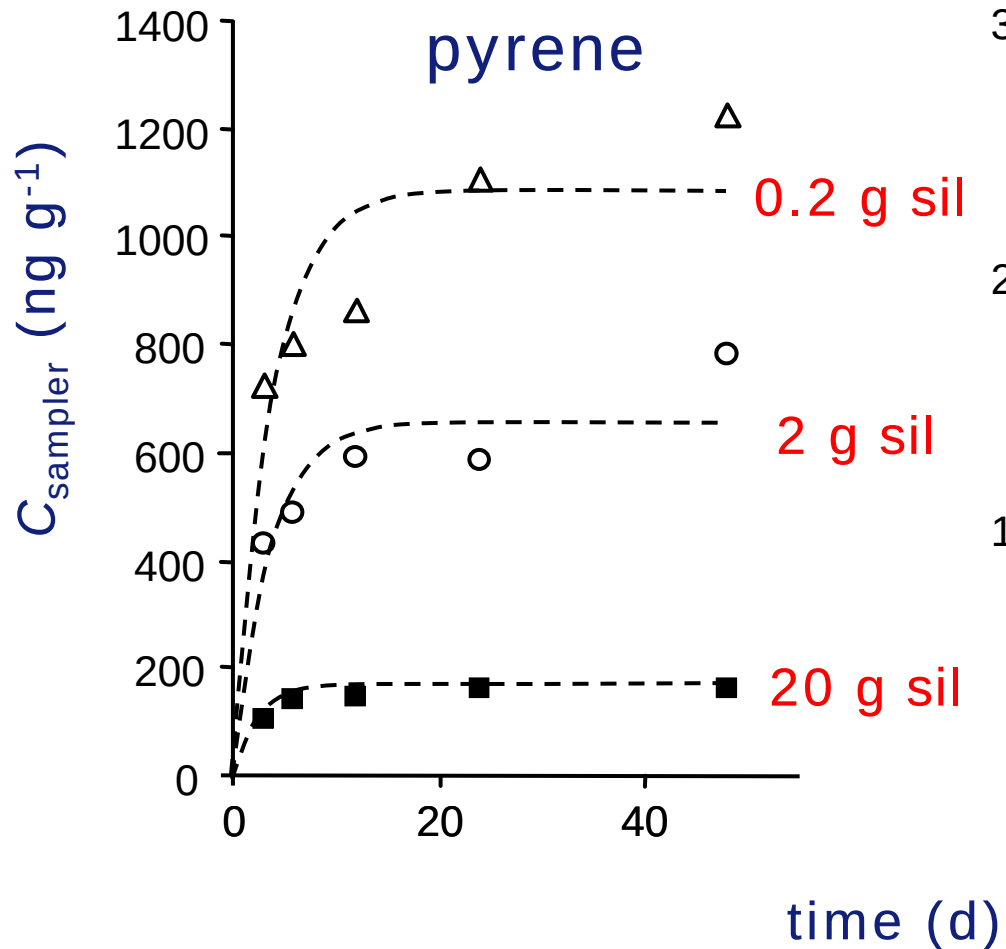
↑ ↑

sniffing depleting



High sampler mass $\Rightarrow$ depletion

20 g dw sediment, $f_{oc}=0.025$

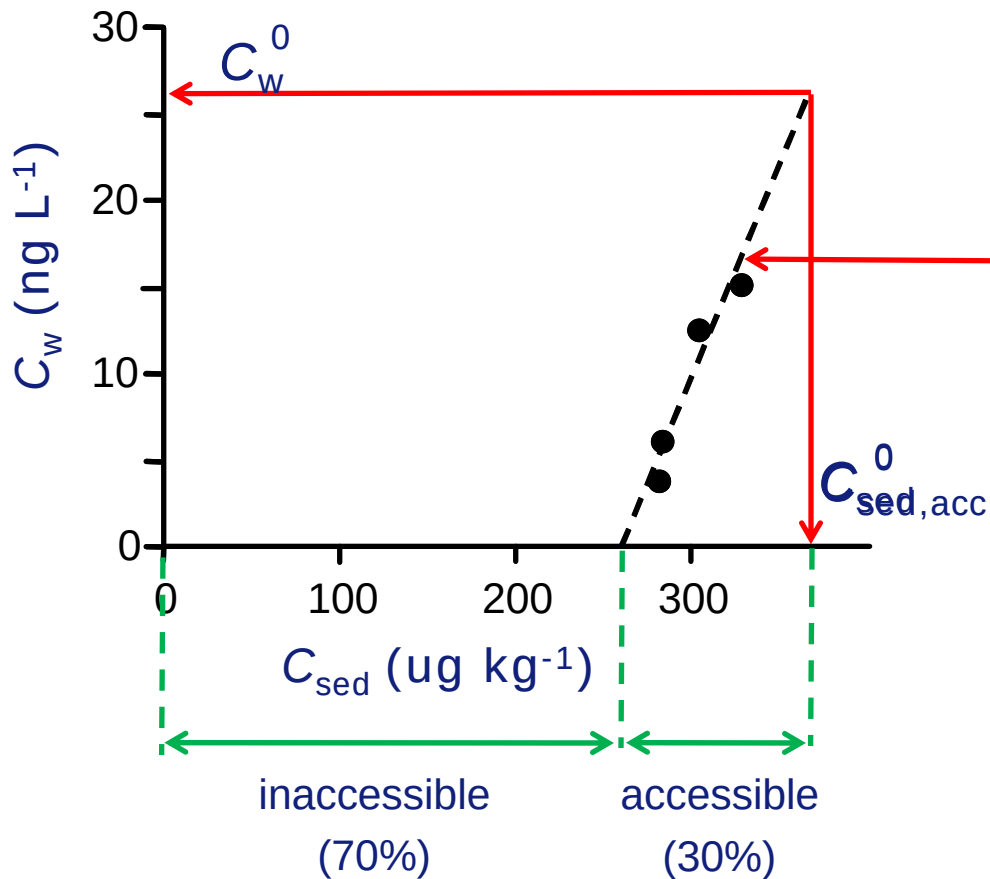




Equilibrate samplers

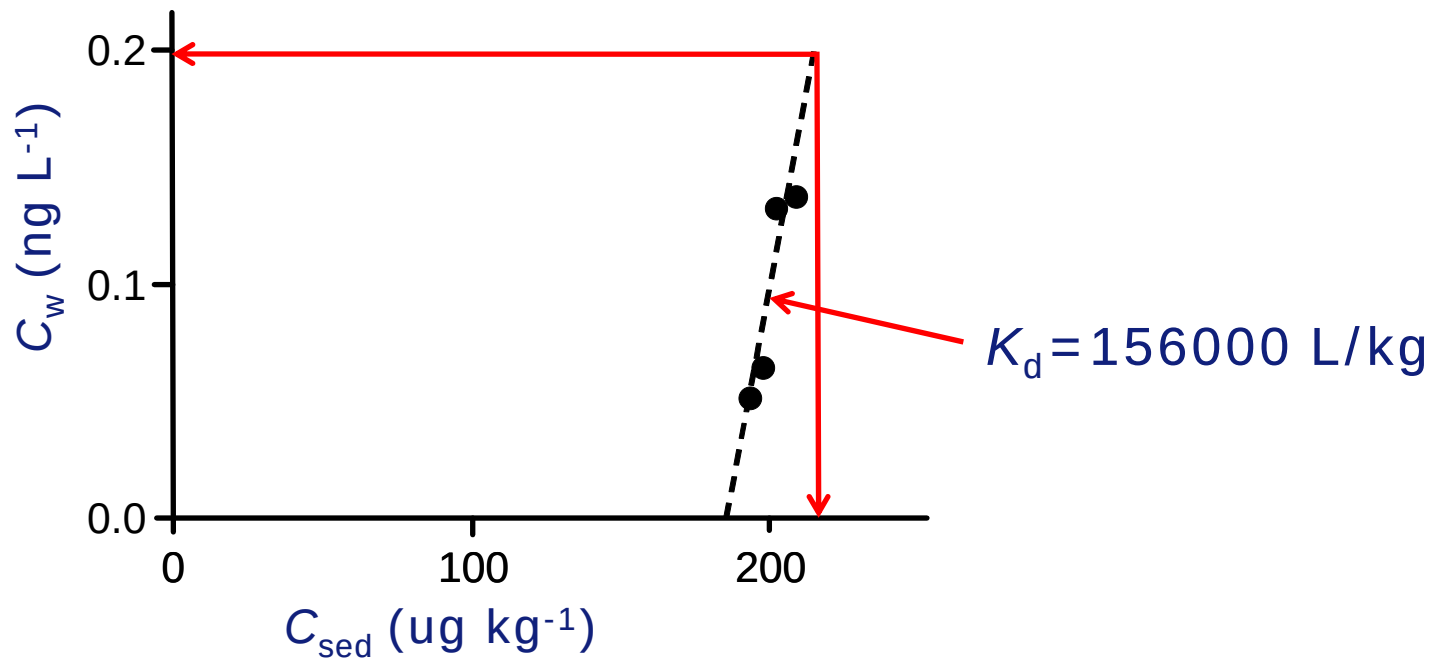
more mass $\Rightarrow$ lower $C_w \Rightarrow$ lower C_{sed}

Fluoranthene



$$K_d = \frac{110\,000 \text{ ng/kg}}{27 \text{ ng/L}} = 4100 \text{ L/kg}$$

Indeno[1,2,3-cd]pyrene



accessible : 14%

inaccessible : 86%



PSDs for sediment quality assessment: achievements & caveats

Achievements

- use R_s and $m_s K_{sw}$ to link PS to batch sampling
- non-depletive $\rightarrow C_w$
(need R_s calibration)
- depletive $\rightarrow$ accessible fraction
(demonstrate equilibrium)
- scaling rules are straightforward (m_{sed} & $m_{sampler}$)

Caveats

- availability of reliable K_{sw} values
- among-manufacturer variability of polymer properties
- limited PSD intercomparison



Evolution of peak pattern

