INVESTMENTS IN EDUCATION DEVELOPMENT

Introduction to Passive Sampling

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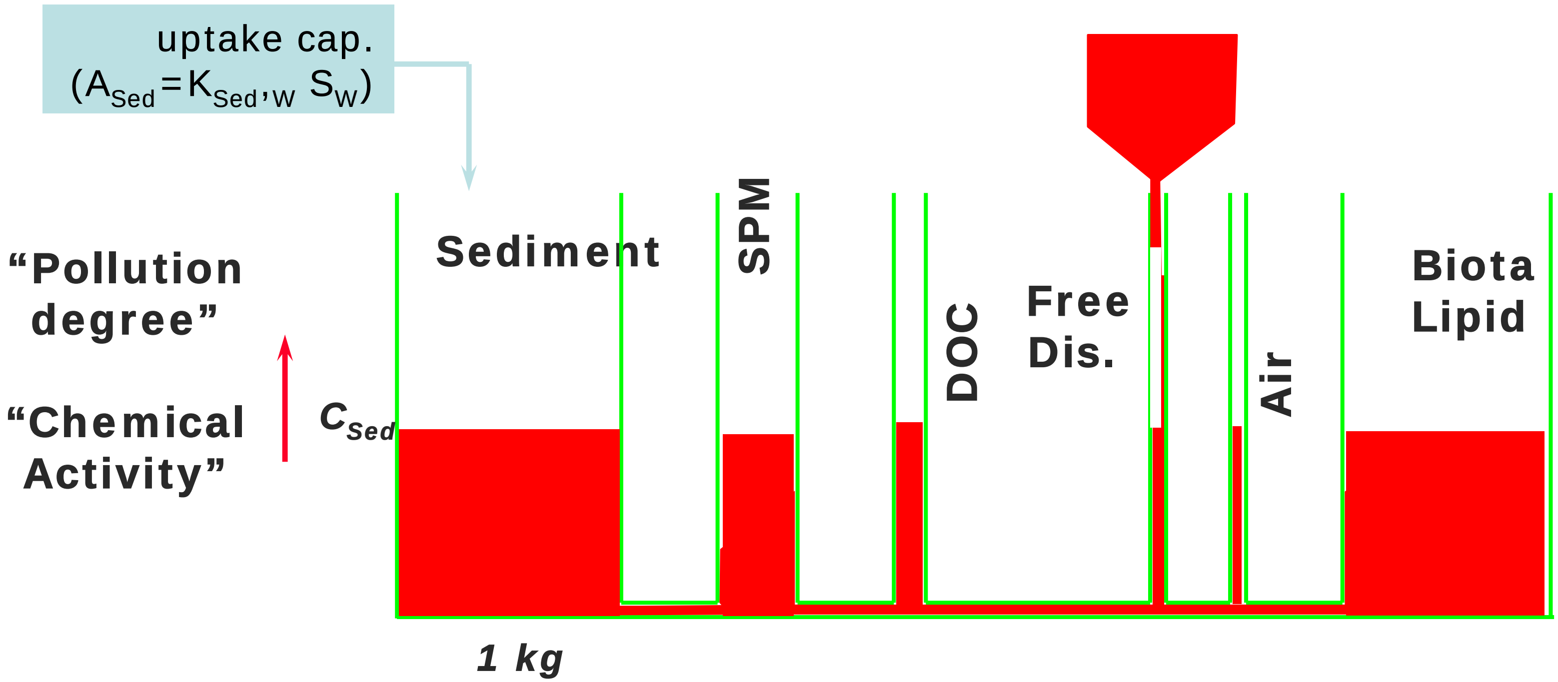
Pollution level in aqueous systems

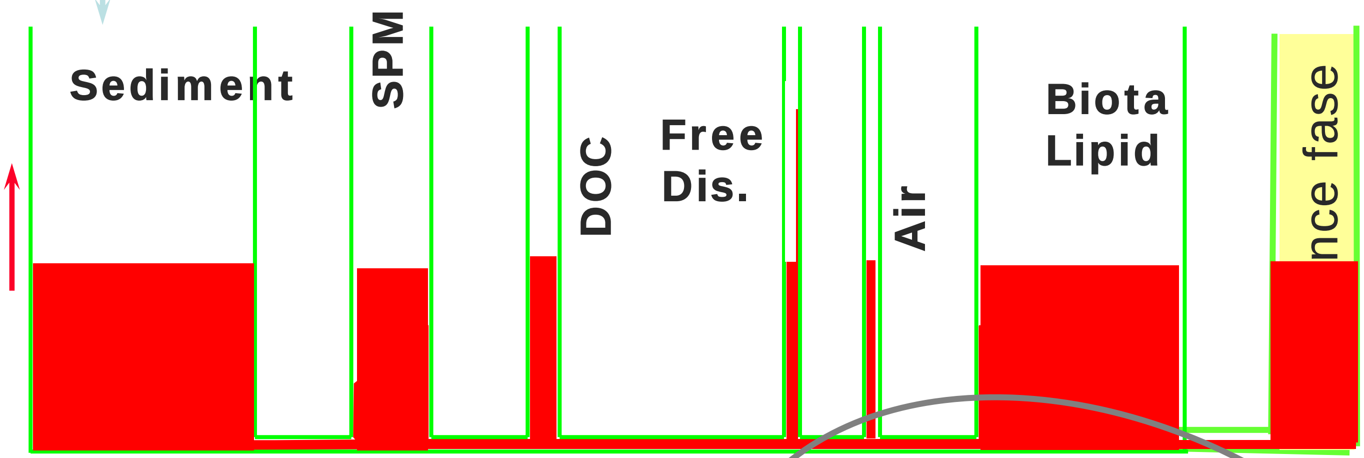


In formula: $$\frac{C_{Sed}}{A_{Sed}} = \frac{C_{SPM}}{A_{SPM}} = \frac{C_{DOC}}{A_{DOC}} = \frac{C_W}{S_W} = \frac{P}{P_0} = \frac{C_{Lipid}}{S_{Lipid}}$$

Pollution level in aqueous systems

uptake cap.
$(A_{Sed} = K_{Sed,W}\, S_W)$

“Chemical activity”



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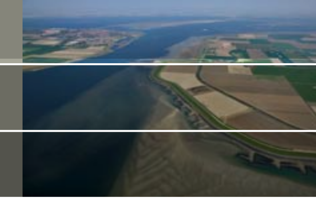
$$K_{Ref\text{-}W} = \frac{S_{Ref}}{S_W} = \frac{C_{Ref}}{C_W}$$


What's on the program

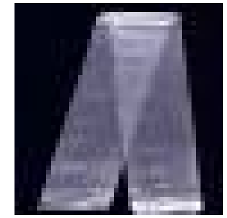
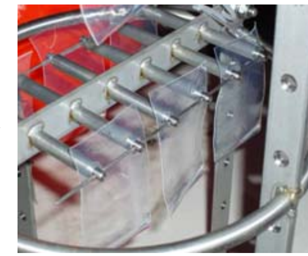
- Different passive samplers
- Procedures, material and methods
- Working principles
- Parameters needed
- Polar samplers

Passive sampler types

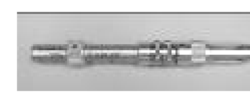
Macro samplers→ extract and multiple analyses

- semipermeable membrane devices "SPMD"
- single-phase strip samplers
  - low-density polyethylene (LDPE)
  - polydimethylsiloxane (PDMS, silicone rubber)
  - polyoxymethylene (POM)
- C18-based disk samplers (ChemCatcher, a.o.
- (Polar compounds: POCIS, C18....)
- (ceramic dosimeter)


Micro passive samplers → all sorbed is injected - one shot

- solid-phase microextraction (SPME)
- stir bar sorptive extraction (SBSE)
- rod samplers (MESCO)




Deployment of SR and SPMD

Ground water

After exposure

Foto by IOEV, Spanish Oceanographic Inst. Vigo, Spain

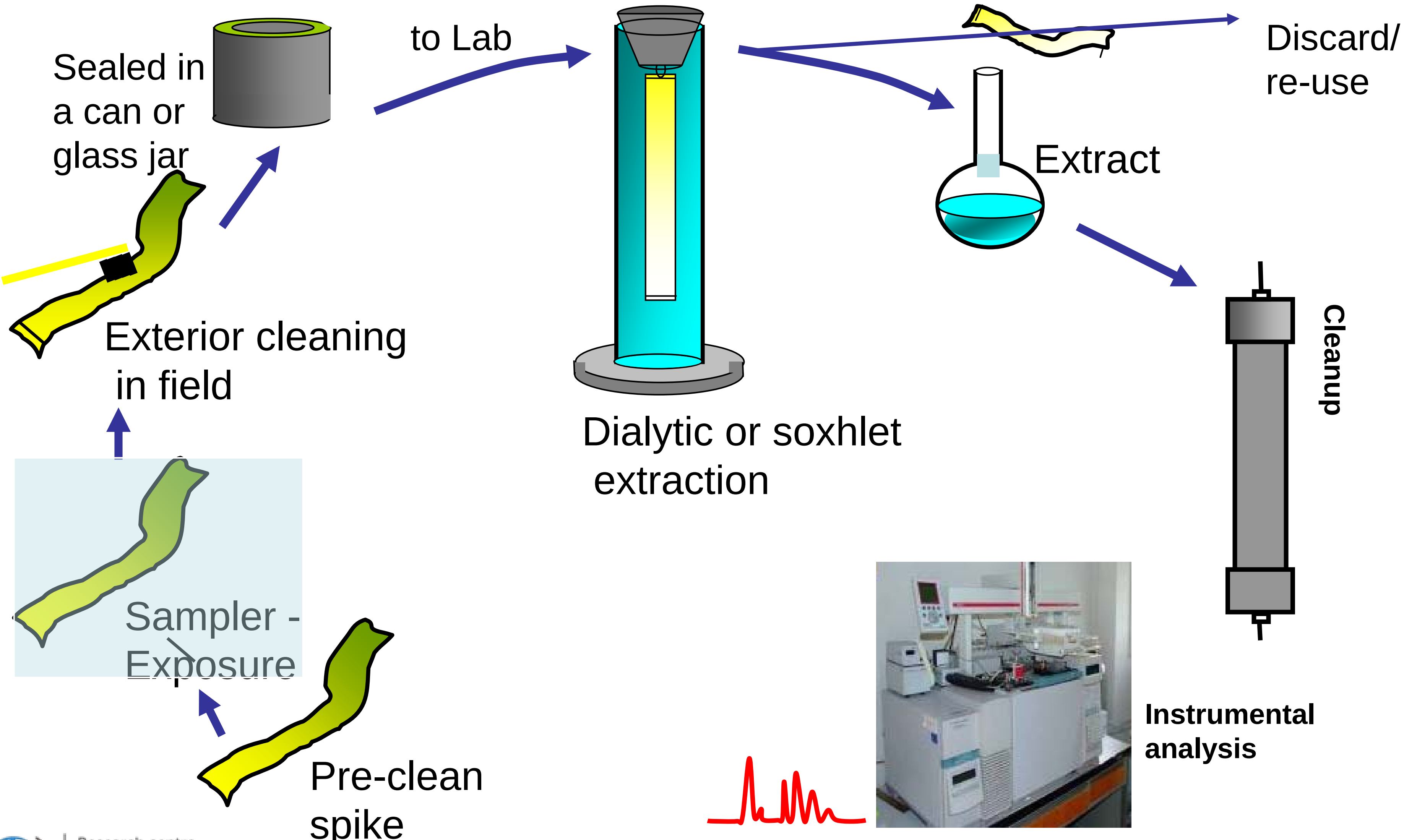
Cleaning sheets after recovery

Cleaning samplers in the lab

During transport and storage redistribution could occur

Better clean samplers in the field with local water and scourer

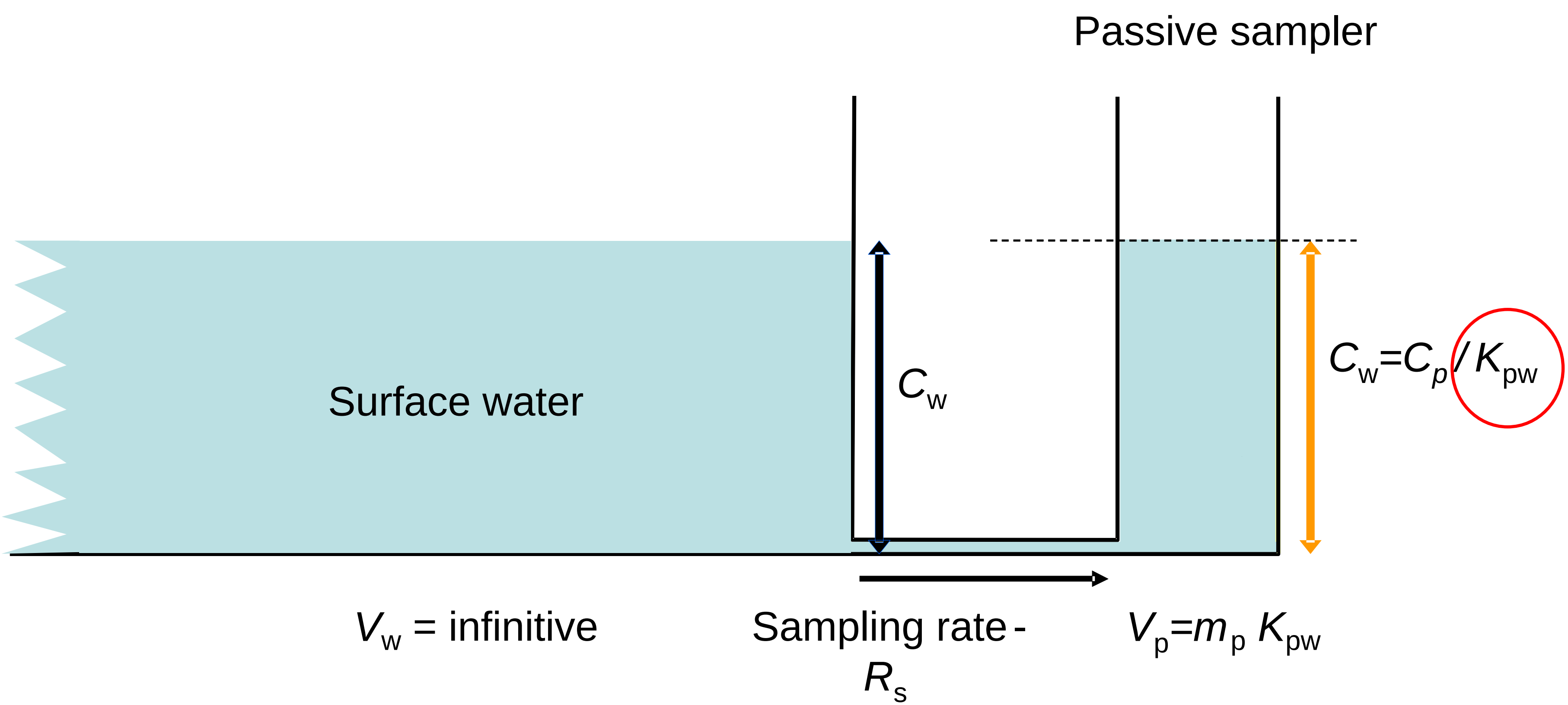
Processing of passive samplers: SPMD



What to do with the data

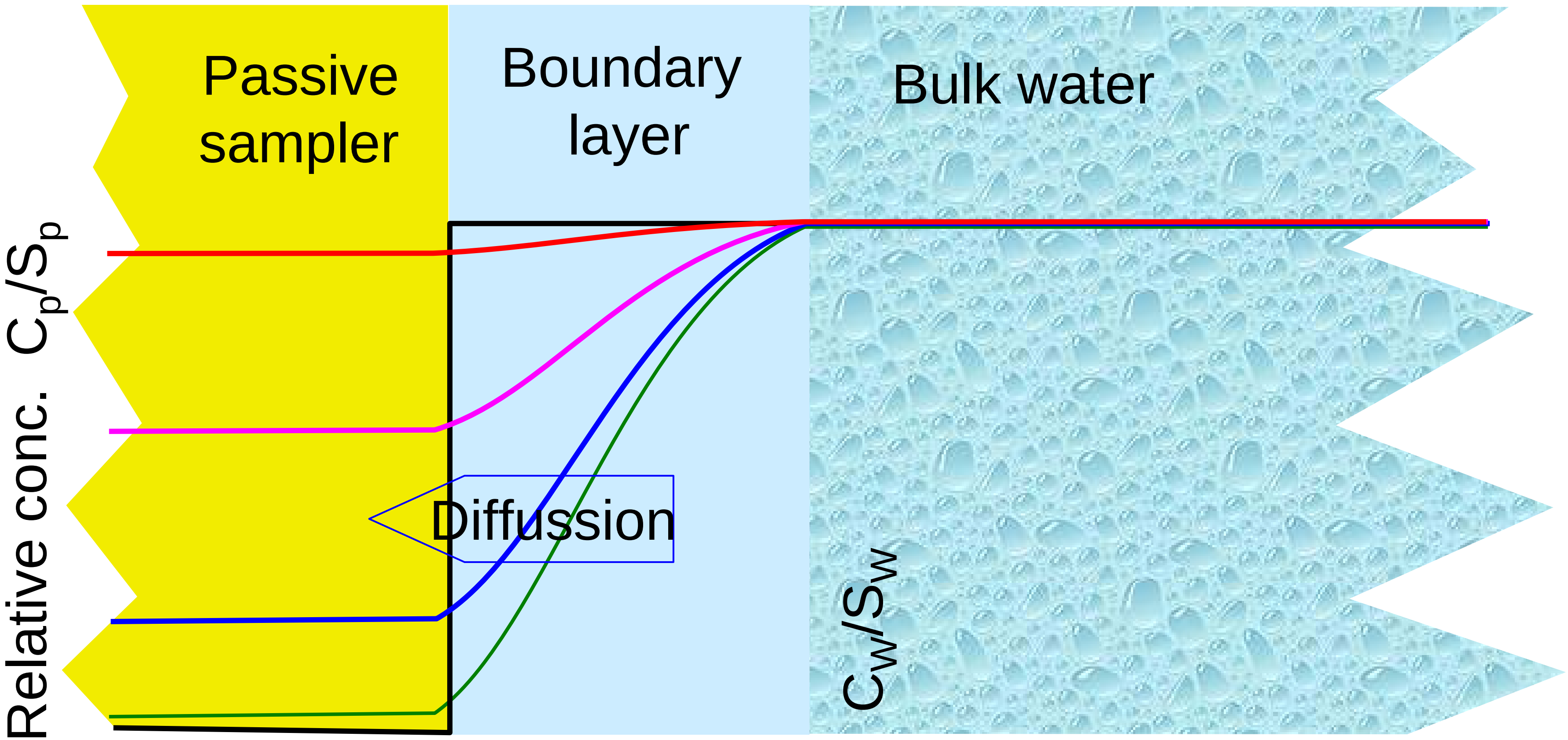
First need to understand the uptake

When equilibrium is attained



Uptake process from water

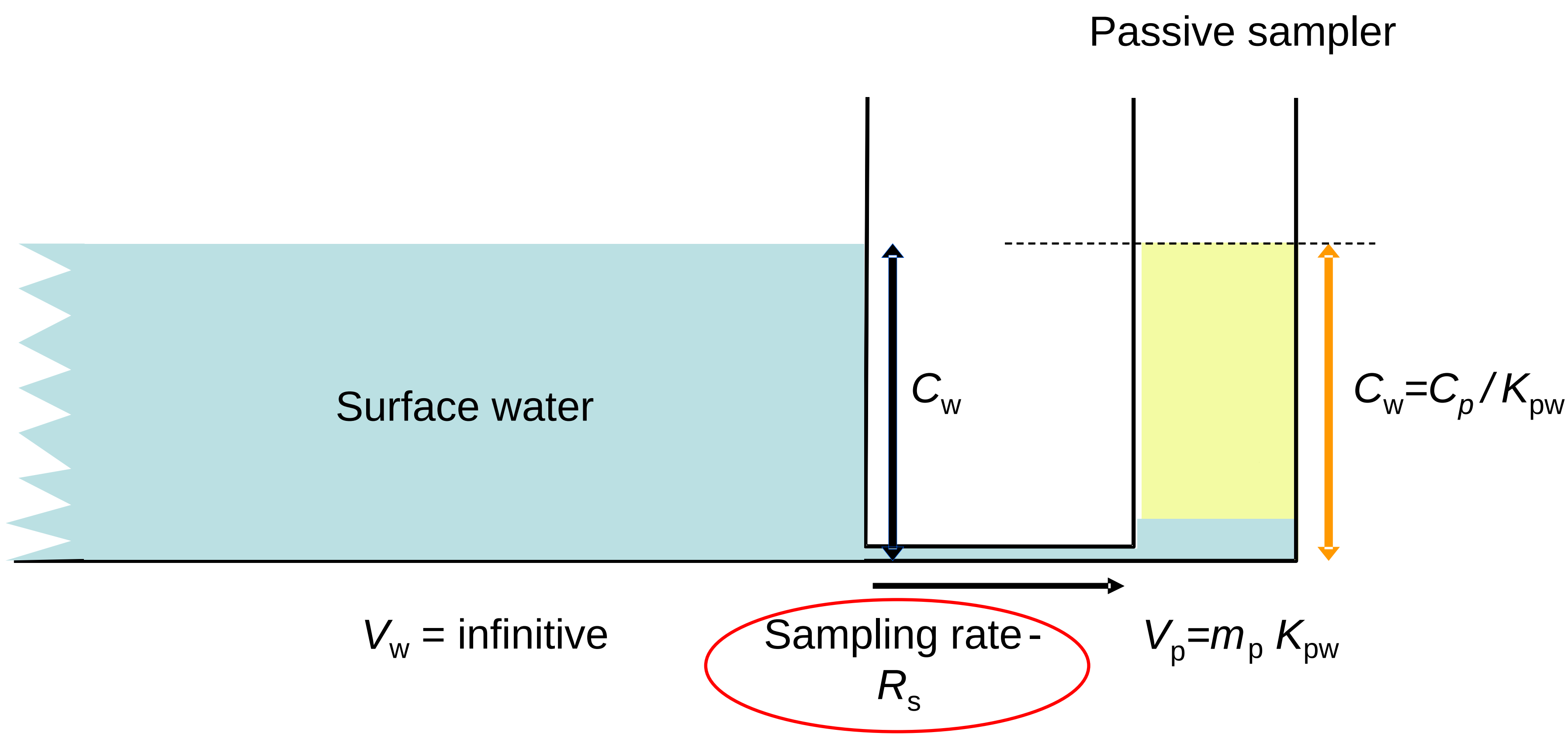
Water Boundary layer controlled



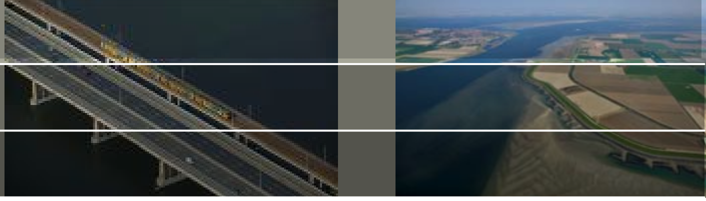
$$\frac{D_p K_{pw}}{\delta_p} \qquad \frac{D_w}{\delta_w}$$

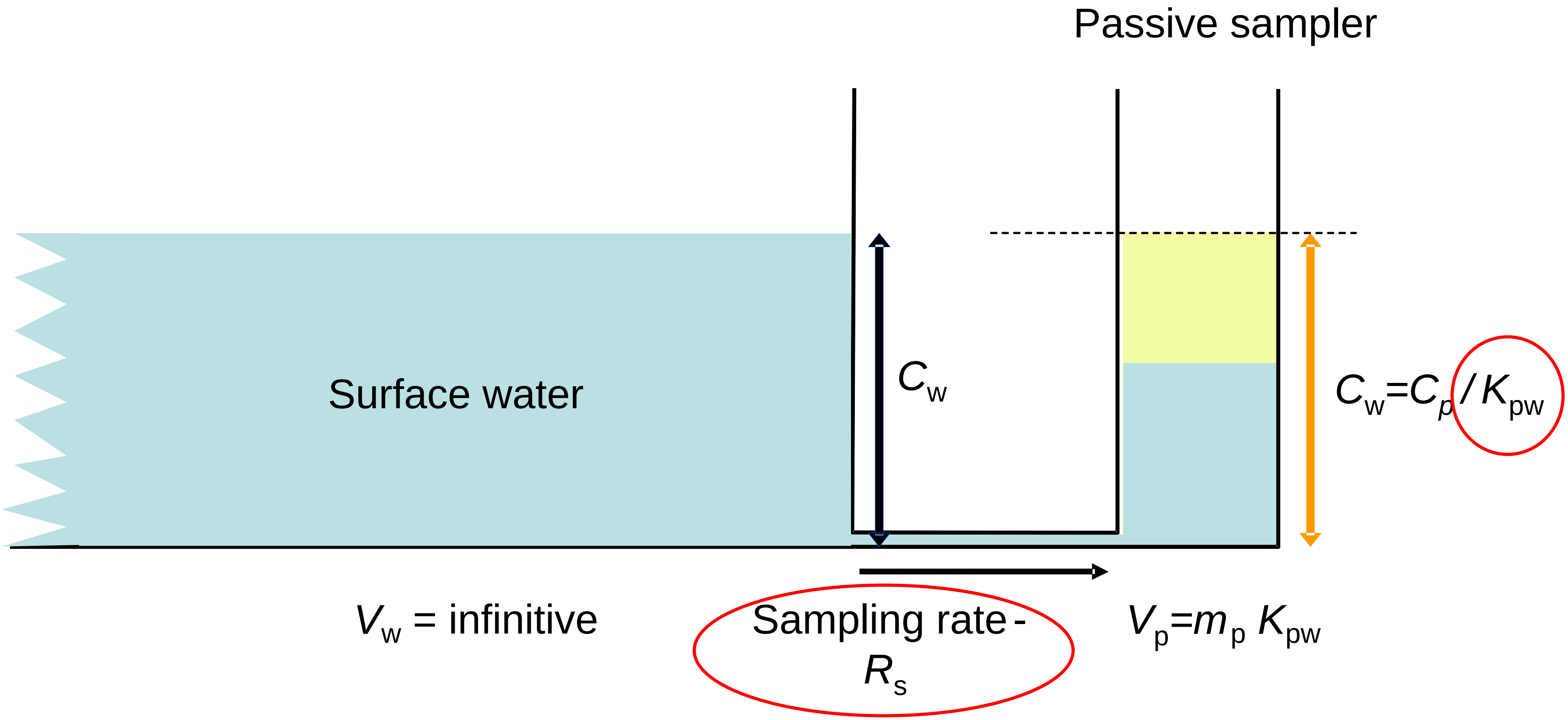
mass transfer coefficients

Uptake process by a passive sampler



Intermediate situation



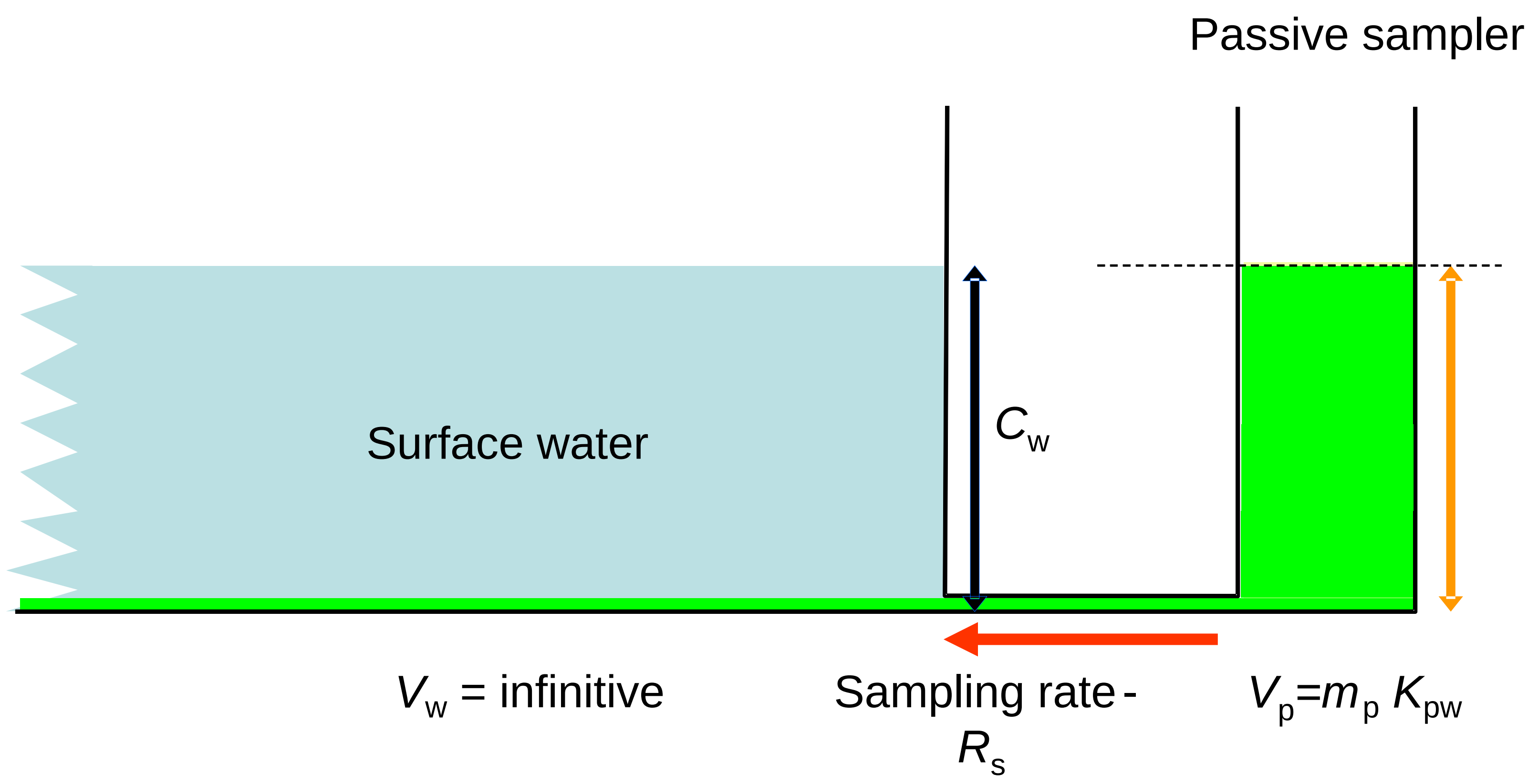


How to estimate sampling rate (R_s)

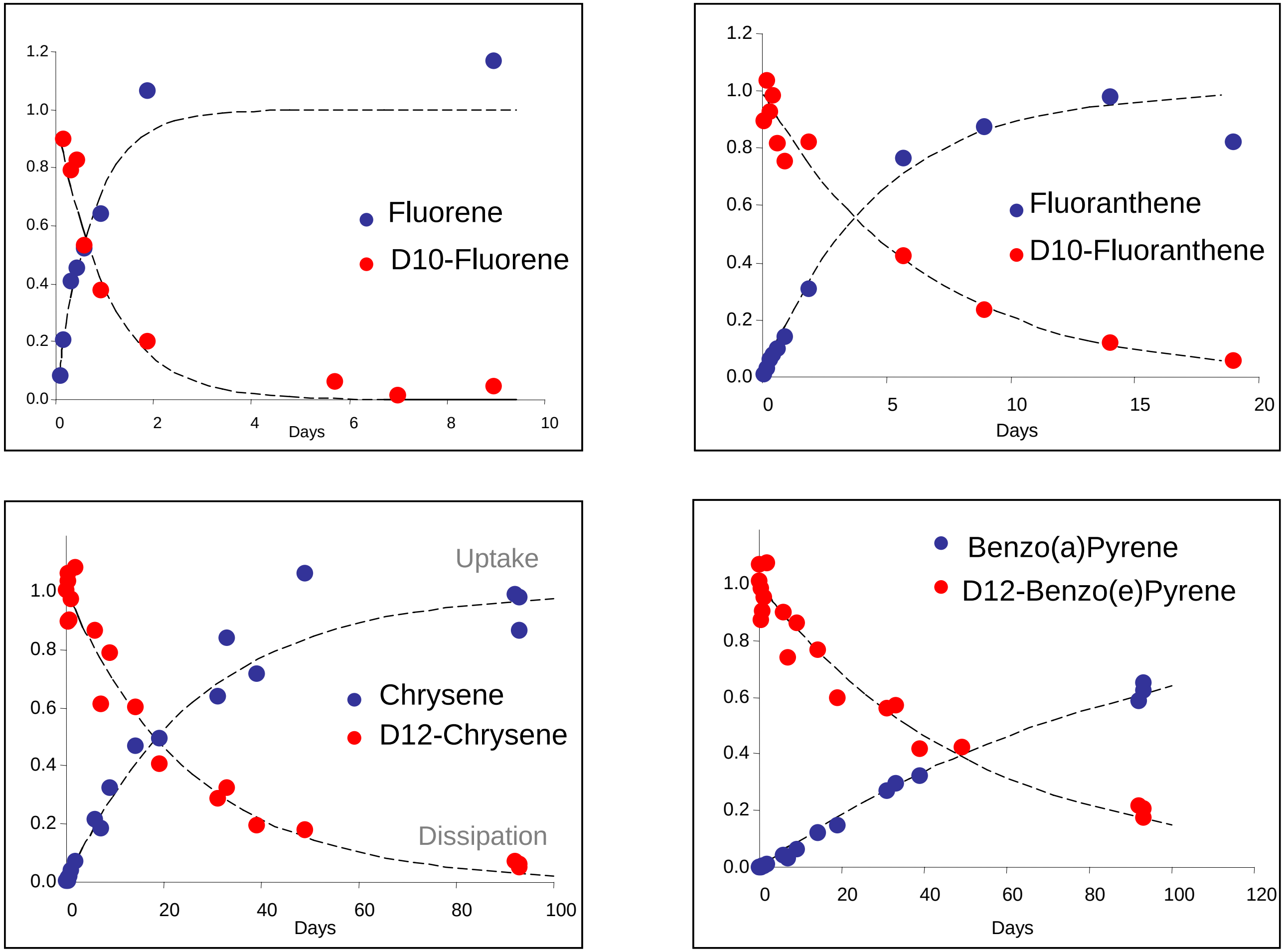
Release and uptake process can be mirrored

Measure release of
performance reference compounds (PRCs)
added prior to exposure

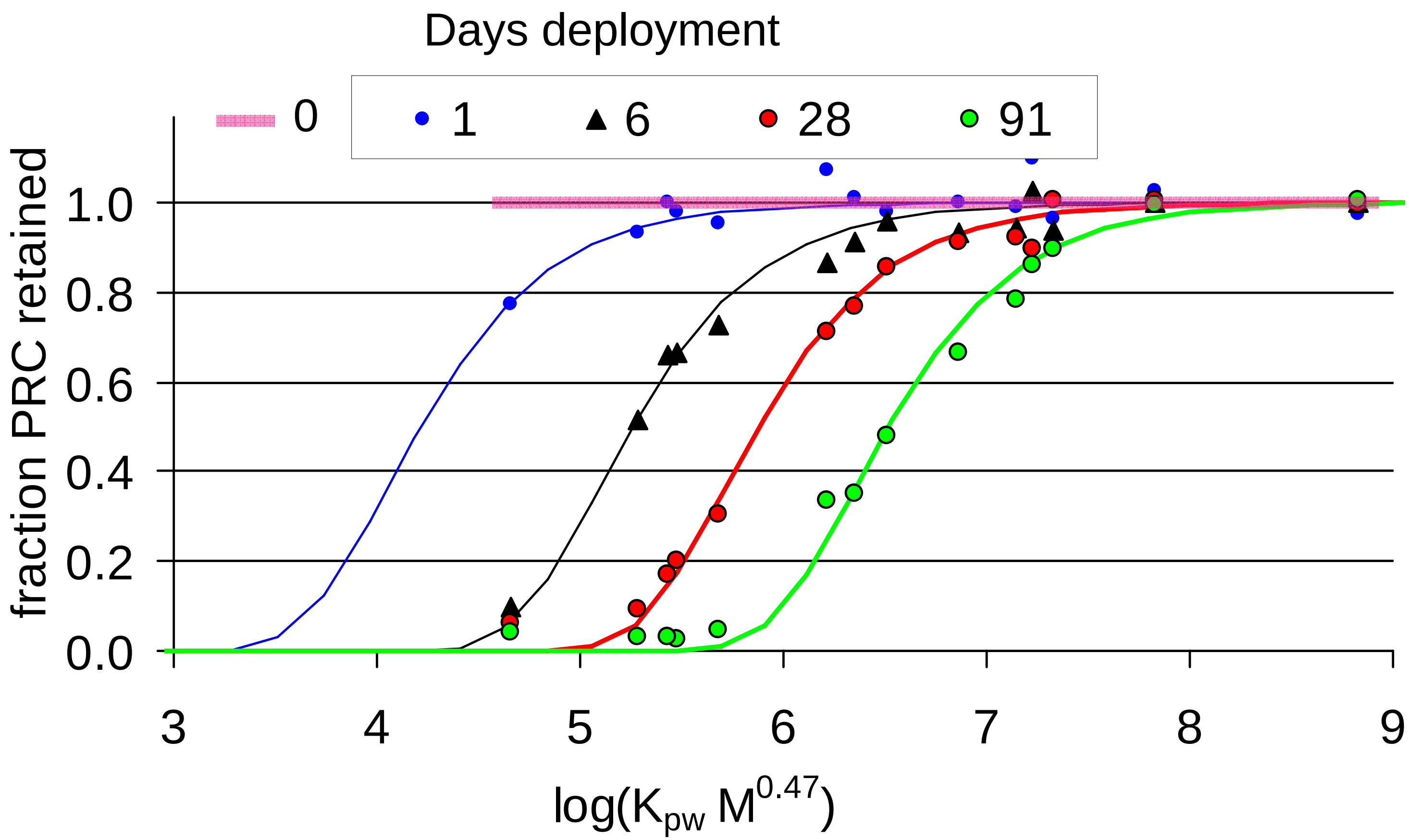
Performanc reference compounds (PRC) release



Sampling rate by PRCs → the exchange is isotropic?



Release of PRCs with time



Data from ECLIPSE project

Required for calculation C_w

reference

Sampler-water partition coefficient (PRCs and targets) [1]

Sampling rate modeled with $R_s = F / M^{0.47}$ [2]

Measured PRC dissipation $f_{exp} = N_t / N_0$ fitted with

$$f_{calc} = e^{-\frac{F\,t}{K_{pw}\,M^{0.47}\,m}}$$

adjustable

Variable, different PRCs

using non-linear regression fit of f_{exp} and f_{calc} [3]

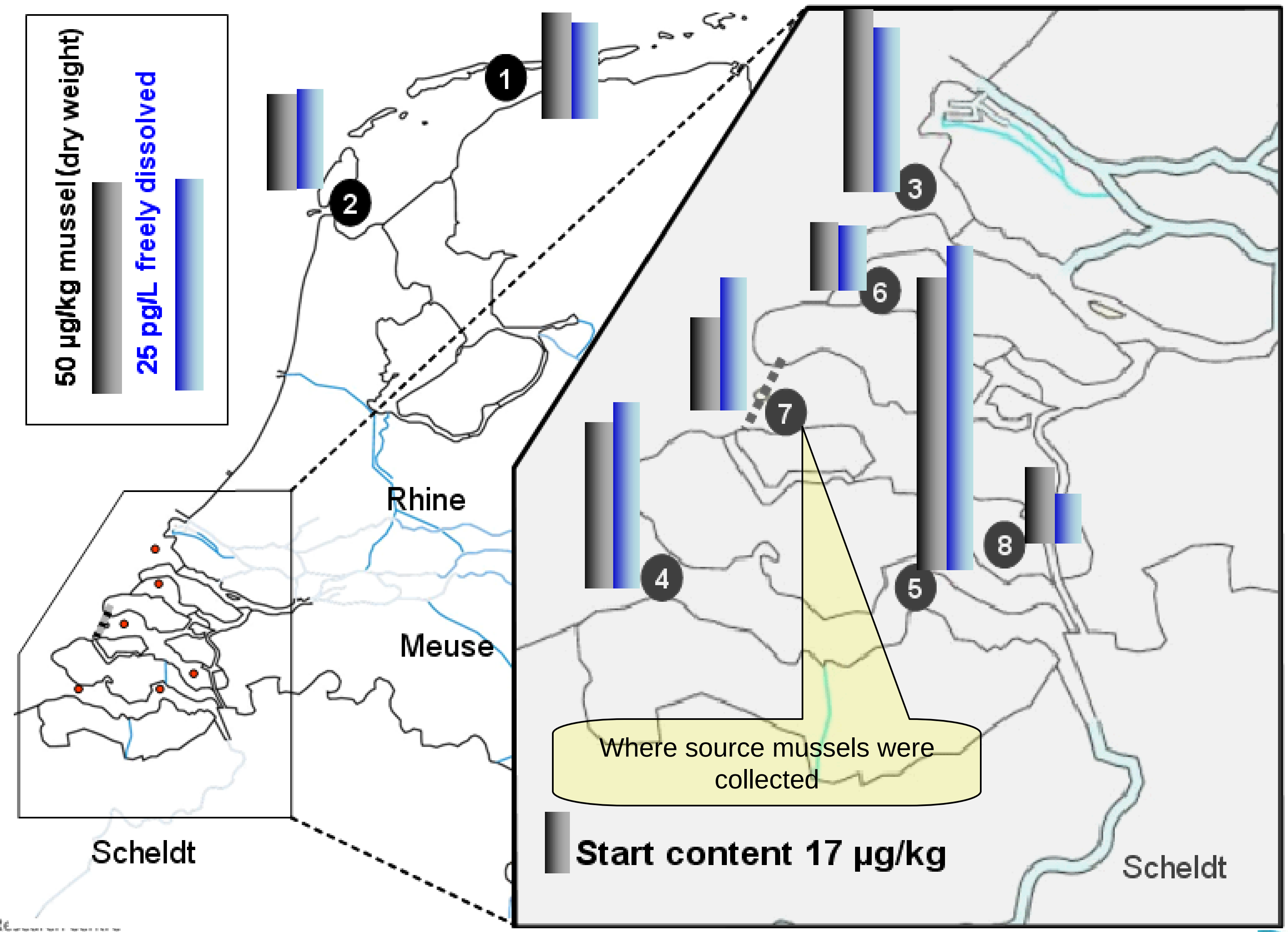
No membrane control on uptake [4]

[1] Smedes et al. EST 2009 [2] Rusina et al EST 2010 [3] Booij and Smedes EST 2010 [4] Rusina et al Chemosphere 2007

A lot of parameters needed !

is that worth while?

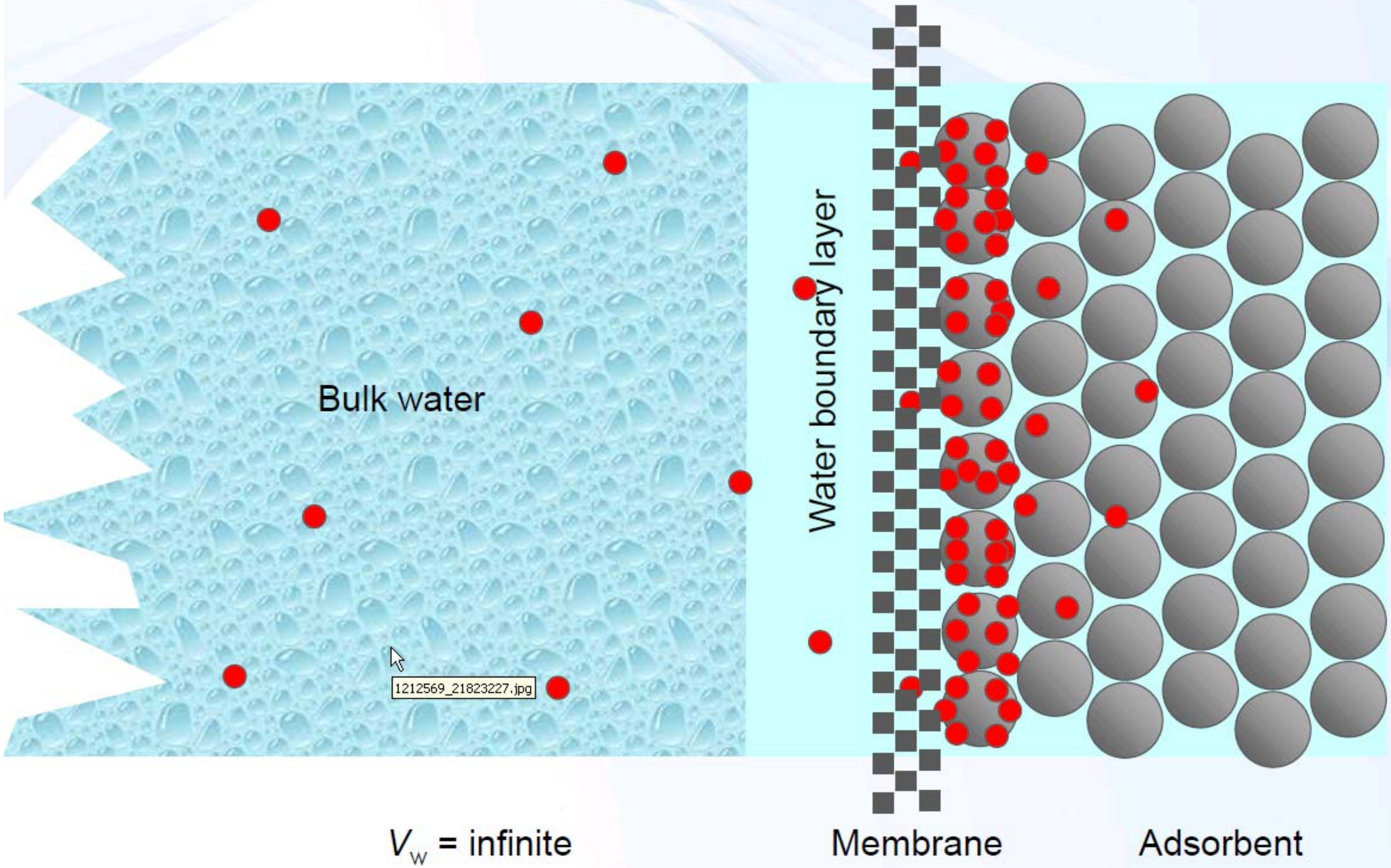
Spatial distribution for PCB 153 in mussels and water



Adsorption passive samplers

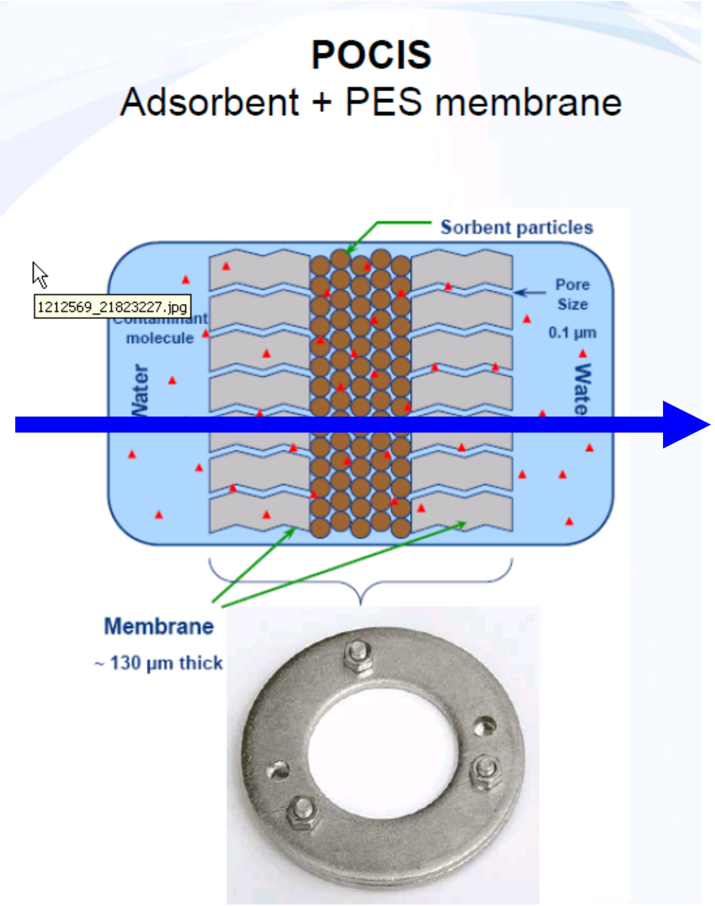
- used for passive sampling of polar compounds
- compounds well soluble in water,
  1. show little absorbtion in polymers
  2. usually present at higher concentrations than hydrophobic compounds
- higher solubility implies more possibility for fluctuations of water concentration – integrative sampling needed

Transport barriers in a samplers for polar compounds



Additional uptake through flow - POCIS

Flow

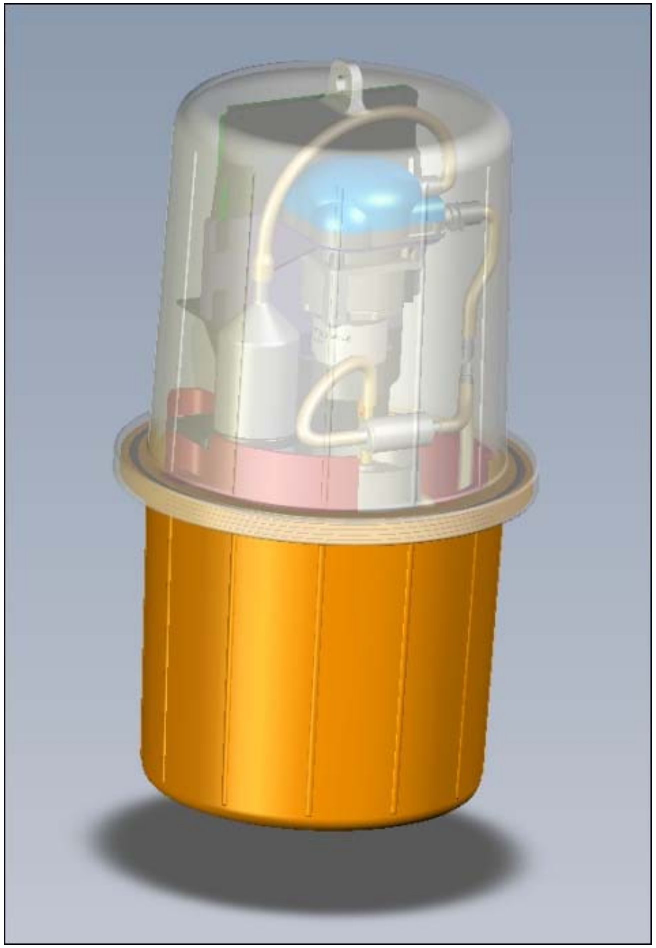


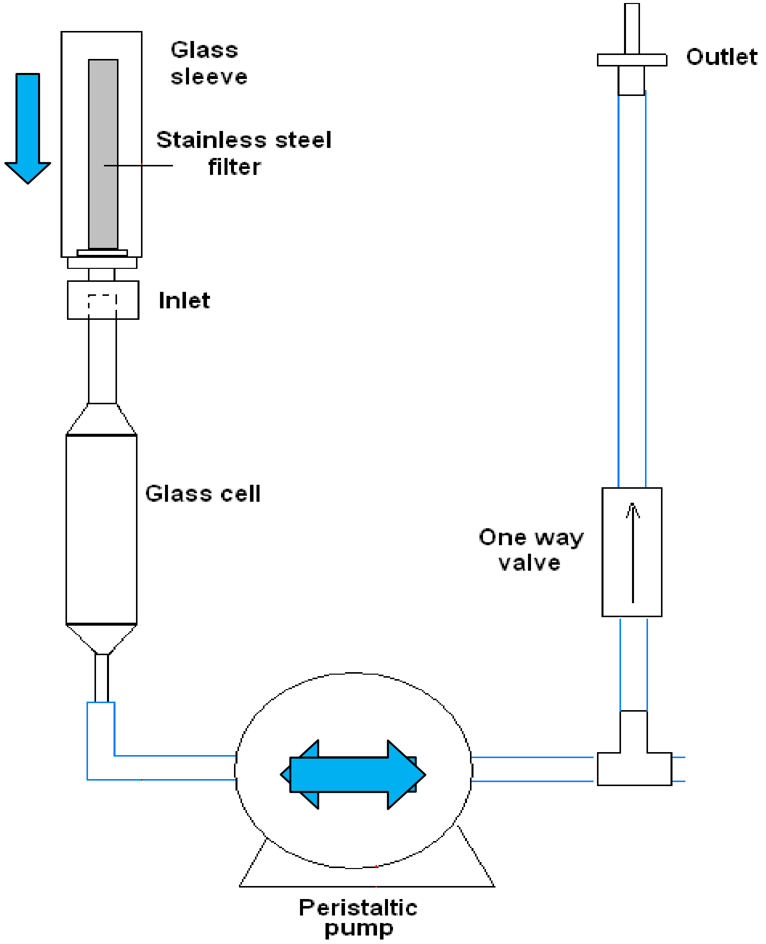
Samplers for polar compounds

- uptake shows the presence of substance
- not easy transformed to accurate C_w
- no clear uptake model yet
- Sampling rates in lab ~0.1-0.3 L/d

Thank you for your attention

Contineous flow integrative samples (CFIS)





Capable of sampling both dissolved and particulate fraction.

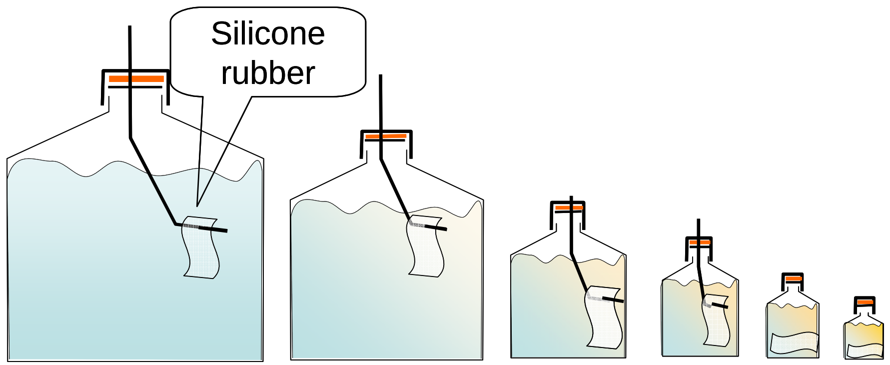
Working principles - calibration

- Uptake process

Equilibrium or linear uptake

Parameters required

K_{pw} determination by cosolvent method



Glass bottle 10 L Glass bottle 0.25 L

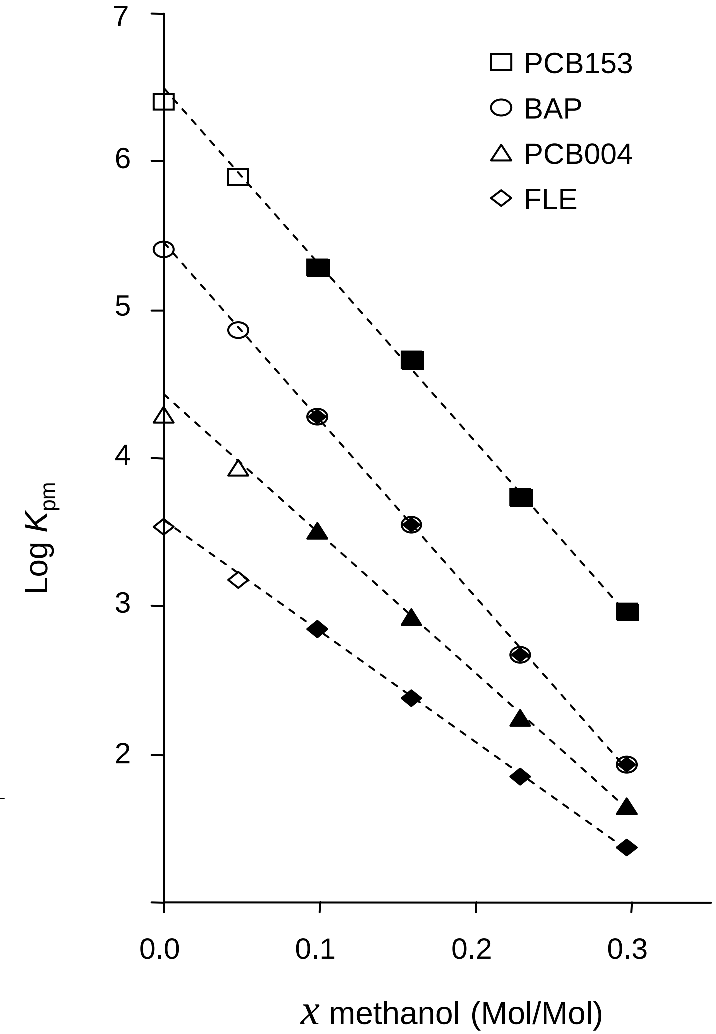
Molfraction methanol

Concentration of analyte

$\log K_{pm}$ decreases

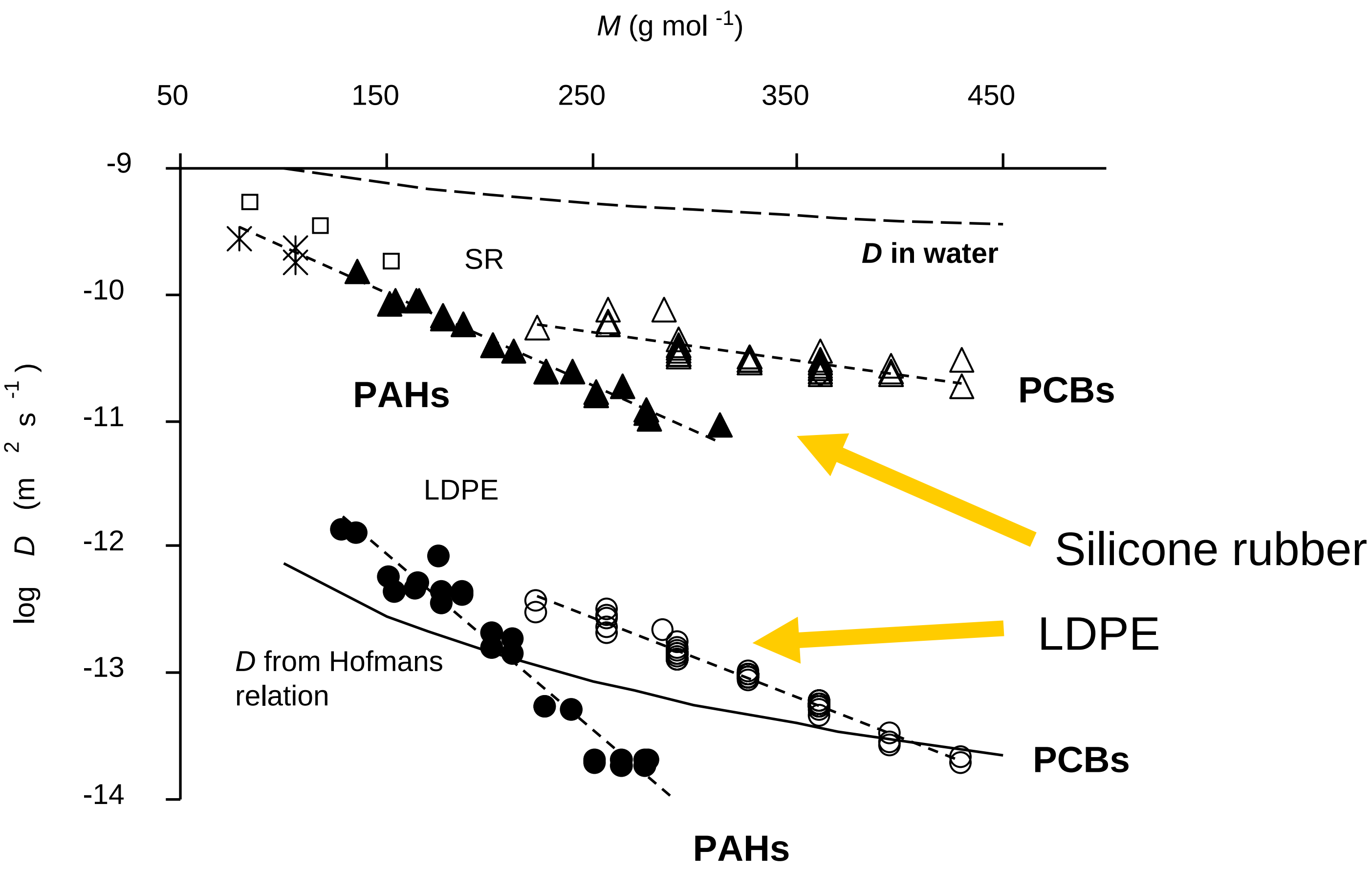
Exposure volume

Final concentration in extract ≈ constant



[1] Smedes et al. EST 2009

Material properties – diffusion of target compounds



[1] Rusina et al, 2010, Appl Polym Sci

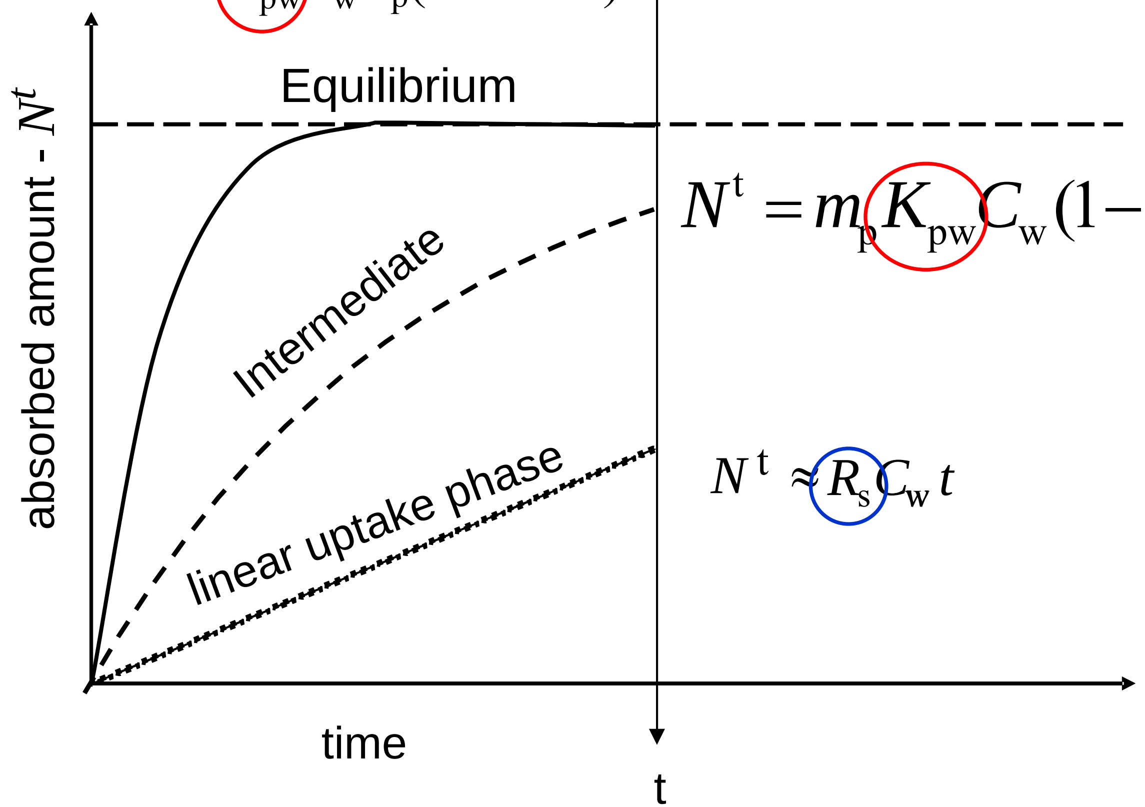
POM

Different stages of the uptake process

N^t amount on the sampler after t days exposure
C_w free dissolved concentration in water
m_p mass sampler
R_s sampling rate
C_p conc. in de sampler

$$K_{pw} = \frac{C_p}{C_w}$$

$$N^t = K_{pw} C_w m_p (= N^{max})$$

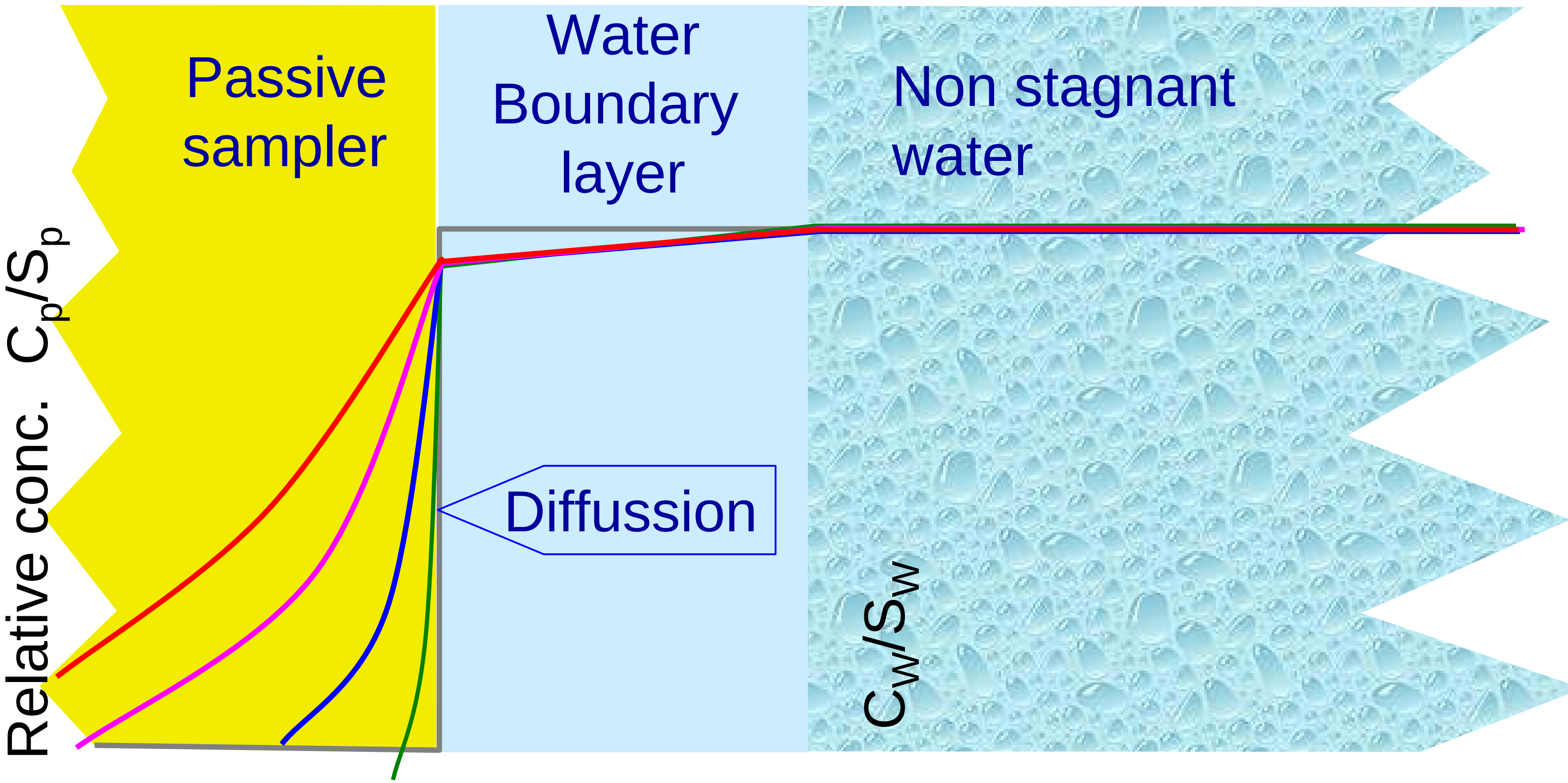


$$N^t = m_p K_{pw} C_w \left(1 - e^{-\frac{R_s t}{m_p K_{pw}}}\right)$$

$$N^t \approx R_s C_w t$$

Uptake process from water

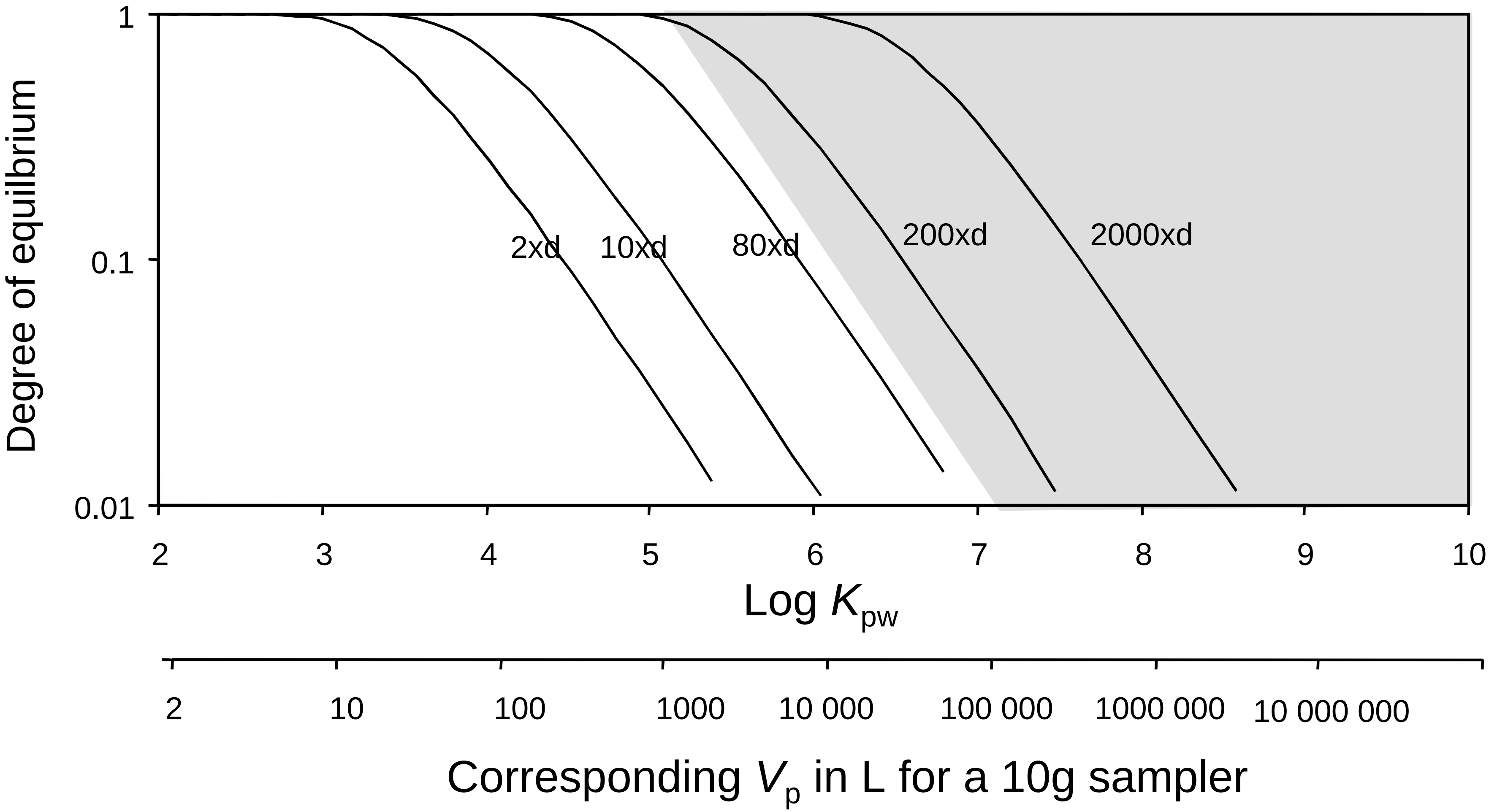
Membrane controlled



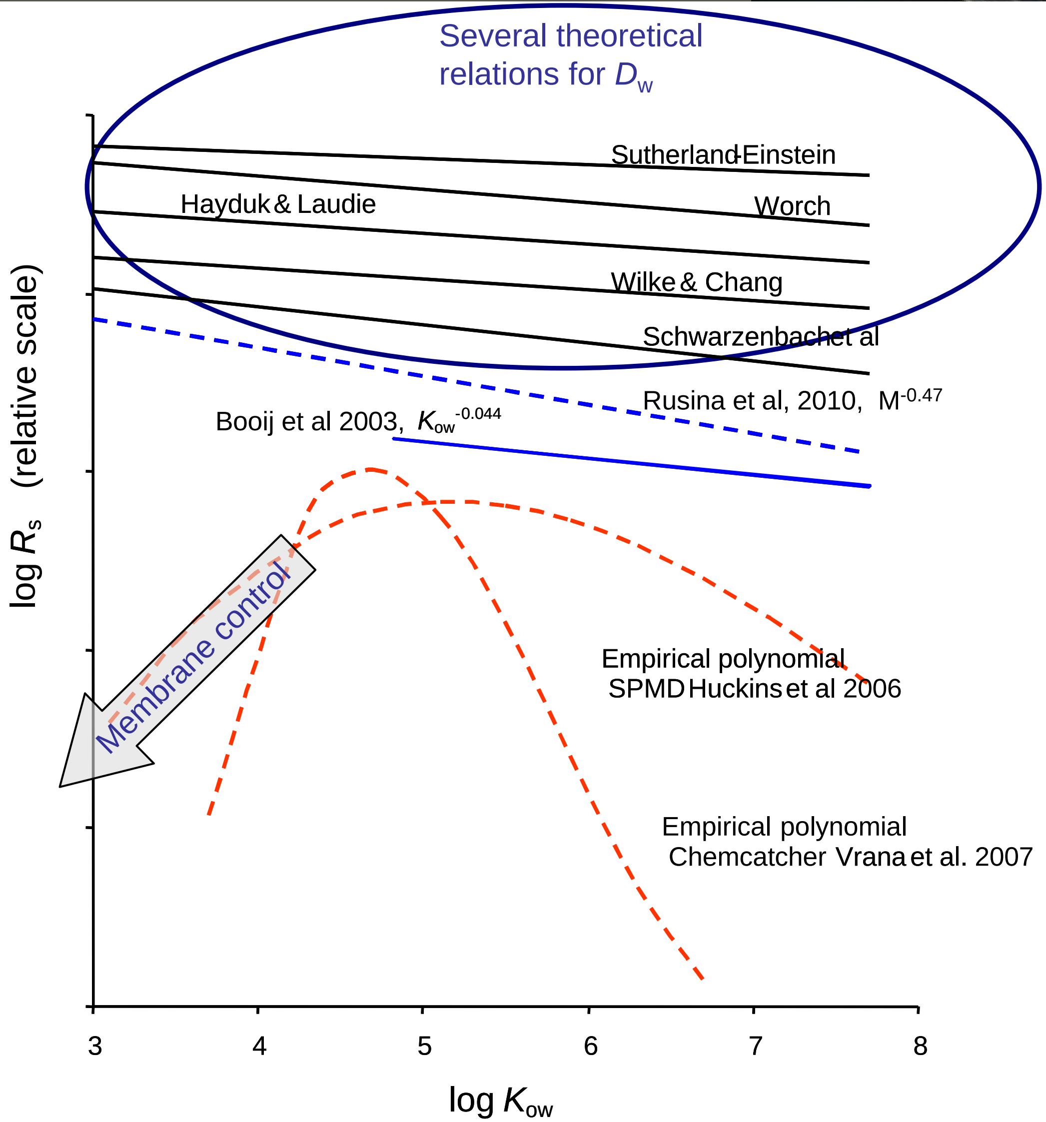
$$\frac{D_p K_{pw}}{\delta_p}$$

$$\frac{D_w}{\delta_w}$$

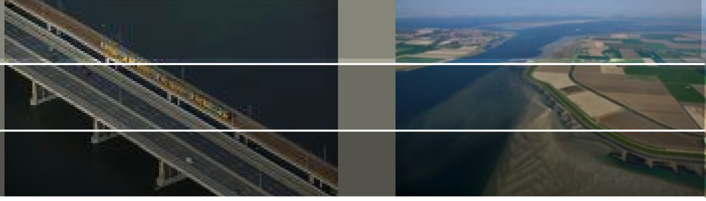
Equilibrium versus logK_{pw} for different time periods



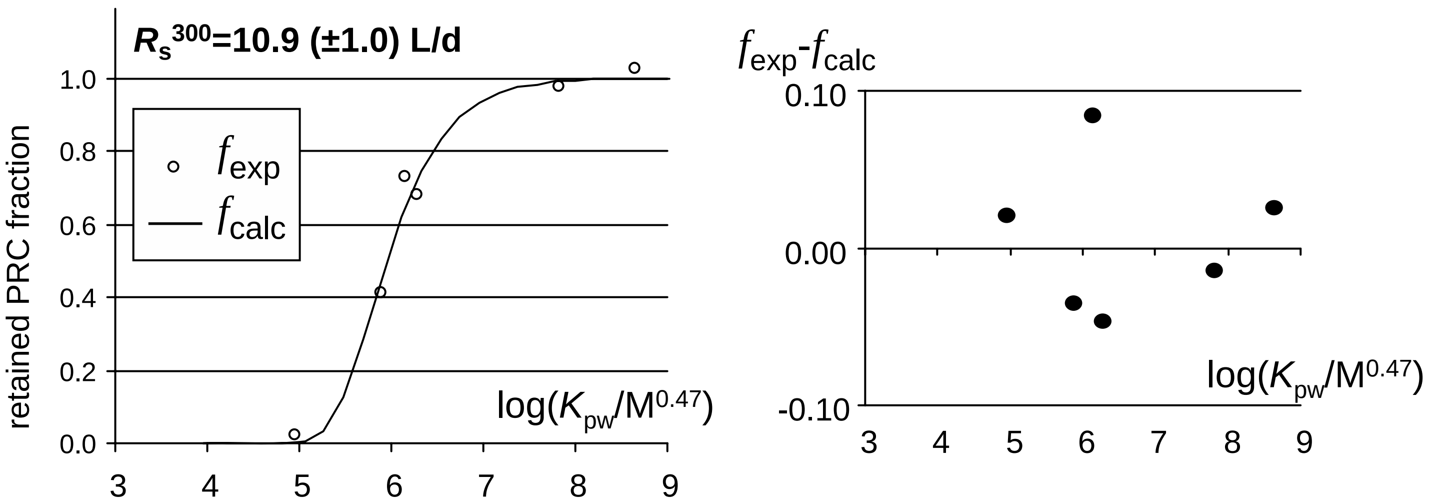
Relation of Rs with hydrophobicity



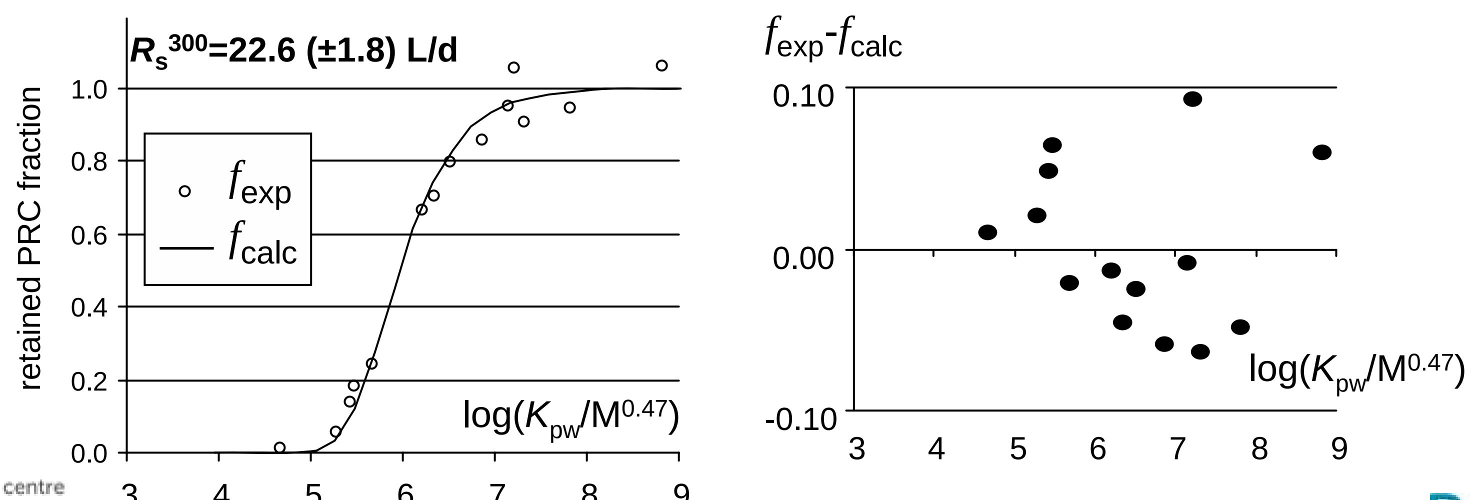
Examples of fiting



2001 Autumn, Station 1 Wadden Sea



2010 Winter, Station 1 Wadden Sea



Biofouled!