Deltares
Enabling Delta Life

Research centre
for toxic compounds
in the environment

Partitioning based Passive Sampling

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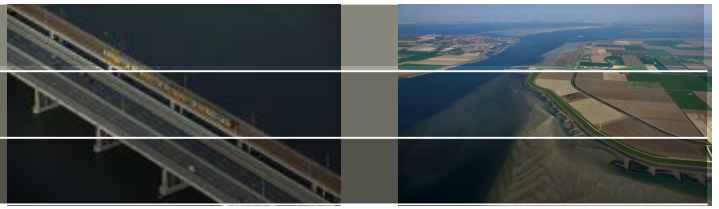
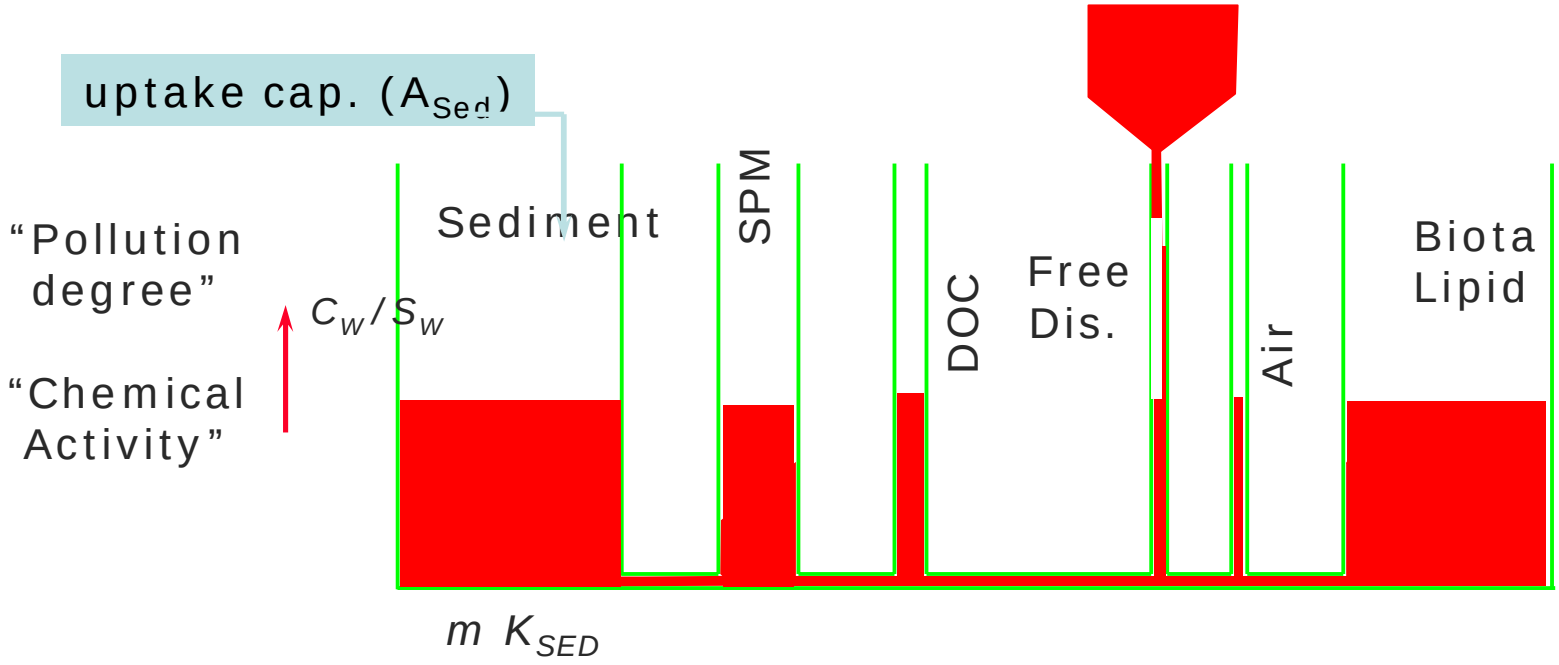
NORMAN Inter-Laboratory Study (ILS) on passive sampling of emerging pollutants
DG Joint Research Centre, 29 – 30 October, 2012, Ispra, Italy

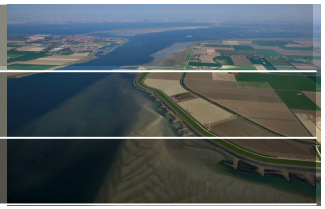
Pollution level in aqueous systems



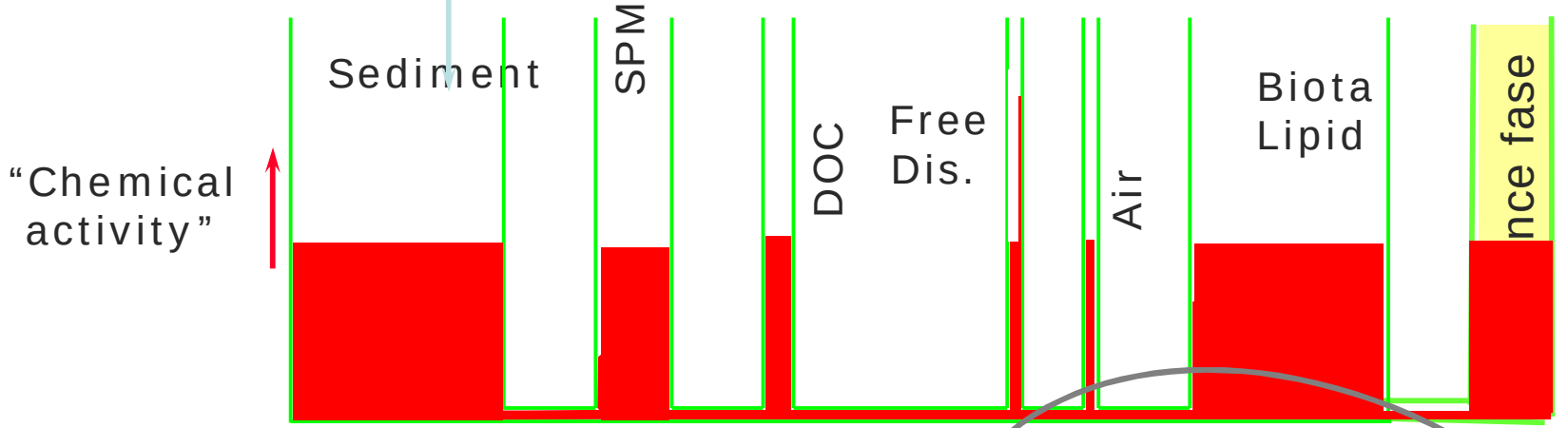


In formula: $\frac{C_{Sed}}{A_{Sed}} = \frac{C_{SPM}}{A_{SPM}} = \frac{C_{DOC}}{A_{DOC}} = \frac{C_W}{S_W} = \frac{P}{P_0} = \frac{C_{Lipid}}{S_{Lipid}}$

Pollution level in aqueous systems



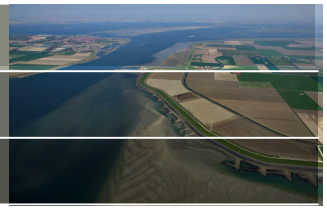
uptake cap. (A_{Sed})



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

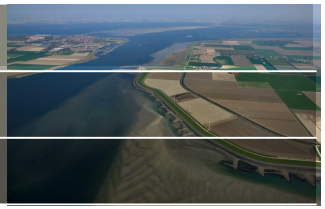
$$K_{Ref\text{-}W} = \frac{S_{Ref}}{S_W} = \frac{C_{Ref}}{C_W}$$

What's on the program



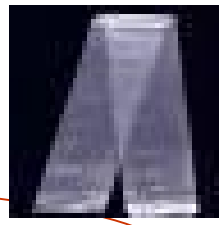
- Different passive samplers
- Procedures, material and methods
- Working principles
- Parameters
- Data processing

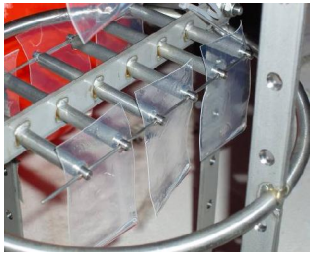
Passive sampler types



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.
- (ceramic dosimeter)
- (Polar compounds: POCIS, C18....)

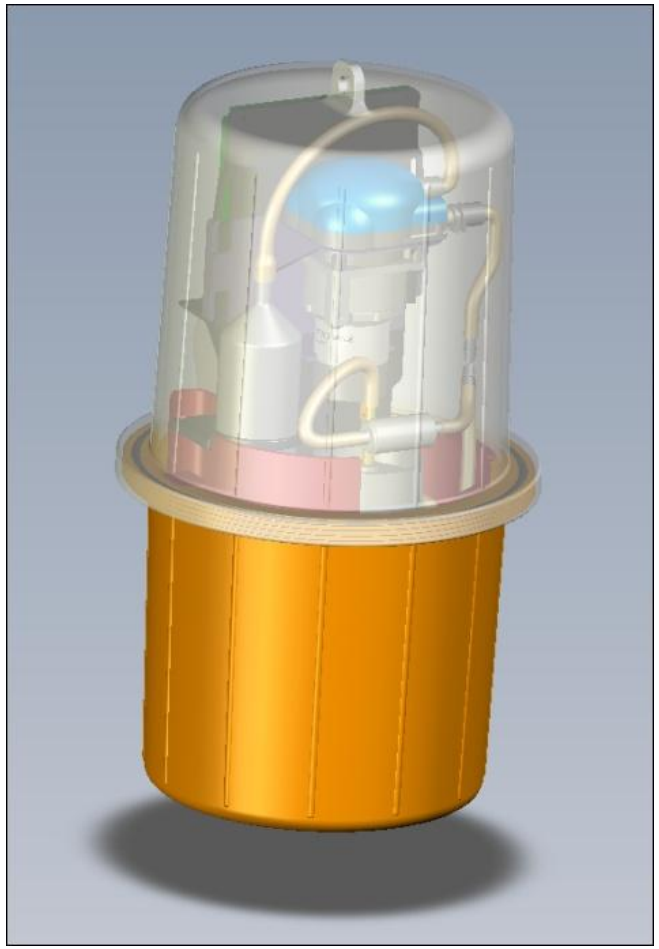


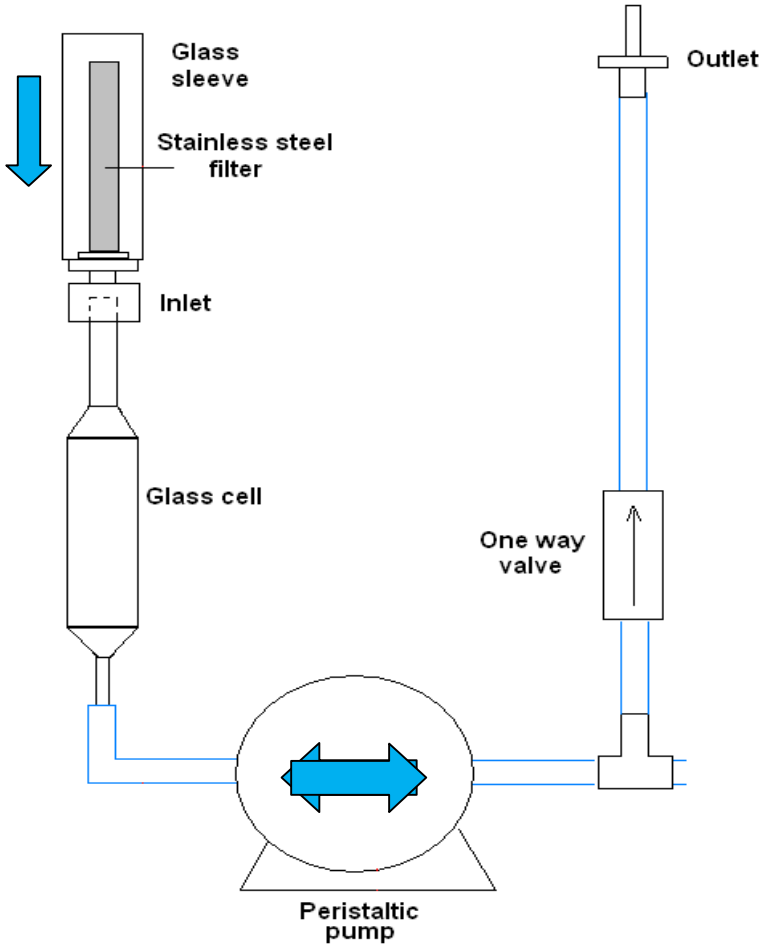


Micro passive samplers → all sorbed is injected - one shot

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

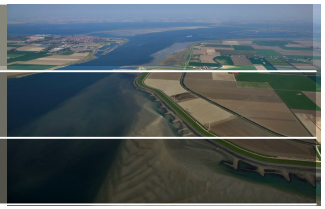
Contineous flow integrative samples (CFIS)



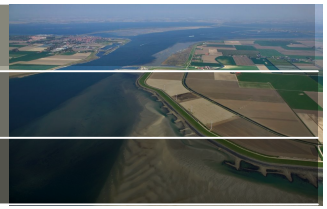


Capable of sampling both dissolved and particulate fraction.

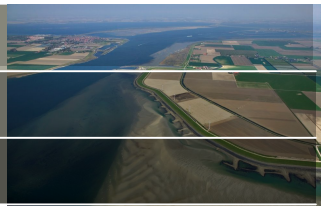
Deployment of SR and SPMD



Ground water



After exposure



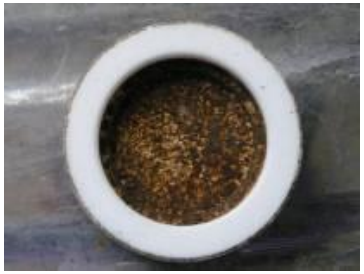
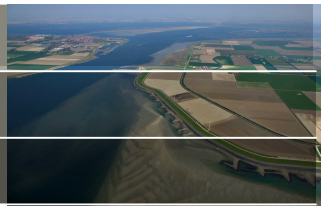
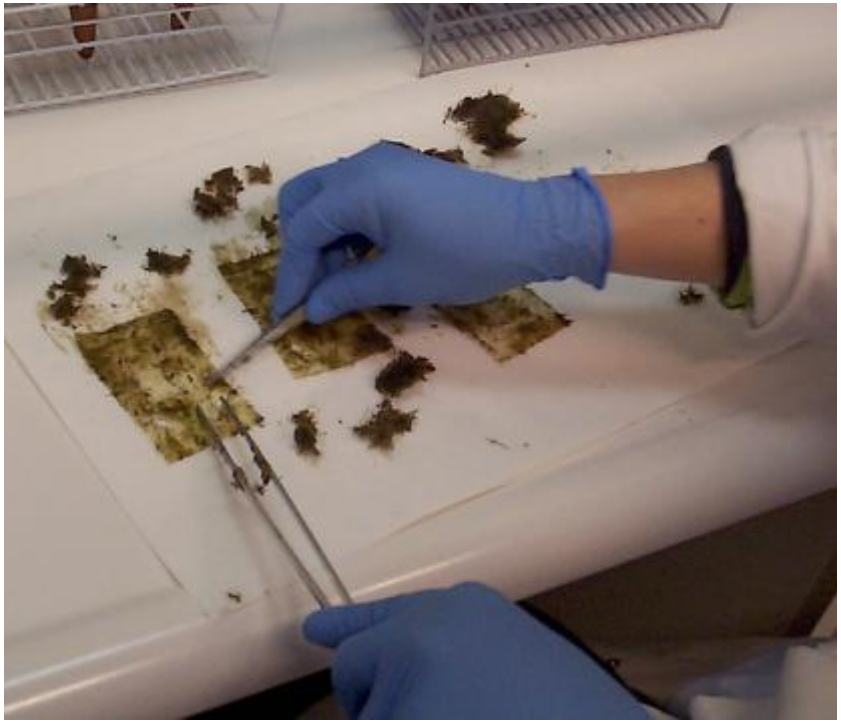


Foto by IOEV, Spanish Oceanographic Inst. Vigo, Spain

Cleaning sheets after recovery



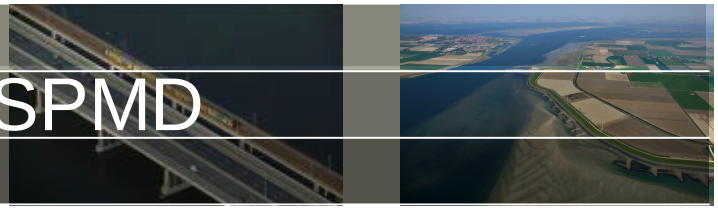
Cleaning samplers in the lab

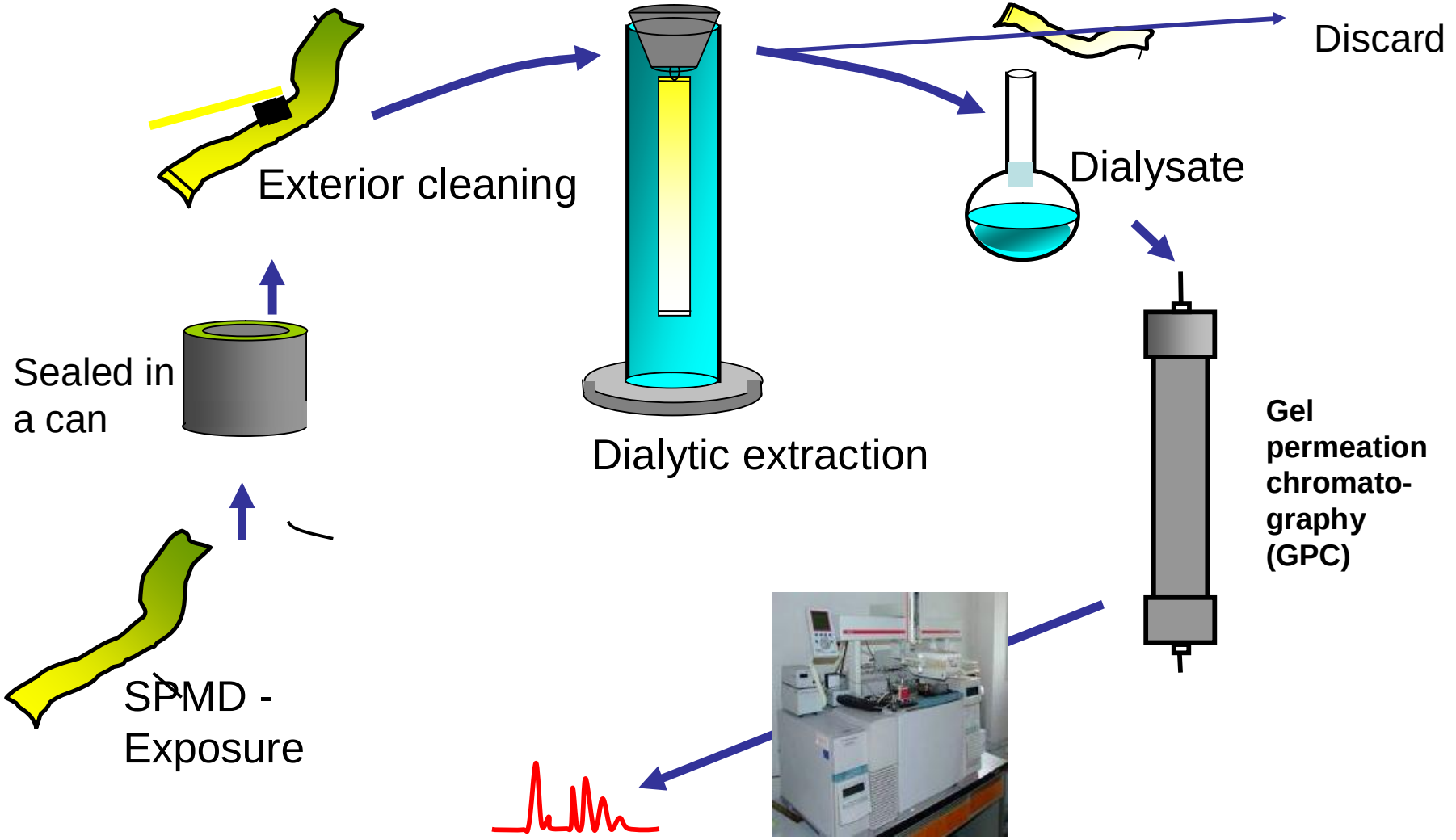


During transport and storage redistribution could occur

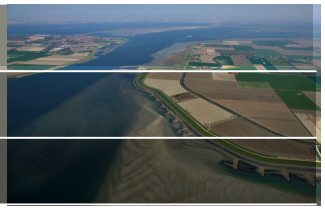
Better clean samplers in the field with local water and scourer

Processing of passive samplers: SPMD





Working principles - calibration

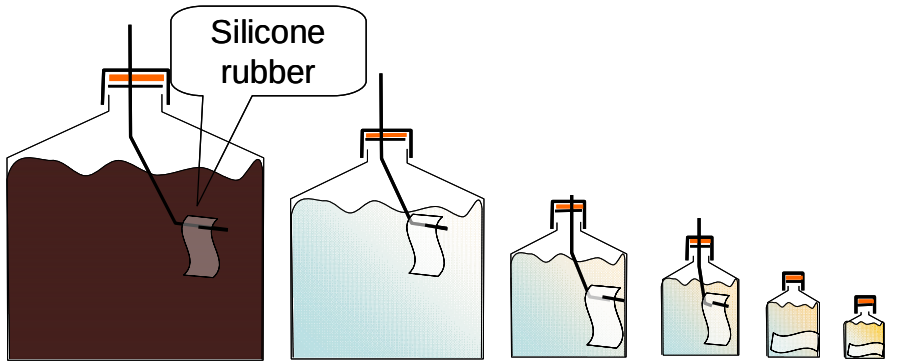


- Uptake process

Equilibrium or linear uptake

Parameters required

K_{pw} determination by cosolvent method



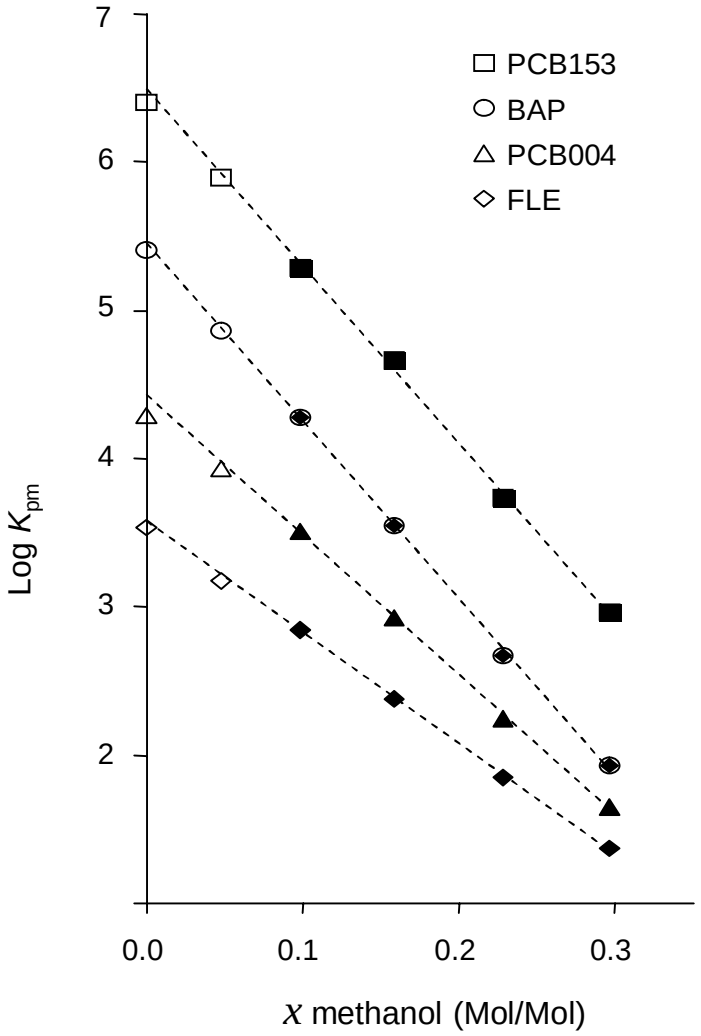
Molfraction methanol

Concentration of analyte

logK_{pm} decreases

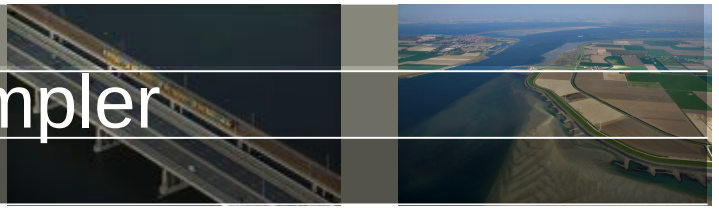
Exposure volume

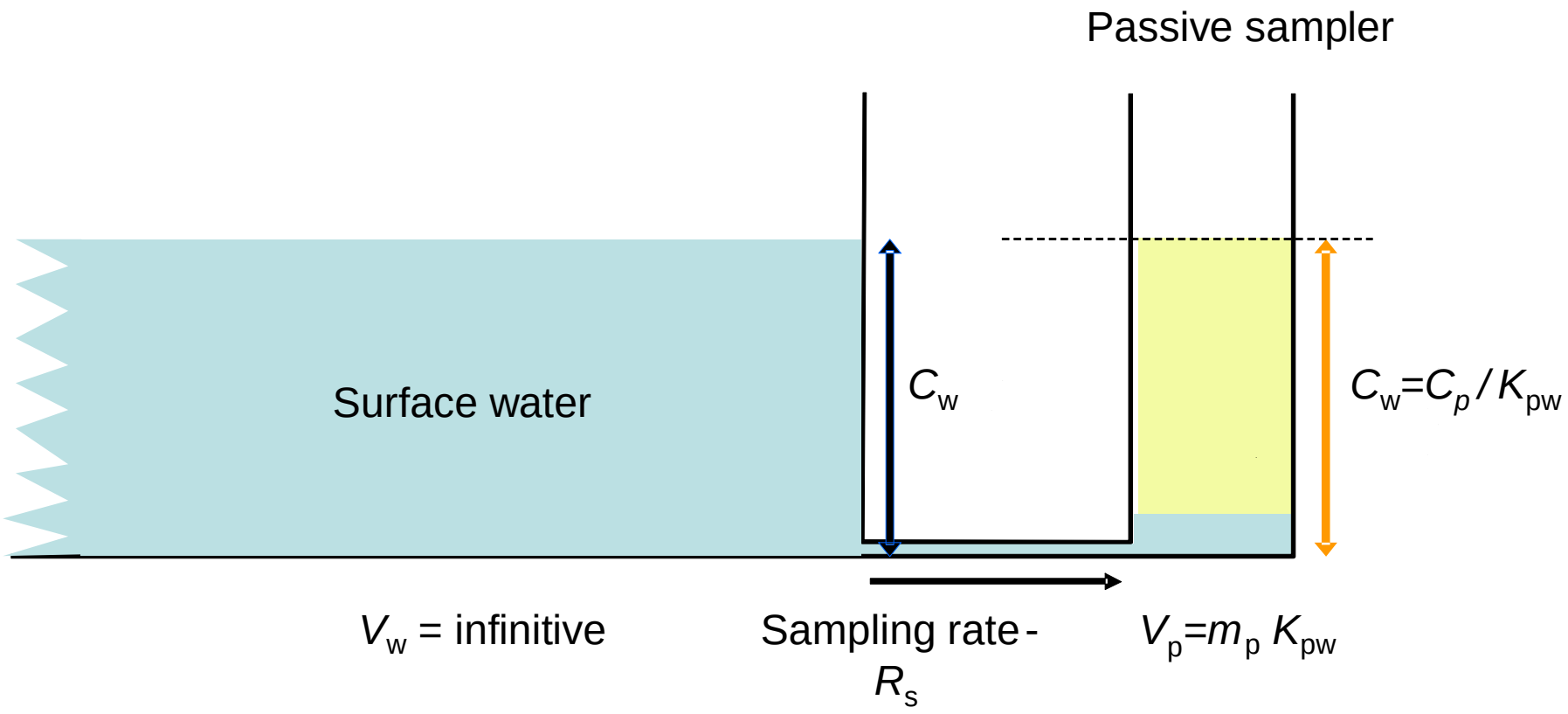
Final concentration in extract ≈ constant



[1] Smedes et al. EST 2009

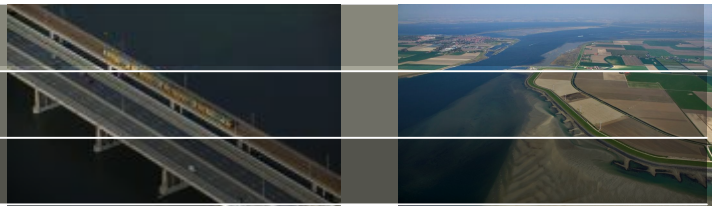
Uptakeprocess by a passive sampler

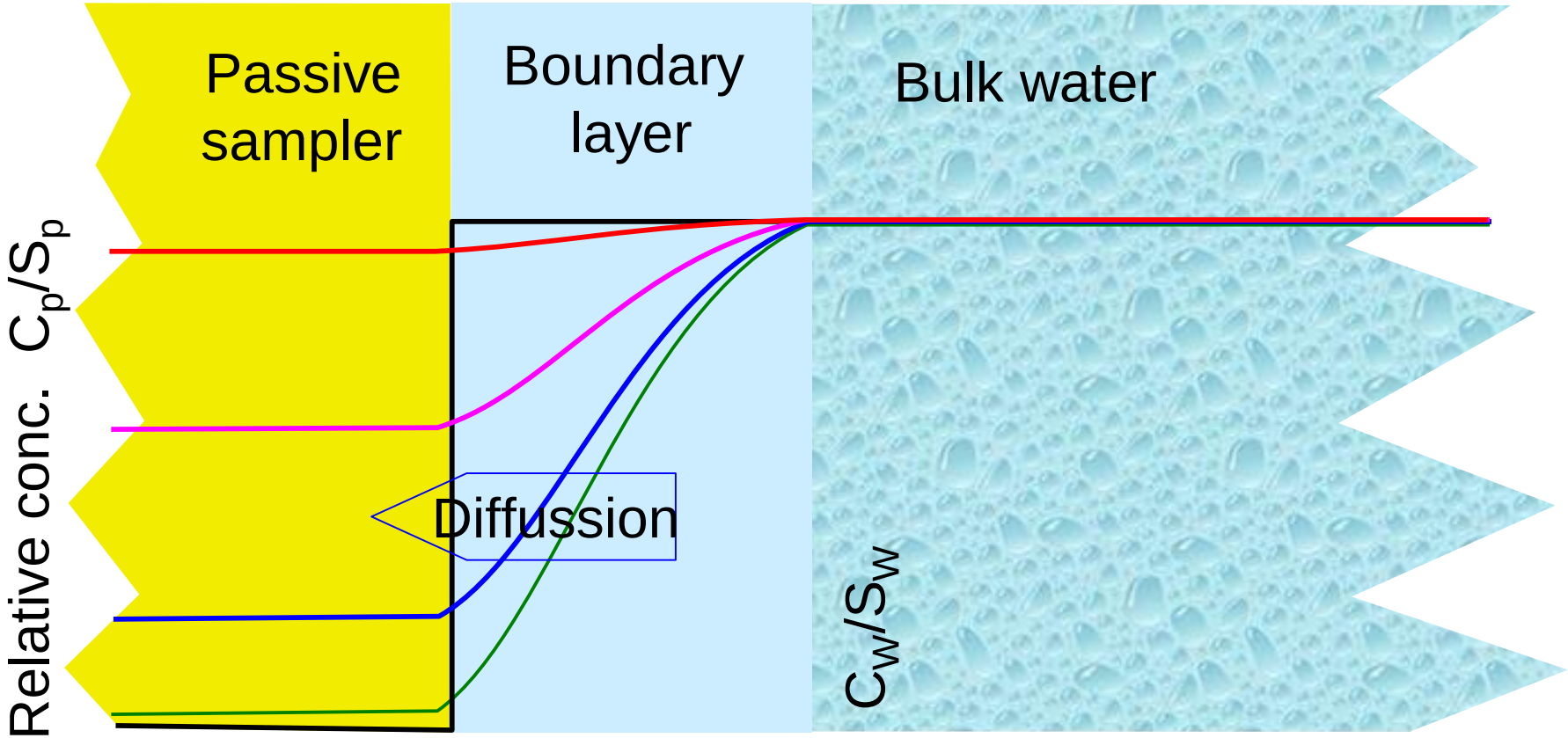




Uptake process from water

Water Boundary layer controlled

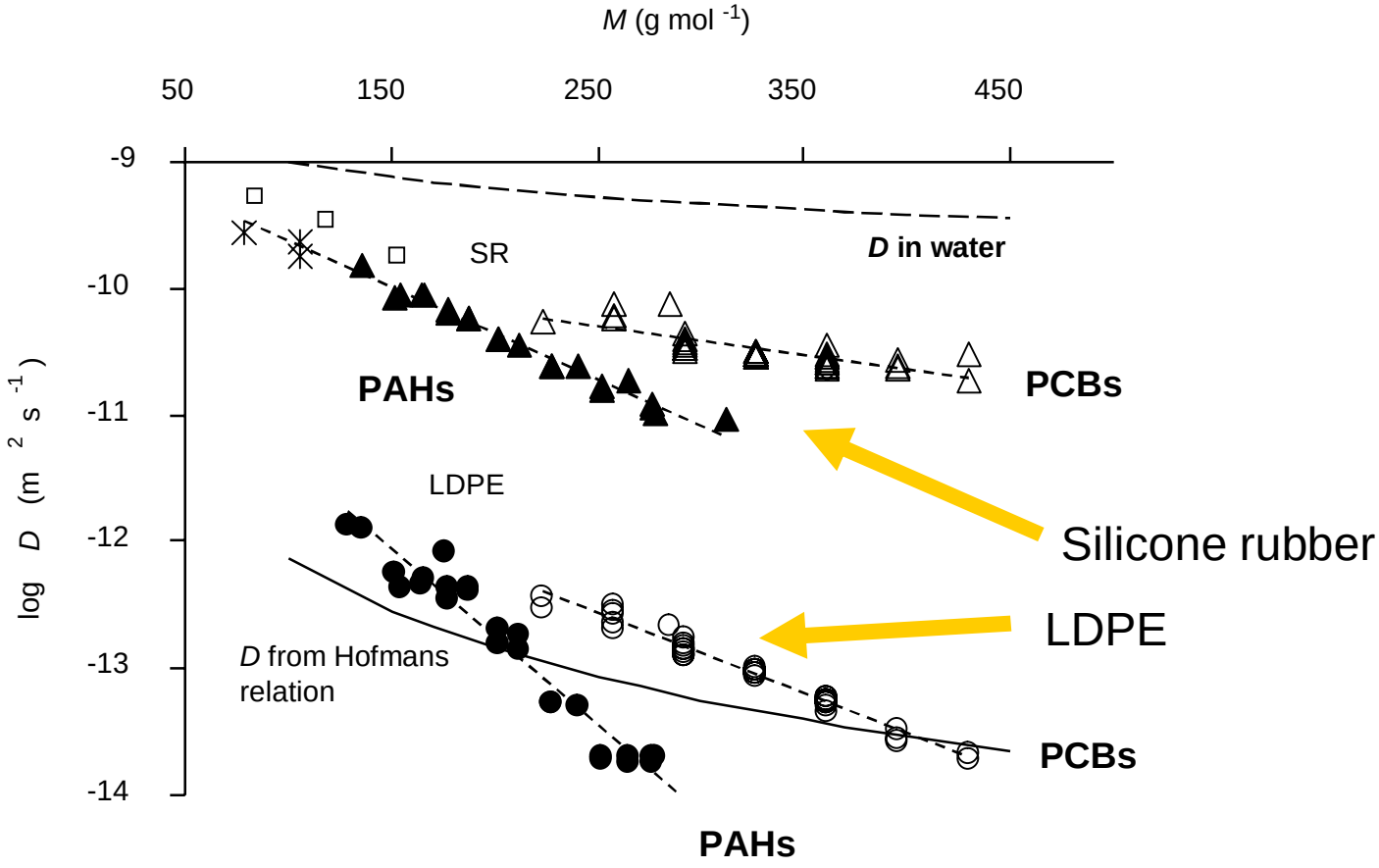




$$\frac{D_p K_{pw}}{\delta_p} \qquad \frac{D_w}{\delta_w}$$

mass transfer coefficients

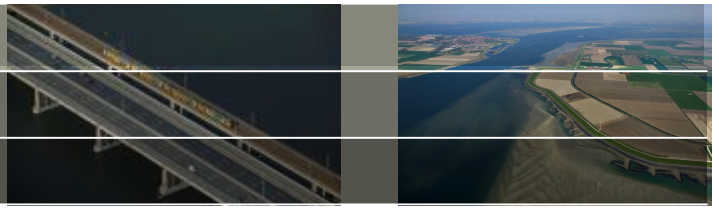
Material properties – diffusion of target compounds

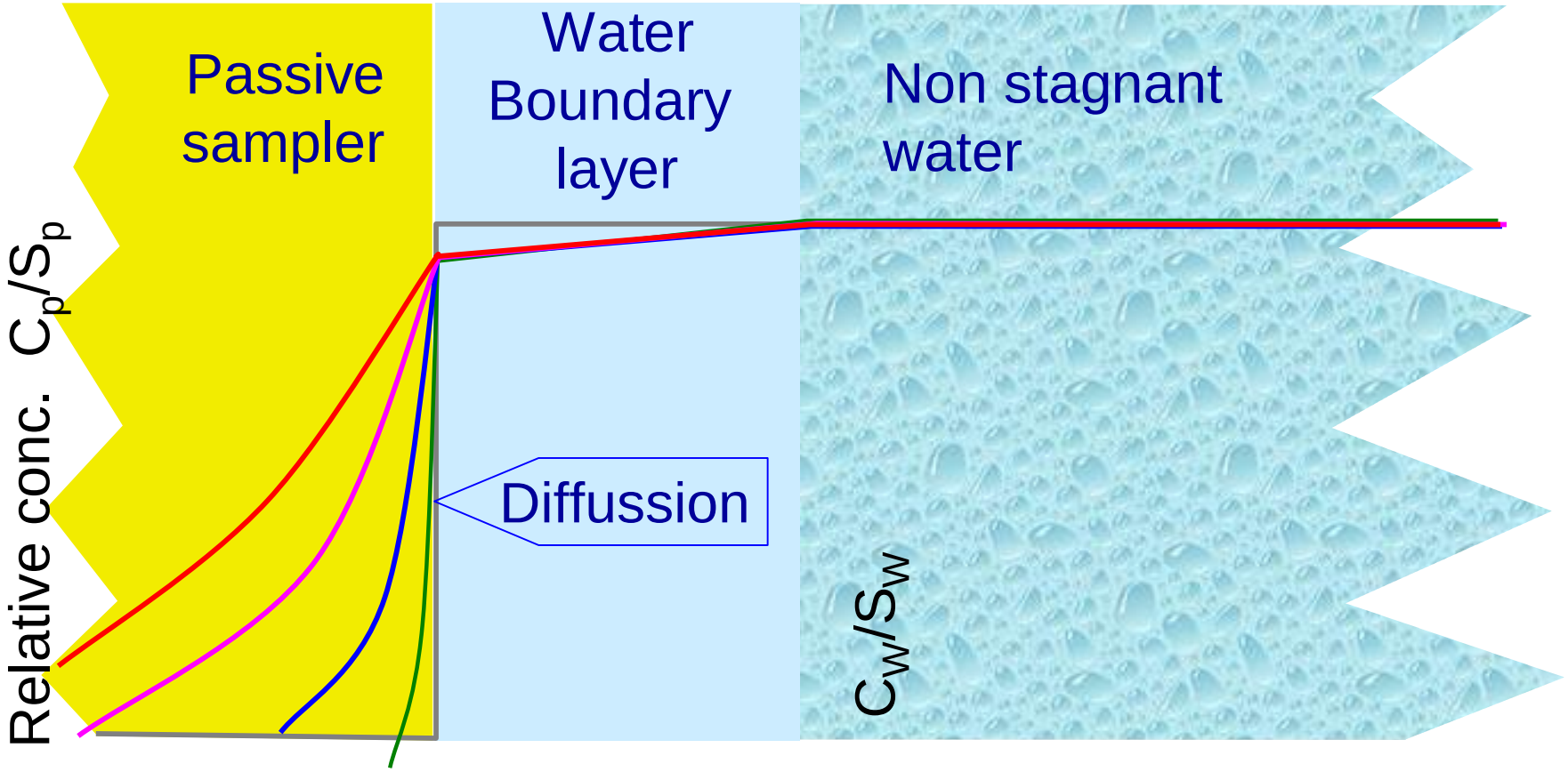


[1] Rusina et al, 2010, Appl Polym Sci

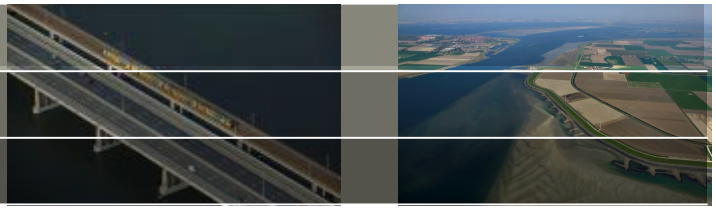
Uptake process from water

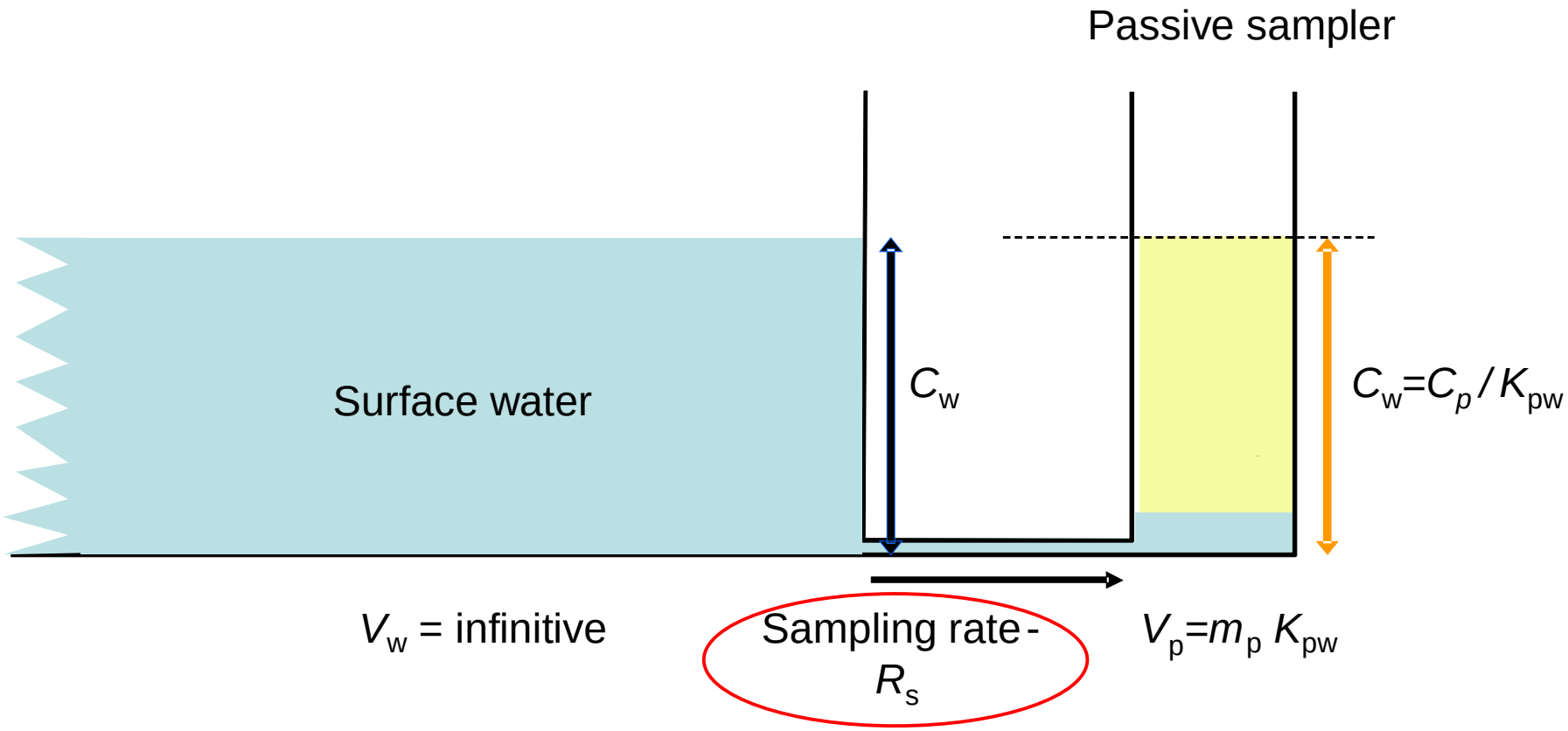
Membrane controlled



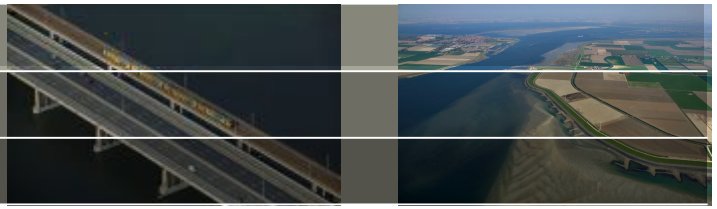


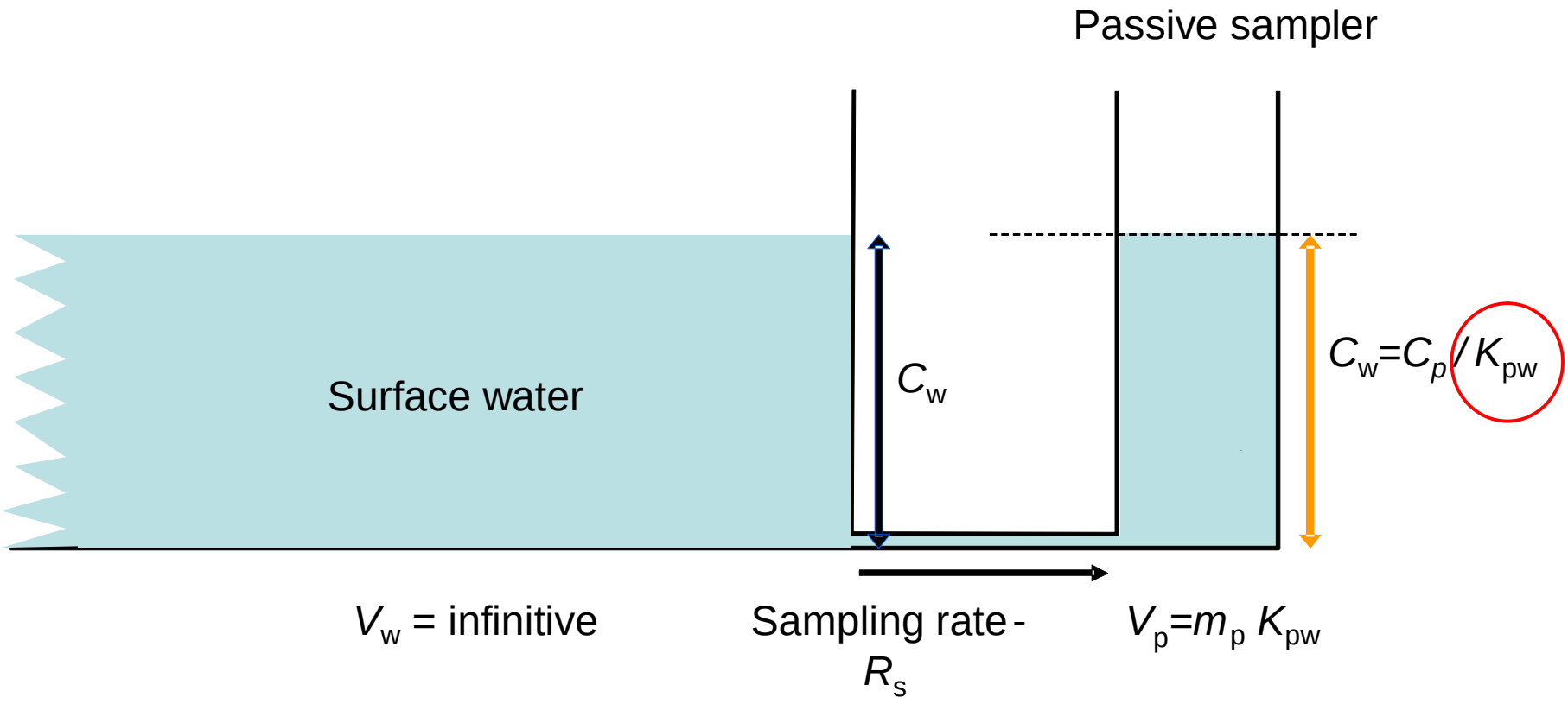
First linear with time



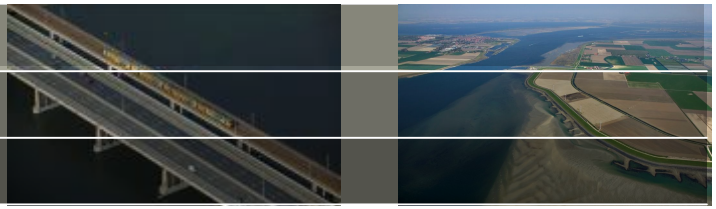


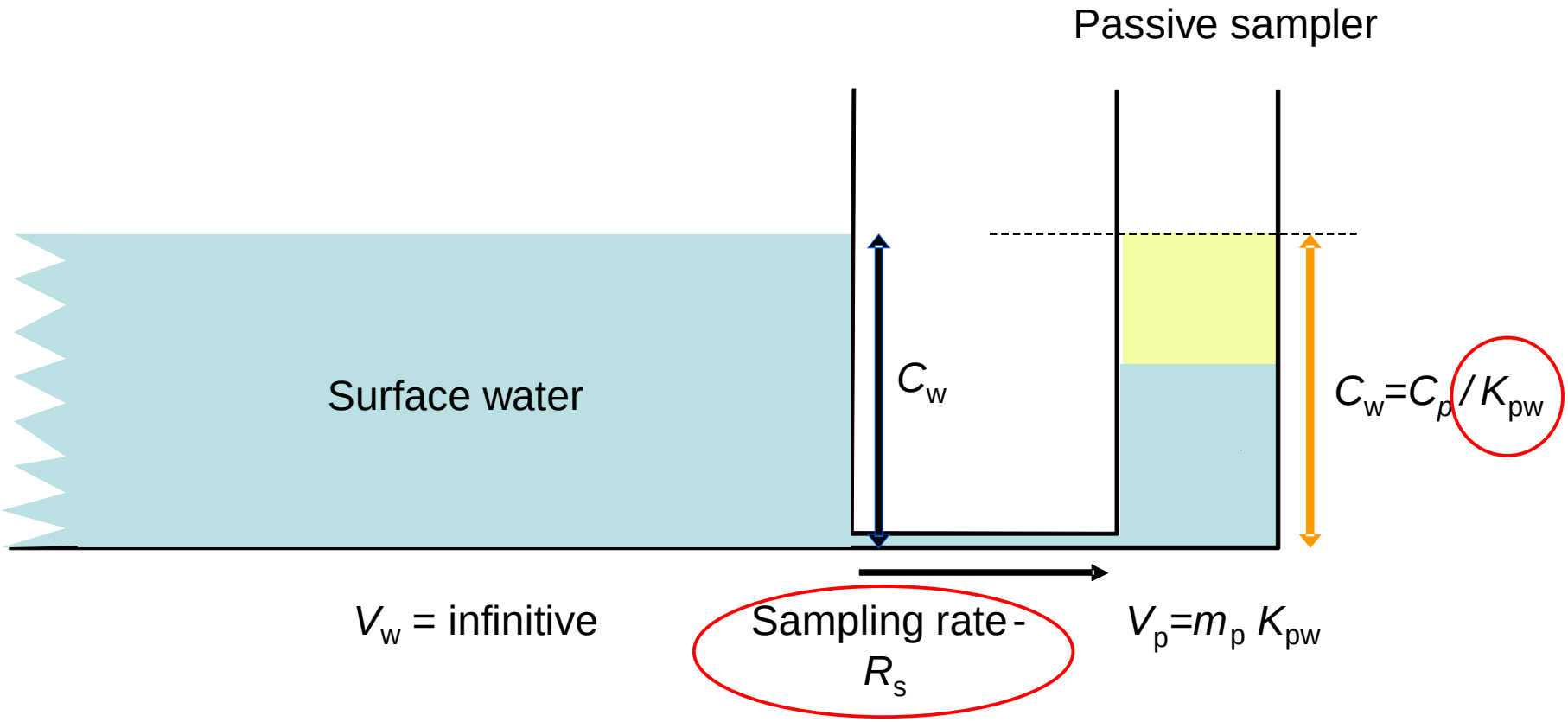
Equlibrium



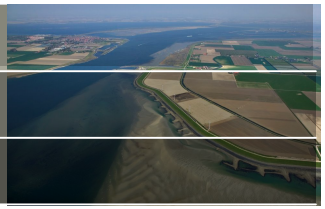

Passive sampler
Surface water
C_w
$C_w = C_p / K_{pw}$
V_w = infinitive
Sampling rate - R_s
$V_p = m_p K_{pw}$

Intermediate situation



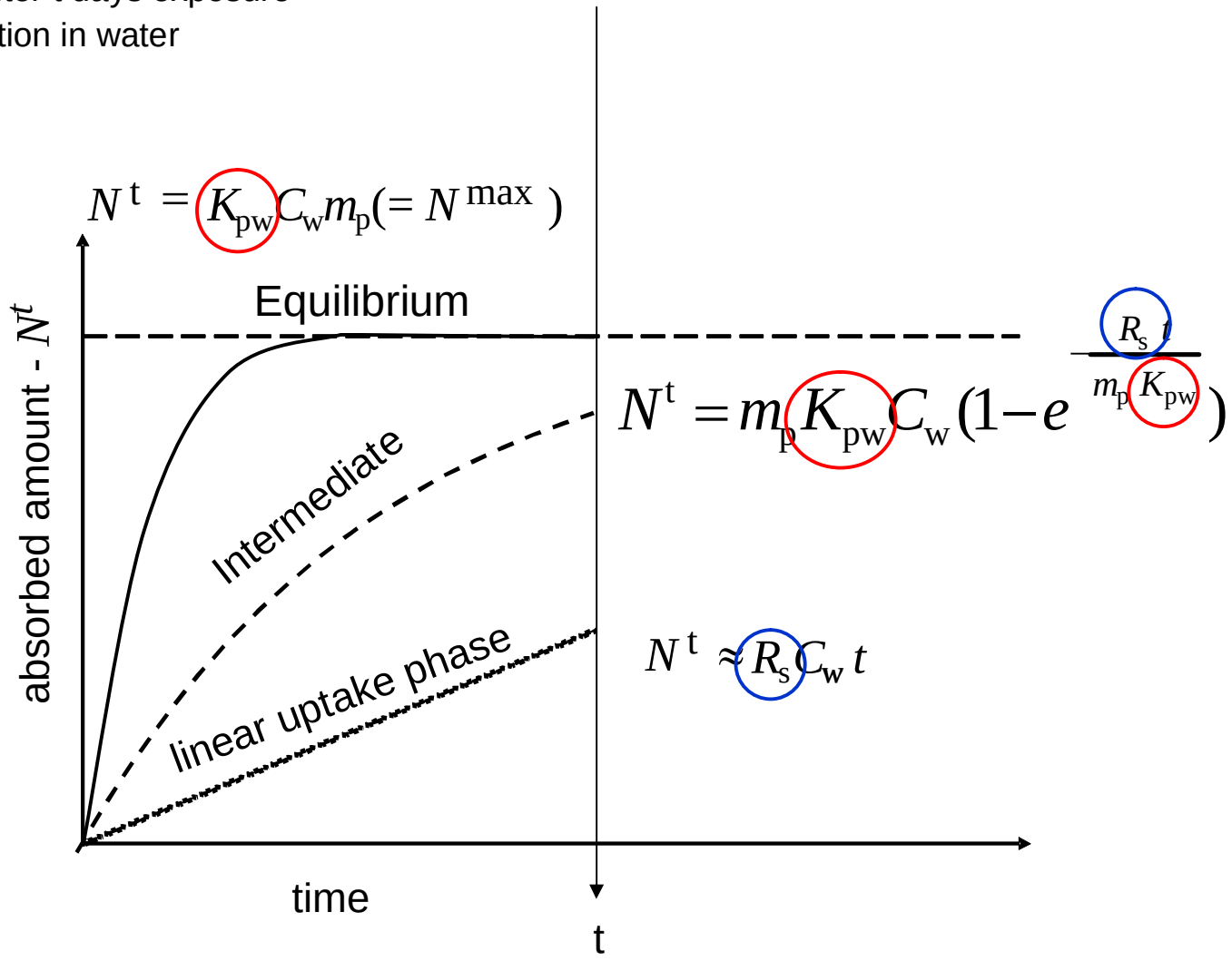


Different stages of the uptake process

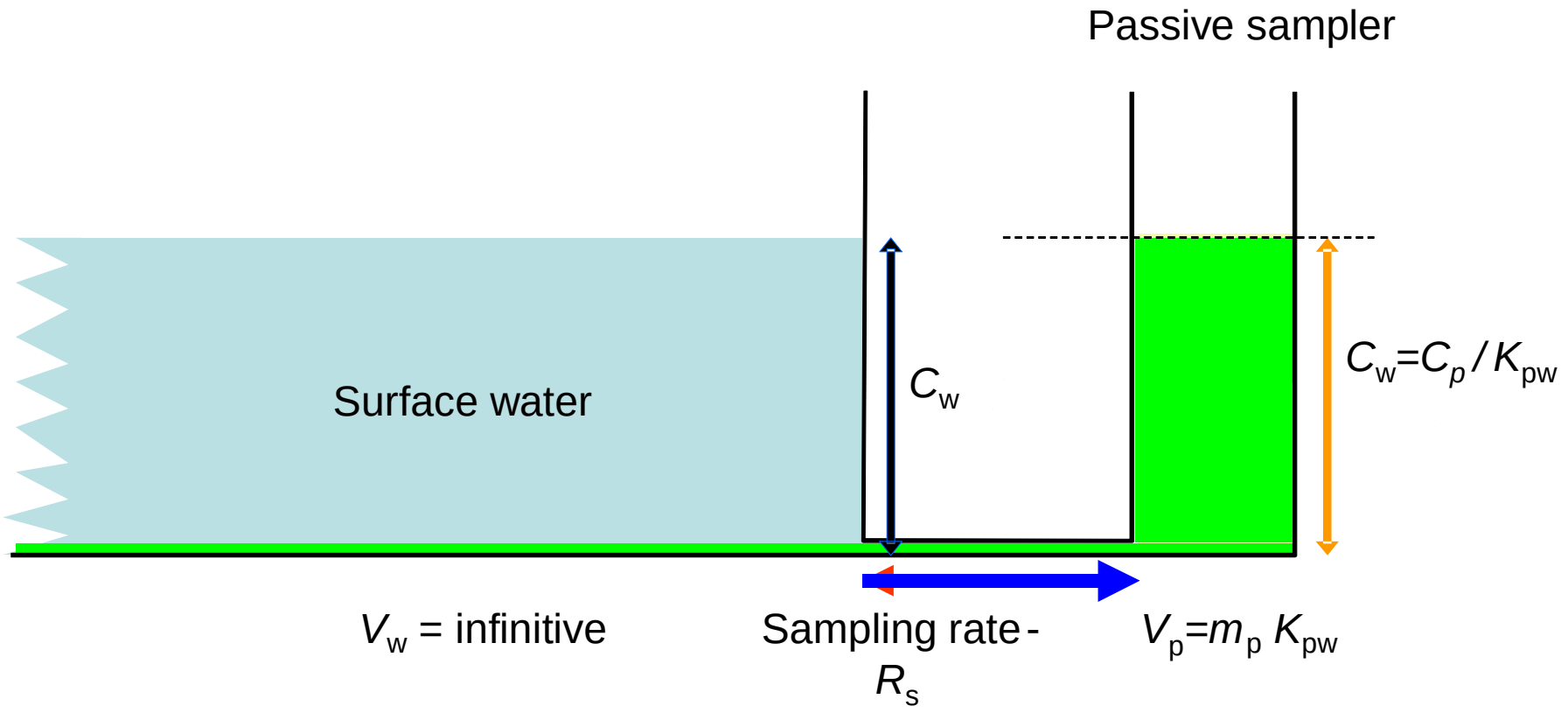


N^t amount on the sampler after t days exposure
C_w free dissolved concentration in water
m_p mass sampler
R_s sampling rate
C_p conc. in de sampler

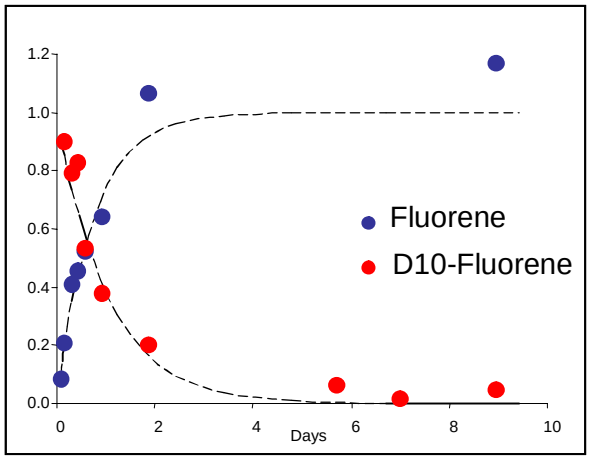
$$K_{pw} = \frac{C_p}{C_w}$$

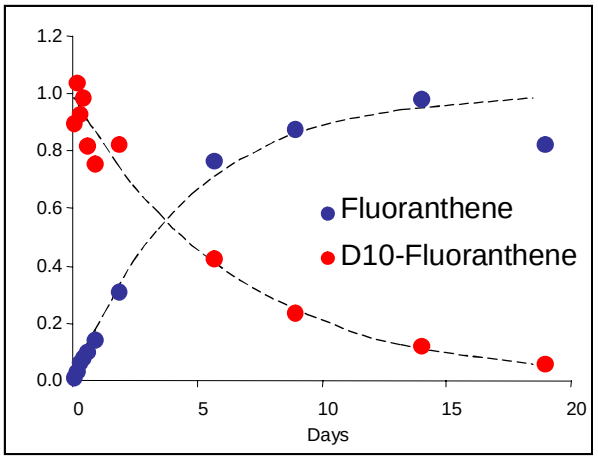


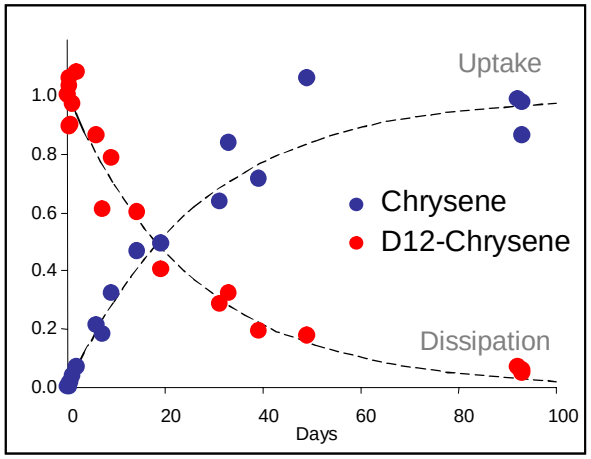
Performanc reference compounds (PRC) release

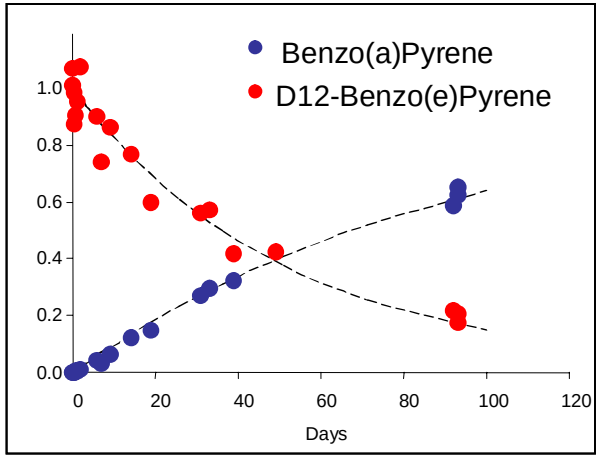


Sampling rate by PRCs → the exchange is isotropic?

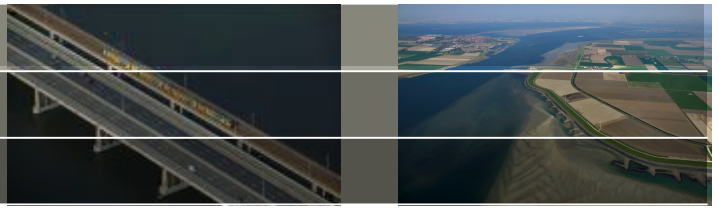


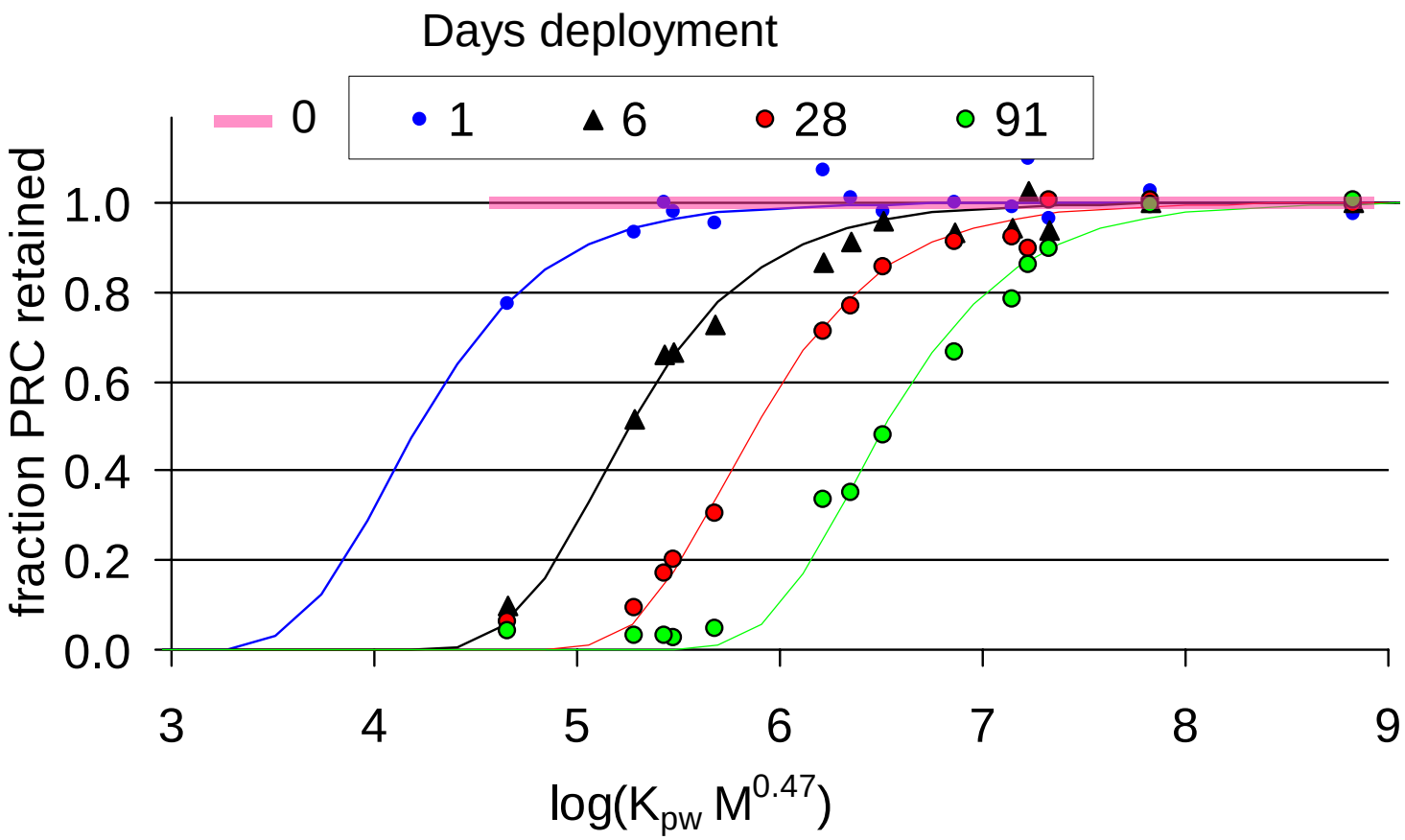






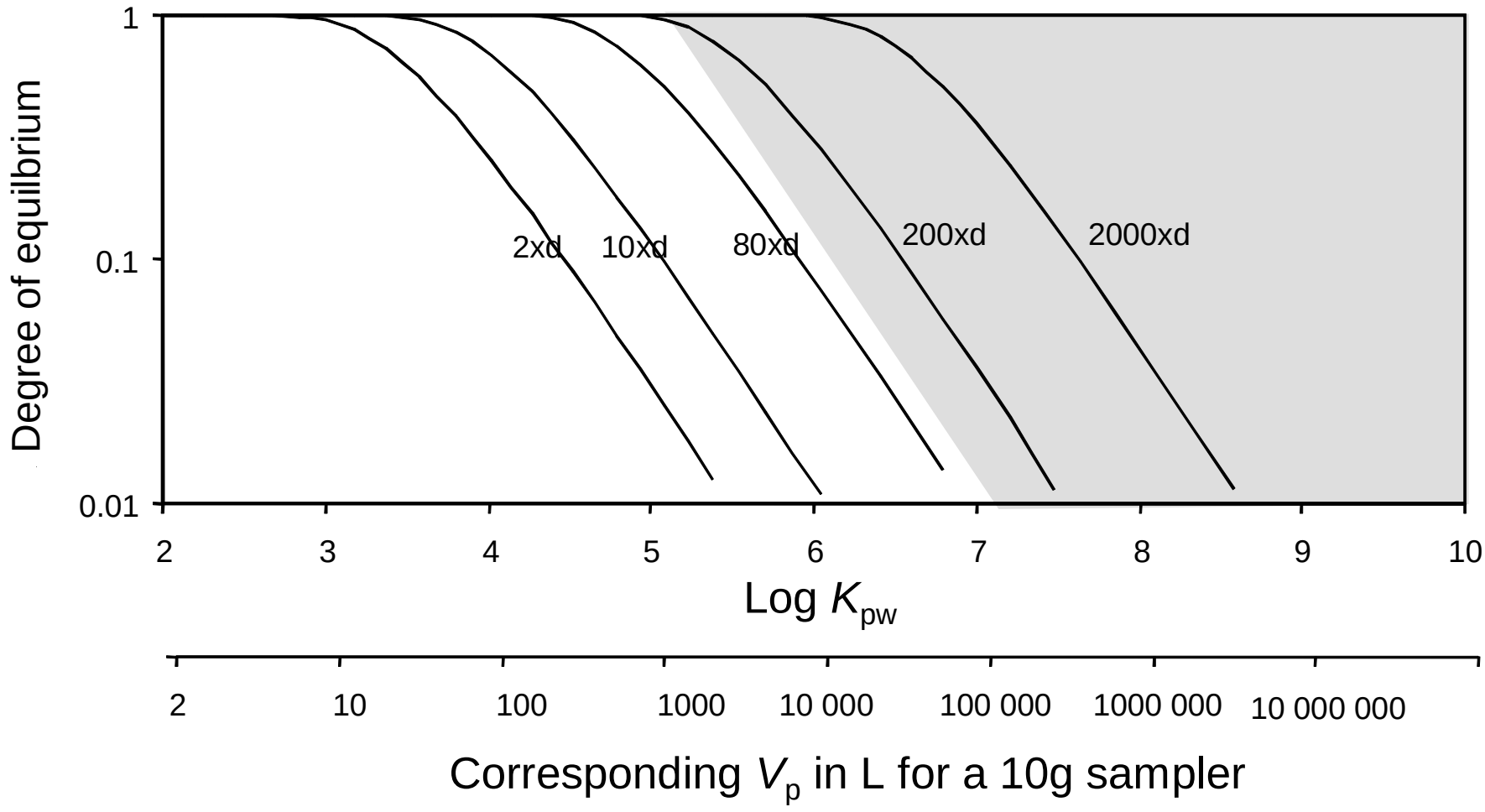
Release of PRCs with time



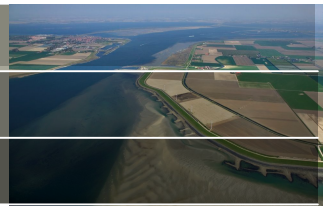


Data from ECLIPSE project

Equilibrium versus logK_{pw} for different time periods



Parameters for calculation C_w



reference

Sampler-water partition coefficient → cosolvent method [1]

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

No membrane control on uptake [3]

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

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

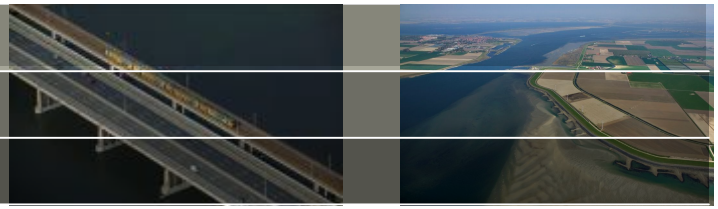
adjustable

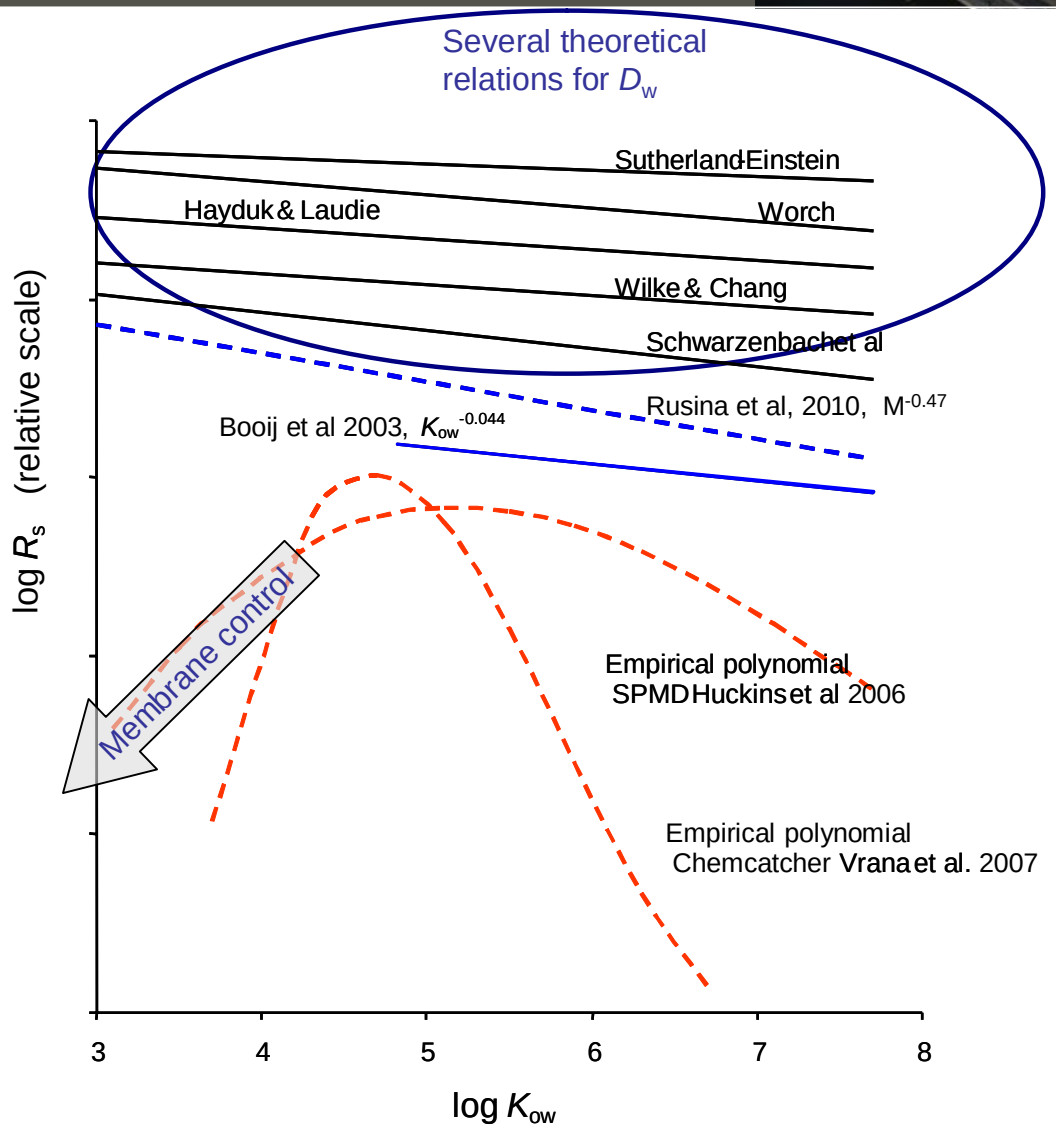
Variable, different PRCs

using non-linear regression fit of f_{exp} and f_{calc} [4]

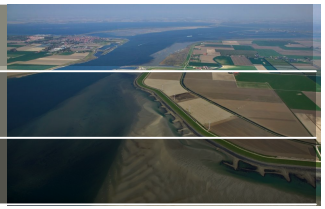
[2] Rusina et al EST 2010 [3] Rusina et al Chemosphere 2007 [4] Booij and Smedes 2010

Relation of Rs with hydrophobicity

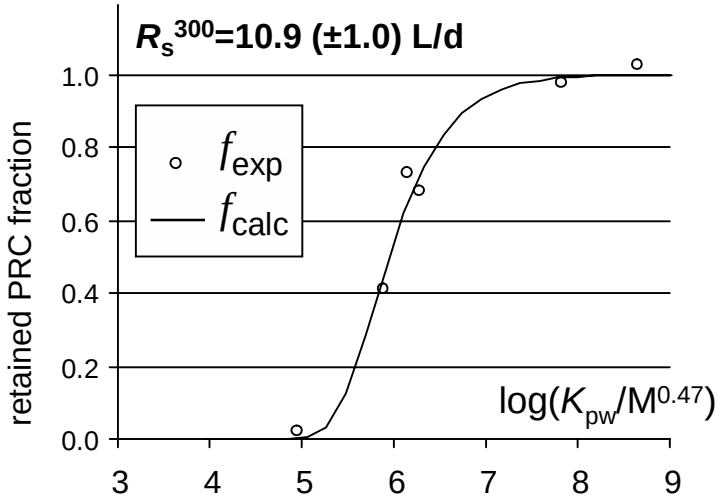


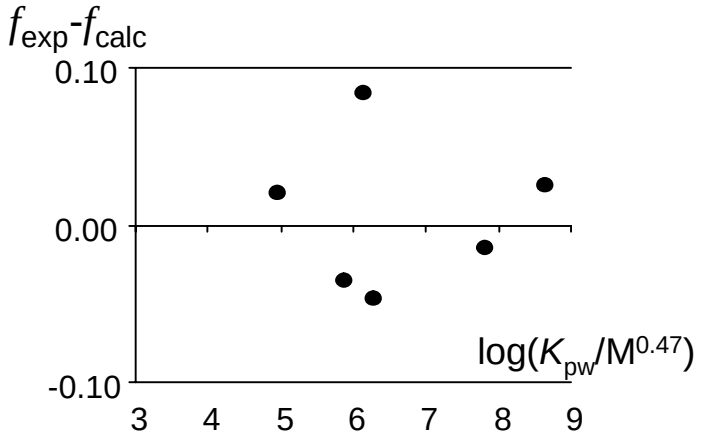


Examples of fiting

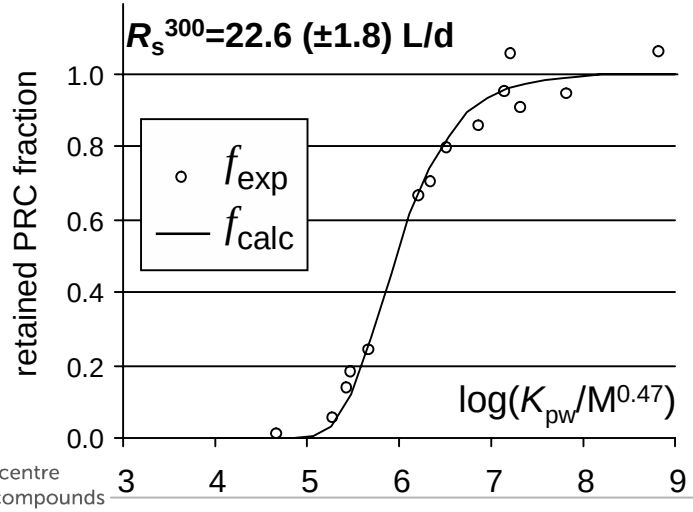


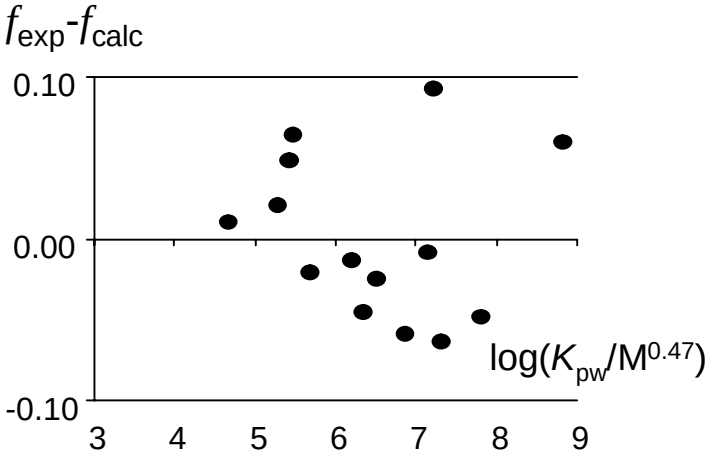
2001 Autumn, Station 1 Wadden Sea



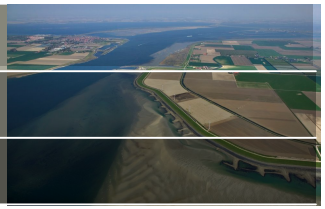


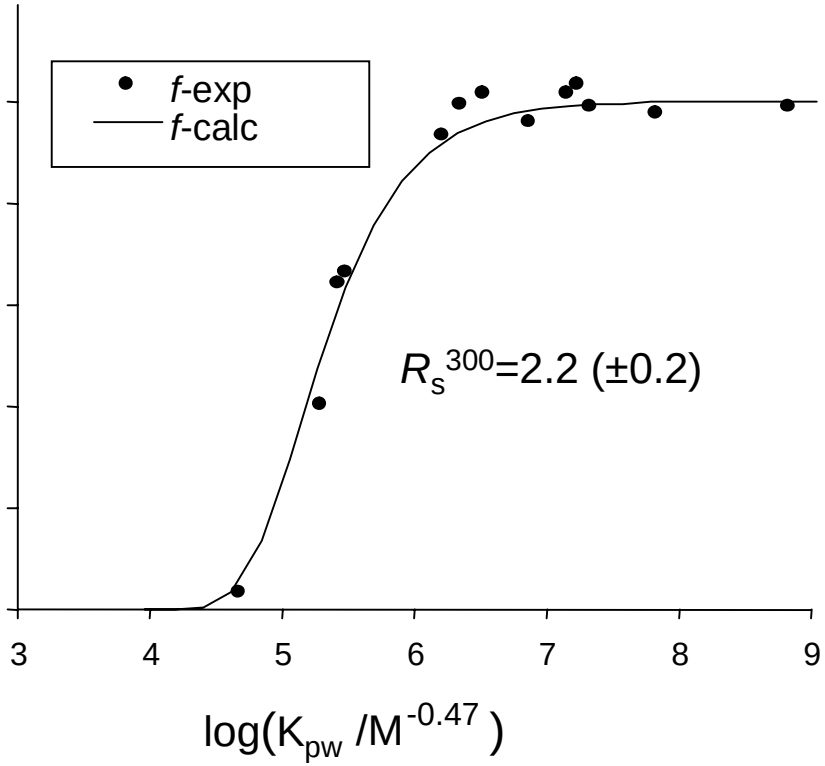
2010 Winter, Station 1 Wadden Sea



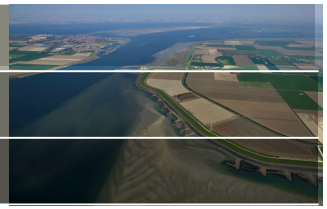


Biofouled!





Caclulation of C_w



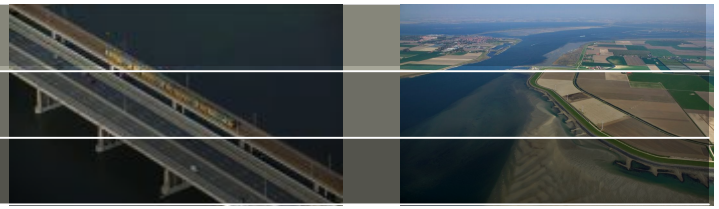
General equation :

$$C_w = \frac{N_t}{K_{pw} m \left(1 - \exp\left(-\frac{R_s \; t}{K_{pw} m}\right)\right)}$$

Inserting model for R_s :

$$C_w = \frac{N_t}{K_{pw} \; m \left(1 - \exp\left(-\frac{FA \; t}{K_{pw} M^{0.47} m}\right)\right)}$$

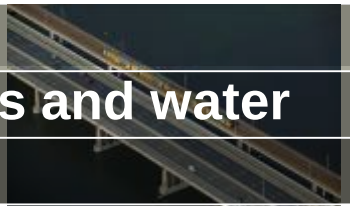
Sampling rates and aqueous concentrations can be calculated retrospectively

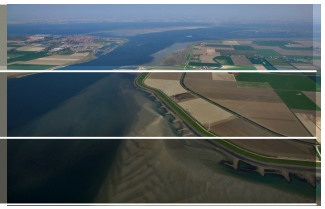


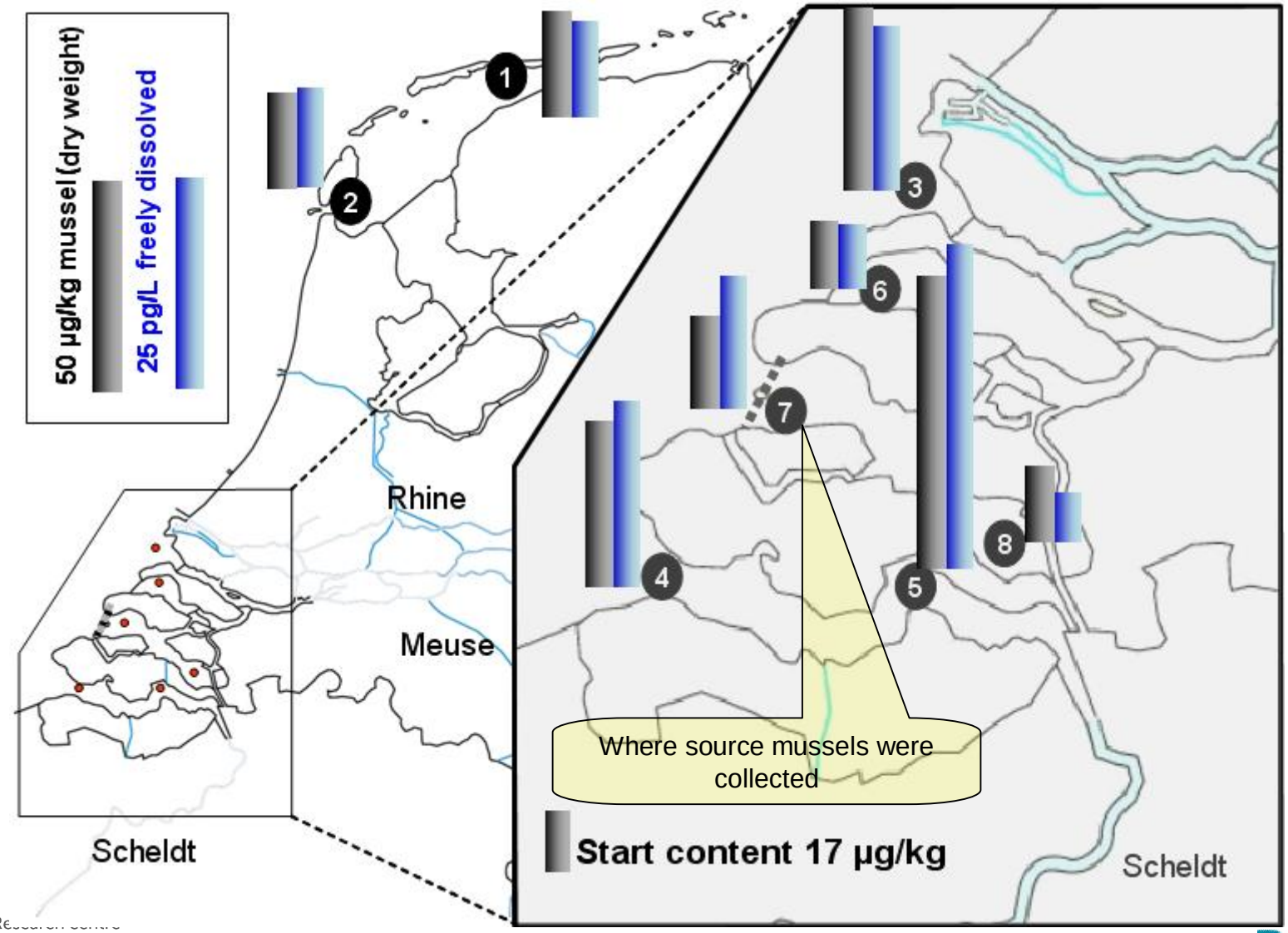
A lot of things to consider,

is that worth while?

Spatial distribution for PCB 153 in mussels and water







NORMAN Inter-Laboratory Study (ILS) on passive sampling of emerging pollutants
DG Joint Research Centre, 29 – 30 October, 2012, Ispra, Italy