Conversion of passive sampling data into concentrations in the sampled media

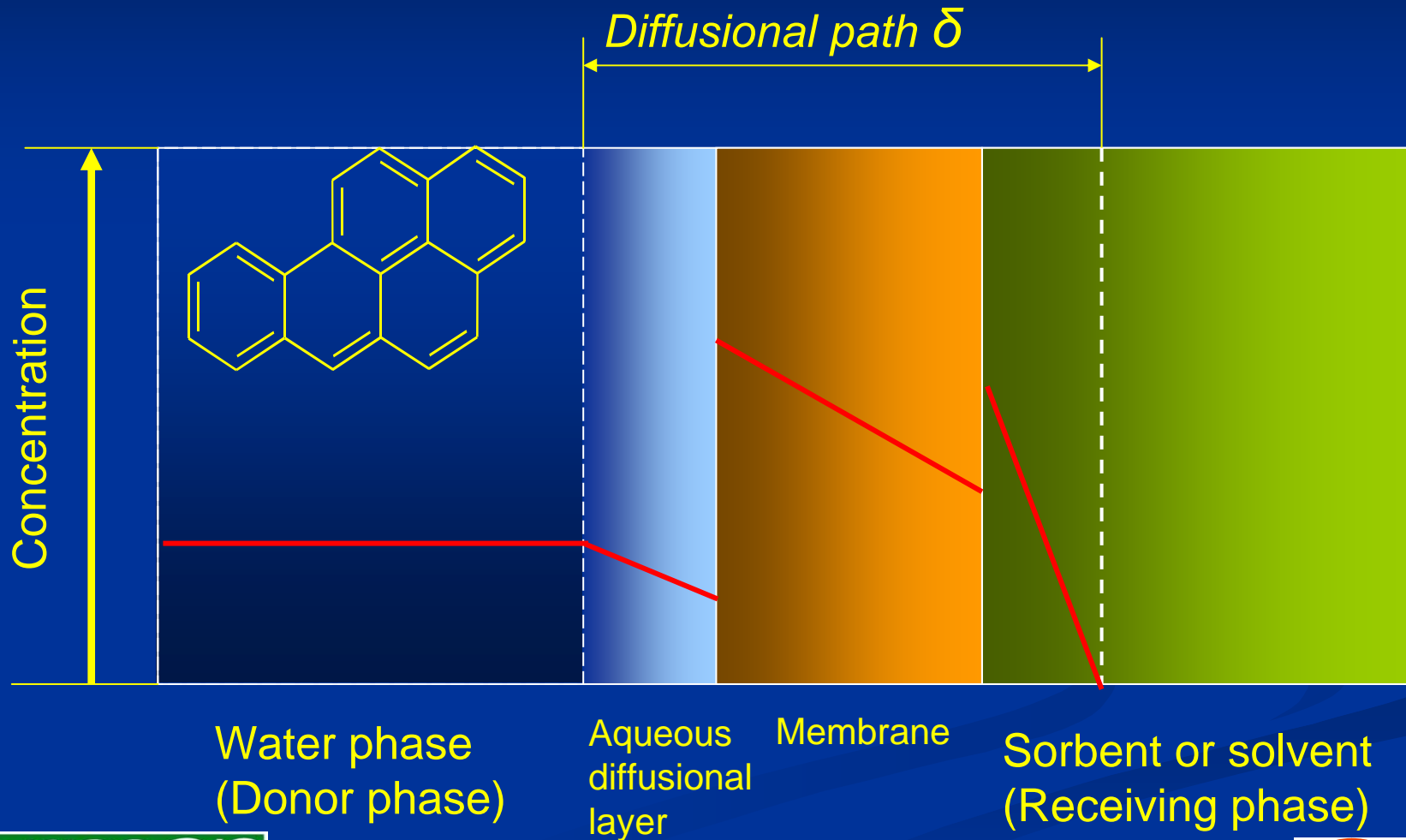## NORMAN expert group meeting
Prague, 27th May 2009

Existing passive sampling techniques

- Sub areas:

  - **hydrophobic** organic compounds, e.g. POPs
  - **polar** (hydrophilic) organic compounds such as pharmaceuticals, polar pesticides and illicit drugs
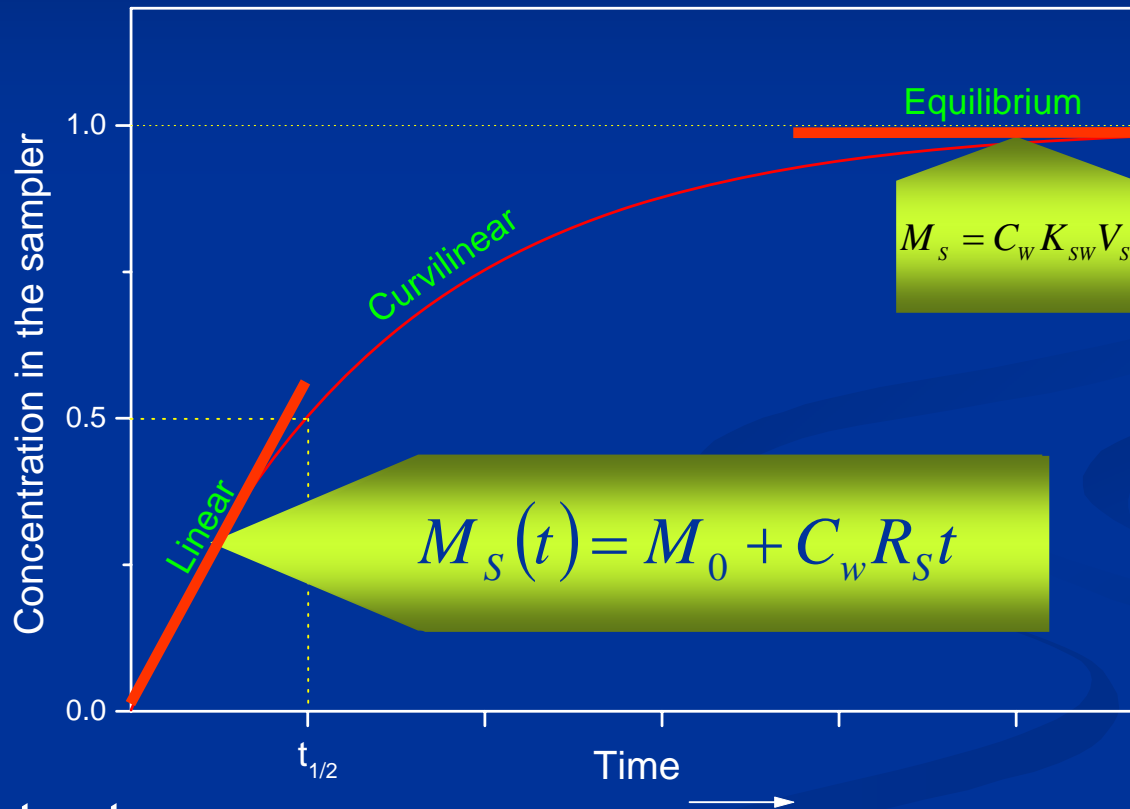 - **trace metals and organometallic** compounds

Time weighted average (TWA) sampling

$$C_{TWA} = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3 + \ldots C_n t_n}{t_1 + t_2 + t_3 + \ldots t_n}$$

Principle of a passive sampler

Diffusional path δ

Concentration

Water phase (Donor phase)

Aqueous diffusional layer

Membrane

Sorbent or solvent (Receiving phase)

Uptake of a chemical by a passive sampler

Concentration in the sampler (y-axis): 0.0, 0.5, 1.0

Equilibrium

$$M_s = C_w K_{sw} V_s$$

Curvilinear

Linear

$$M_s(t) = M_0 + C_w R_S t$$

$$\frac{dM_s}{dt} \sim C_w$$

$t_{1/2}$

Time

C_W = constant

R_S = substance specific sampling rate [L d^{-1}]

Uptake kinetics of a contaminant into passive sampler

$$C_S(t) = C_{S0} + \left(C_W K_{SW} - C_{S0}\right)\left[1 - \exp\left(-\frac{k_o A \alpha}{K_{SW} V_S}\right)t\right]$$

$$C_S(t) = K_{SW} C_W \underbrace{\left[1 - \exp(-k_e t)\right]}_{\text{uptake}} + \underbrace{C_{S0} \exp(-k_e t)}_{\text{elimination}}$$

Uptake of a compound to a passive sampler

$$C_S(t) = K_{SW} C_W [1 - \exp(-k_e t)] + C_{S0} \exp(-k_e t)$$

uptake   elimination

$C_W \neq 0 \quad C_{S0} = 0:$ **uptake**

$$C_S(t) = K_{SW} C_W [1 - \exp(-k_e t)]$$
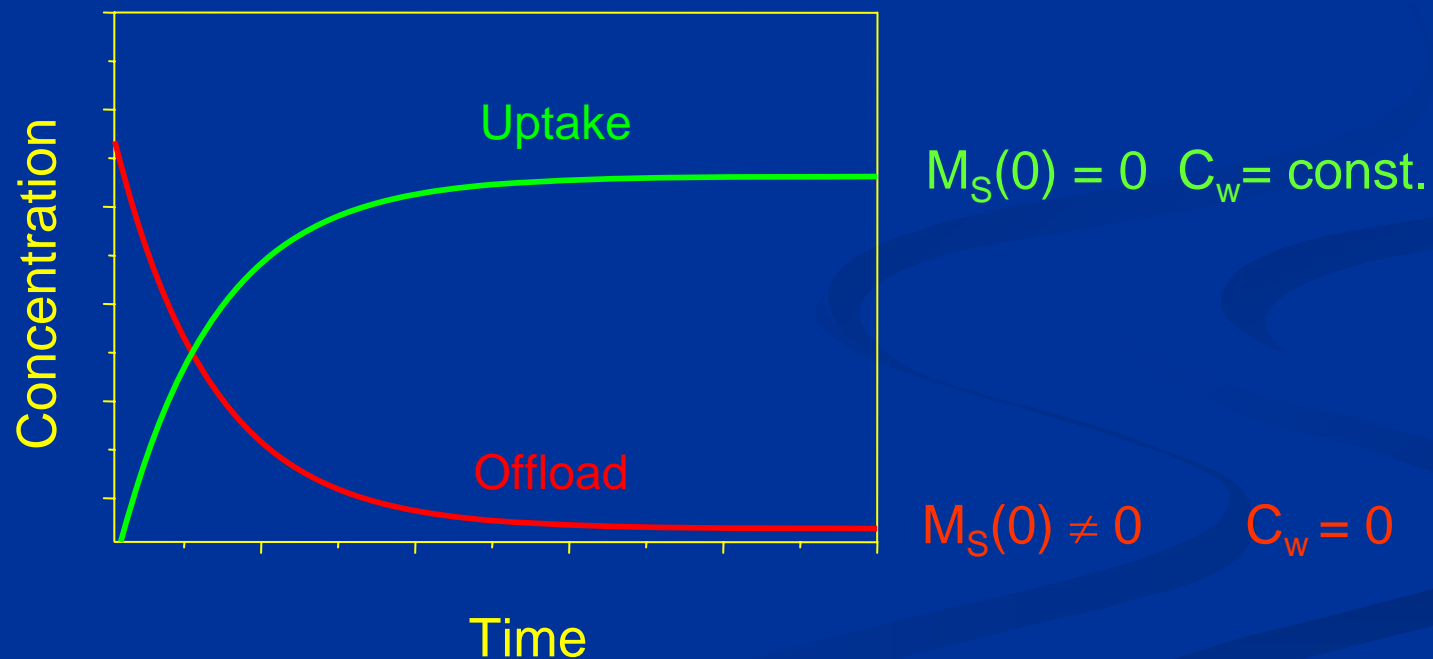
Elimination of a compound from a passive sampler

$$C_S(t) = K_{SW} C_W \; [1 - \exp(-k_e t)] + C_{S0} \exp(-k_e t)$$

uptake   elimination

$C_W = 0$ $C_{S0} \neq 0$:   **only elimination**

$$C_S(t) = C_{S0} \exp(-k_e t)$$

Correlation between uptake and offload – PRC concept

In ideal case: both uptake and offload are governed by the same mass transfer law – isotropic exchange kinetics.
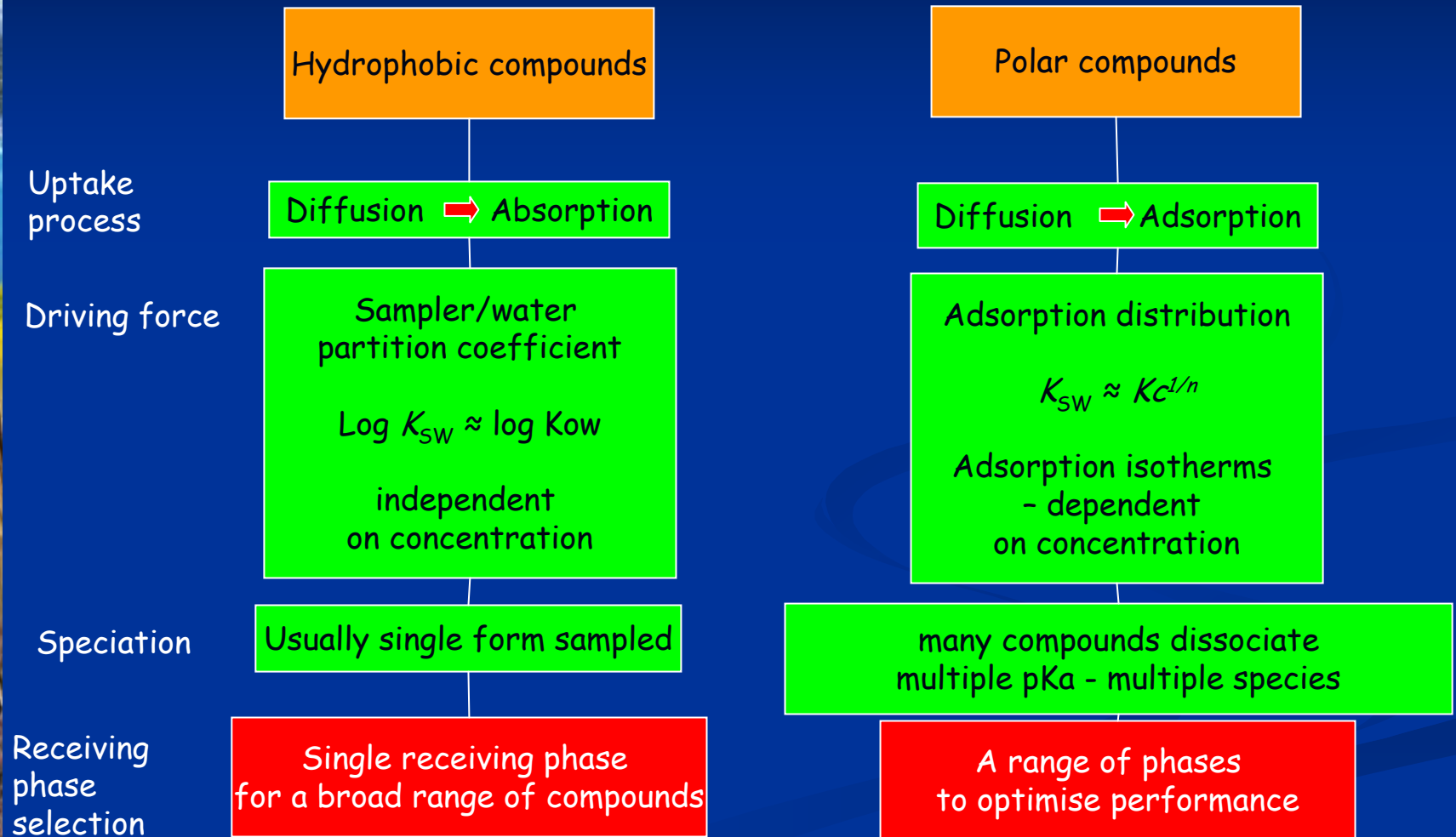
Mass transfer in a passive sampler

■ The overall resistance ($1/k_{\text{ov}}$) to the uptake of a chemical into the passive sampler is given by a sum of particular resistances to mass transfer:

Membrane   Water   Acceptor

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iw} D_i} = \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_W}{D_W} + \frac{\delta_S}{D_S K_{SW}}$$

$$k_i = \frac{D_i}{\delta_i}$$
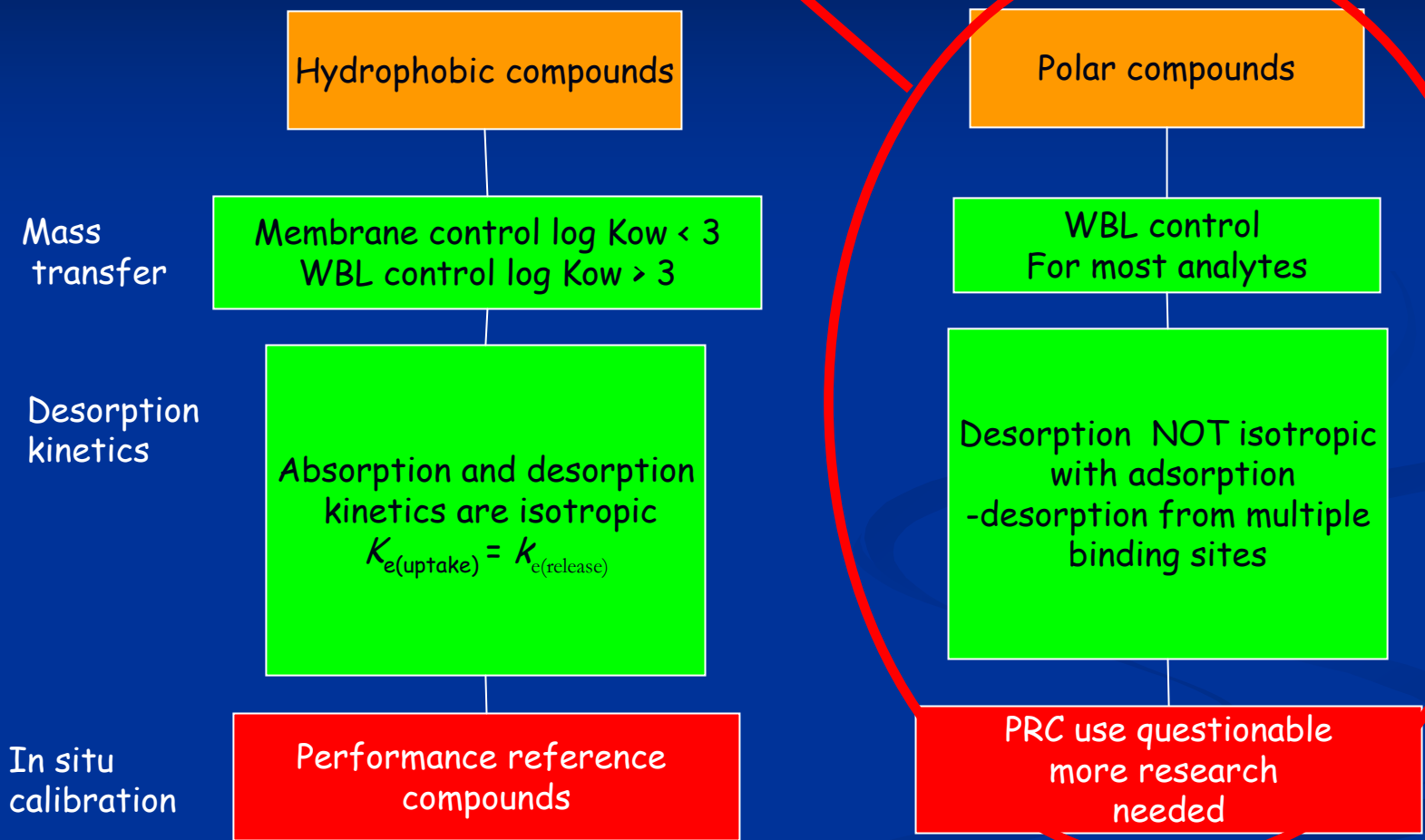
Differences in sampling principles

	Hydrophobic compounds	Polar compounds
Uptake process	Diffusion ➡ Absorption	Diffusion ➡ Adsorption
Driving force	Sampler/water partition coefficient Log K_{SW} ≈ log Kow independent on concentration	Adsorption distribution K_{SW} ≈ $Kc^{1/n}$ Adsorption isotherms – dependent on concentration
Speciation	Usually single form sampled	many compounds dissociate multiple pKa - multiple species
Receiving phase selection	Single receiving phase for a broad range of compounds	A range of phases to optimise performance

norman

IPSW 2009
Prague

Differences in sampling principles

Most emerging compounds

Hydrophobic compounds

Polar compounds

Mass transfer

Membrane control log Kow < 3
WBL control log Kow > 3

WBL control
For most analytes

Desorption kinetics

Absorption and desorption kinetics are isotropic
$K_{e(uptake)} = k_{e(release)}$

Desorption NOT isotropic with adsorption
-desorption from multiple binding sites

In situ calibration

Performance reference compounds
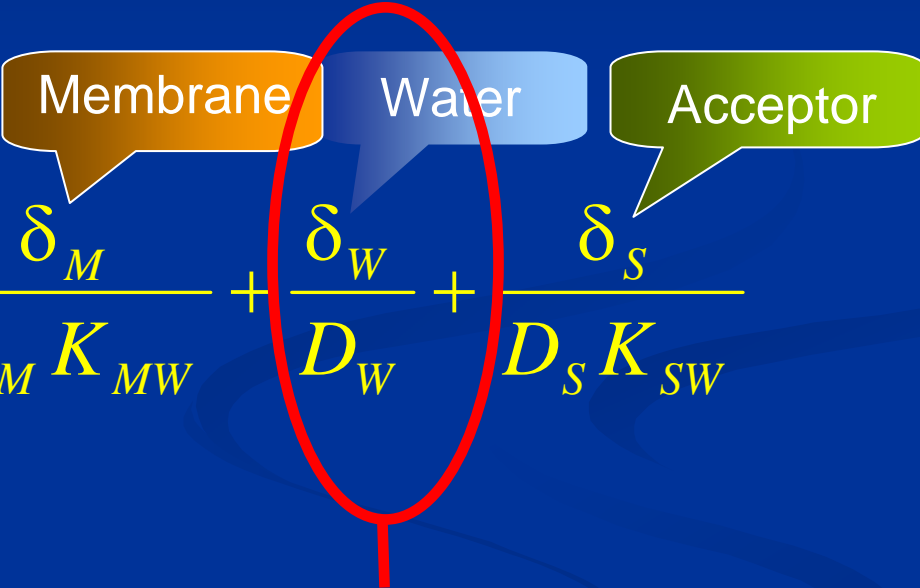
PRC use questionable more research needed

Problems with adsorption based samplers

- Sorption distribution coefficients are not constant, nonlinear adsorption isotherms

- Competitive sorption is likely

- Effect of pH not sufficiently characterised for dissociating compounds

- Absorption is often WBL controlled, thus sampling sensitive to flow turbulence

- Desorption is not isokinetic with adsorption – PRC applicability is questionable

Resistances to Mass transfer in a passive sampler

Membrane | Water | Acceptor

$$\frac{1}{k_{ov}} = \sum_i \frac{\delta_i}{K_{iw} D_i} = \frac{\delta_M}{D_M K_{MW}} + \frac{\delta_W}{D_W} + \frac{\delta_S}{D_S K_{SW}}$$
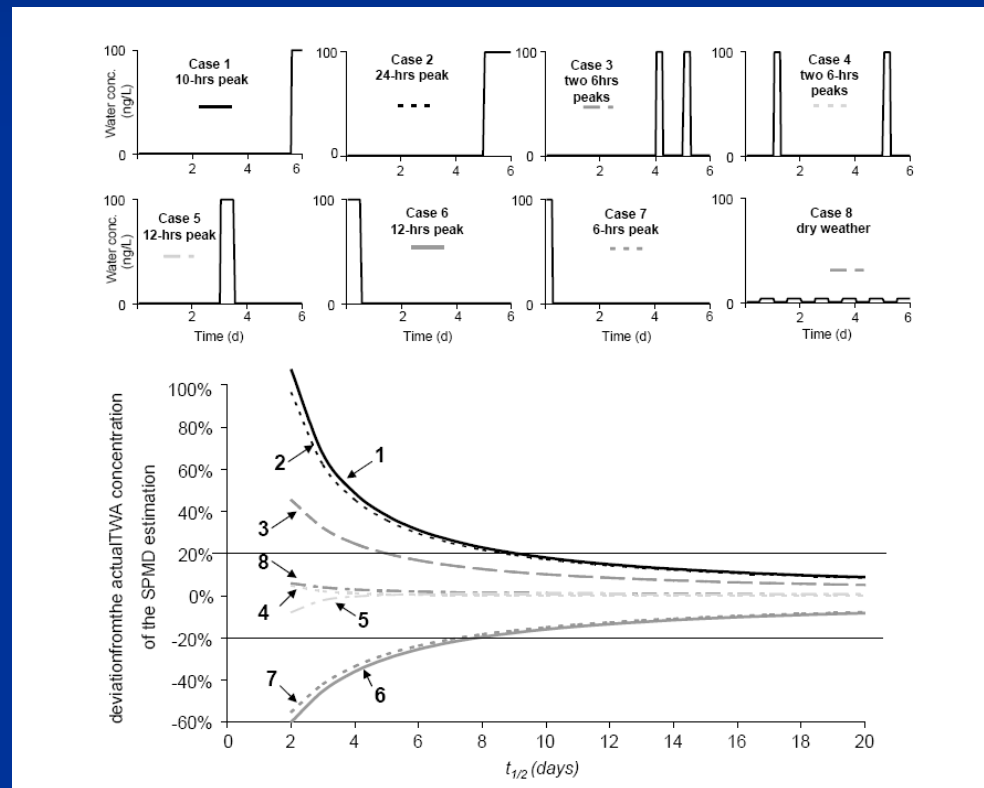
Highly variable resistance

$$k_i = \frac{D_i}{\delta_i}$$

Problems with all samplers

- TWA uncertainty when concentrations fluctuate

C. Gourlay-Francé et al. / Chemosphere 73 (2008) 1194–1200