



# Adsorption based sampling

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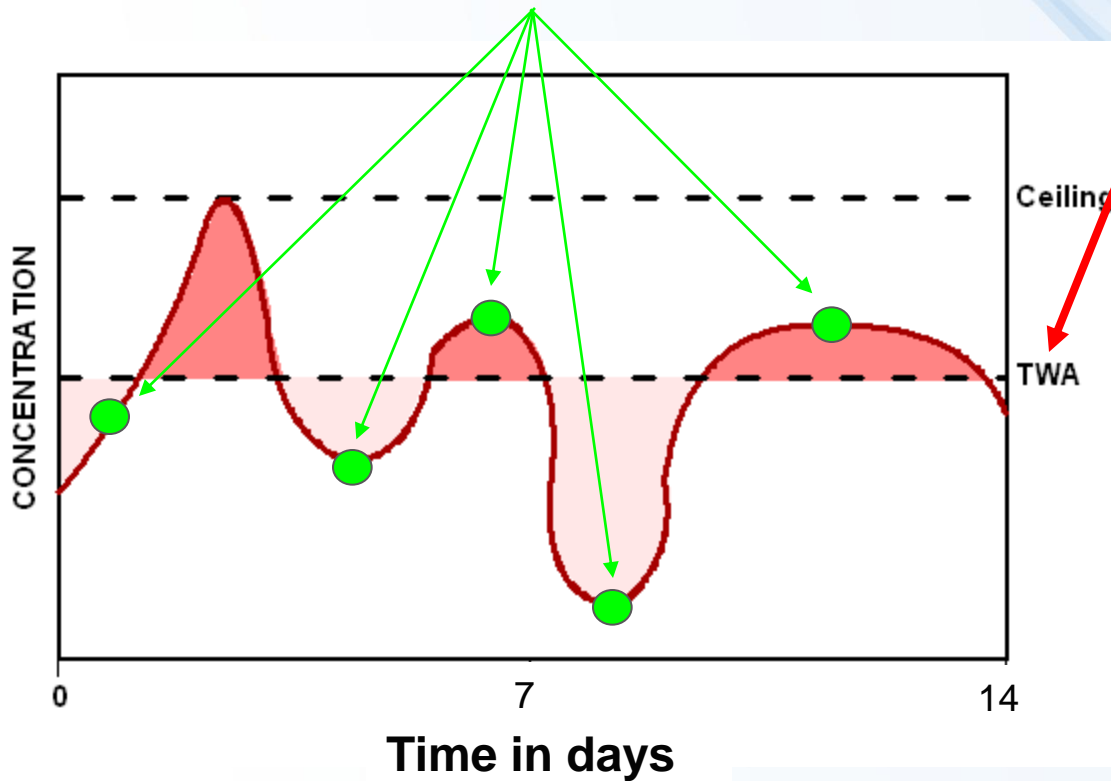
## Why adsorption passive sampling sampling?

- passive sampling of polar compounds
- soluble in water, can be present at higher concentrations than hydrophobic compounds
- higher solubility implies more possibility for fluctuations of water concentration
  - integrative sampling needed

# Variation in pollution over time

Concentrations  
In individual  
Spot samples

TWA = time-weighted  
average



## Need for methods with very low limits of quantification

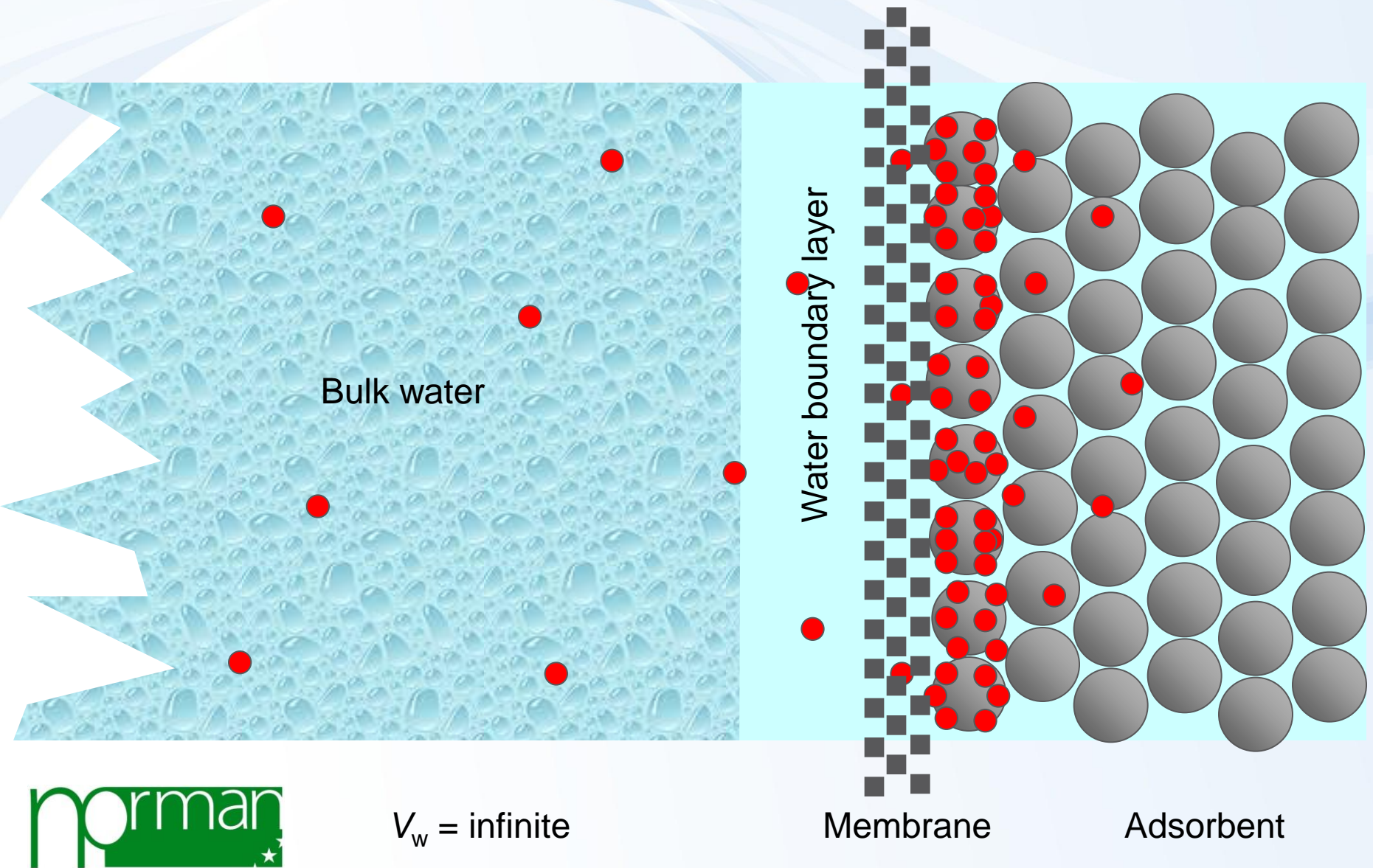
- Analytical Methods for the new proposed Priority Substances of the European Water Framework Directive (WFD)
- methods limits of quantification (LOQs) are compared with one third (1/3) of the EQS, mandatory for WFD compliance monitoring
- Example EQS:
  - Cypermethrin 80 pg/l (8 pg/l for coastal salt waters)
  - Dichlorvos 60 pg/l in coastal waters
  - Dicofol 32 pg/l in coastal waters
  - 17-alpha-ethinylestradiol 35 pg/l (7 pg/l in coastal waters)
  - 17-beta-estradiol 80 pg/l in coastal waters
  - Heptachlor/epoxide 0.2 pg/l (10 fg/l in coastal waters)
  - BDEs 49 fg/l (2.4 fg/l in coastal waters)

polar substances

# Why adsorption passive sampling sampling?

- partition/absorption polymers have low uptake capacity for polar compounds
- **adsorption materials** with strong bonding and high bonding capacity of polar compounds used in construction

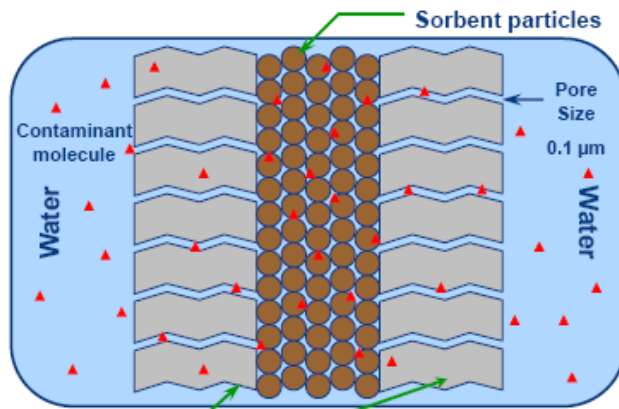
# Transport barriers in a samplers for polar compounds



# Adsorption based samplers

## POCIS

Adsorbent + PES membrane

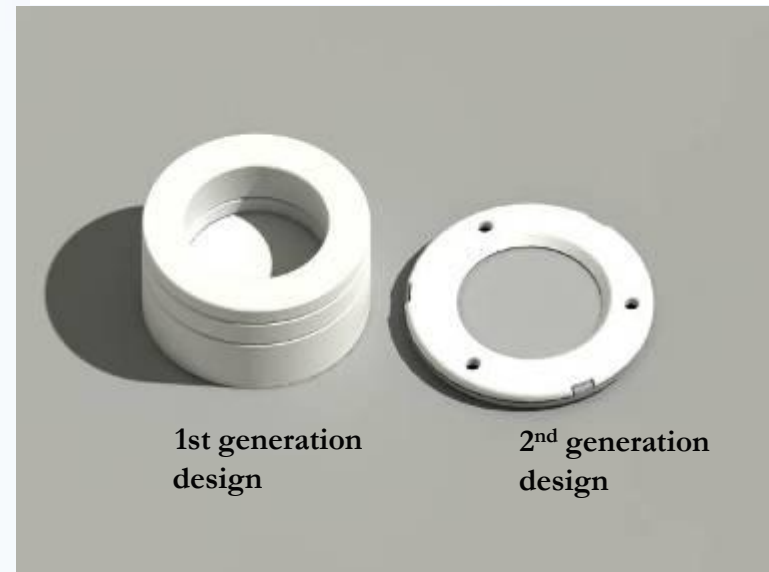
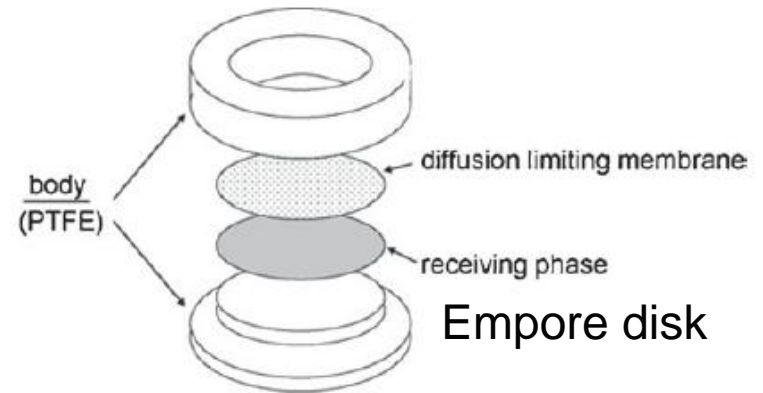


Membrane  
~ 130 μm thick



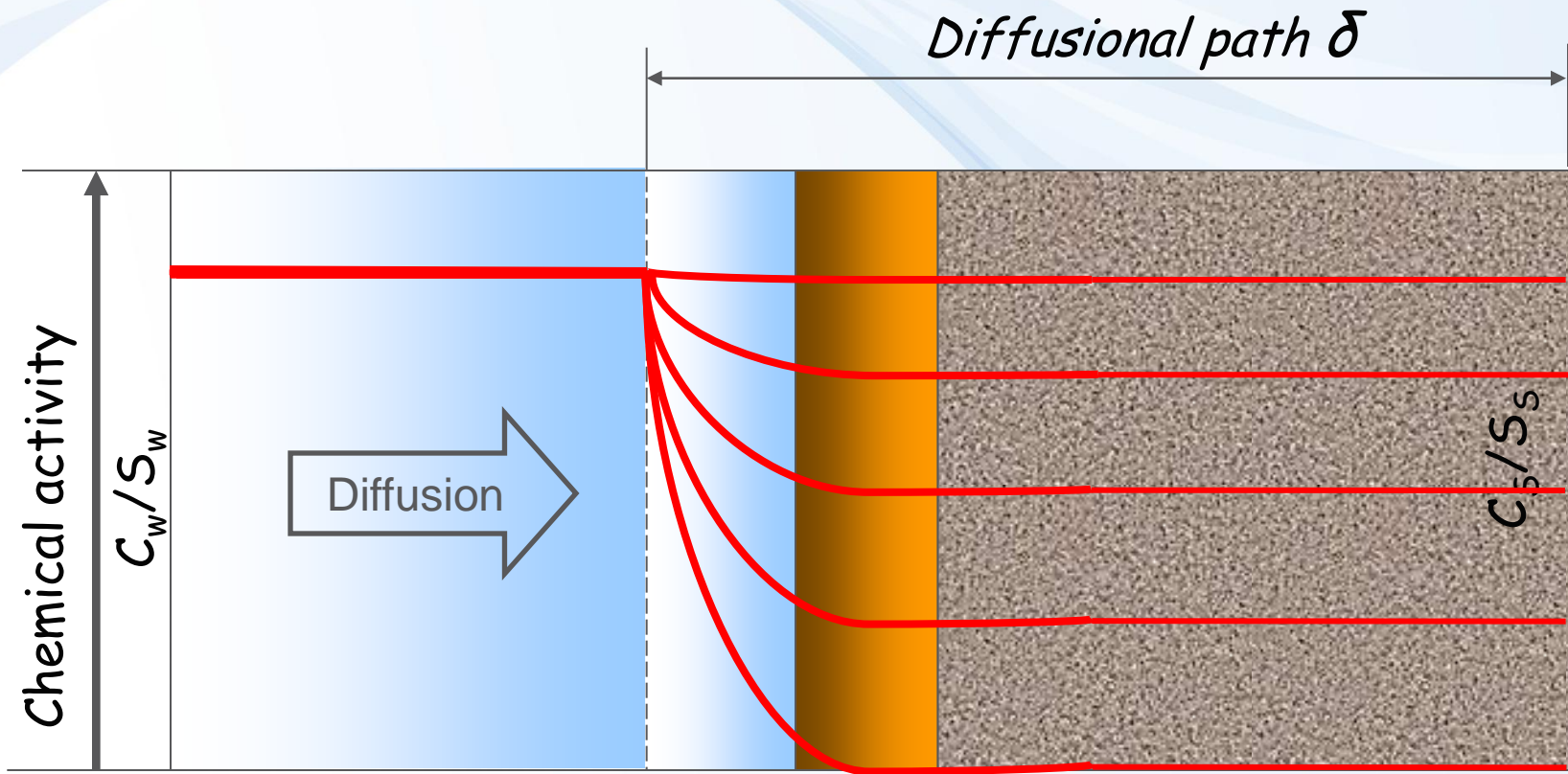
## Chemcatcher

Empore disk +/- PES membrane





# Principle of a passive sampler: uptake process from water



Bulk water

Water boundary layer (WBL)

Membrane

Sorbent (Receiving phase)

Mass transfer coefficients:

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

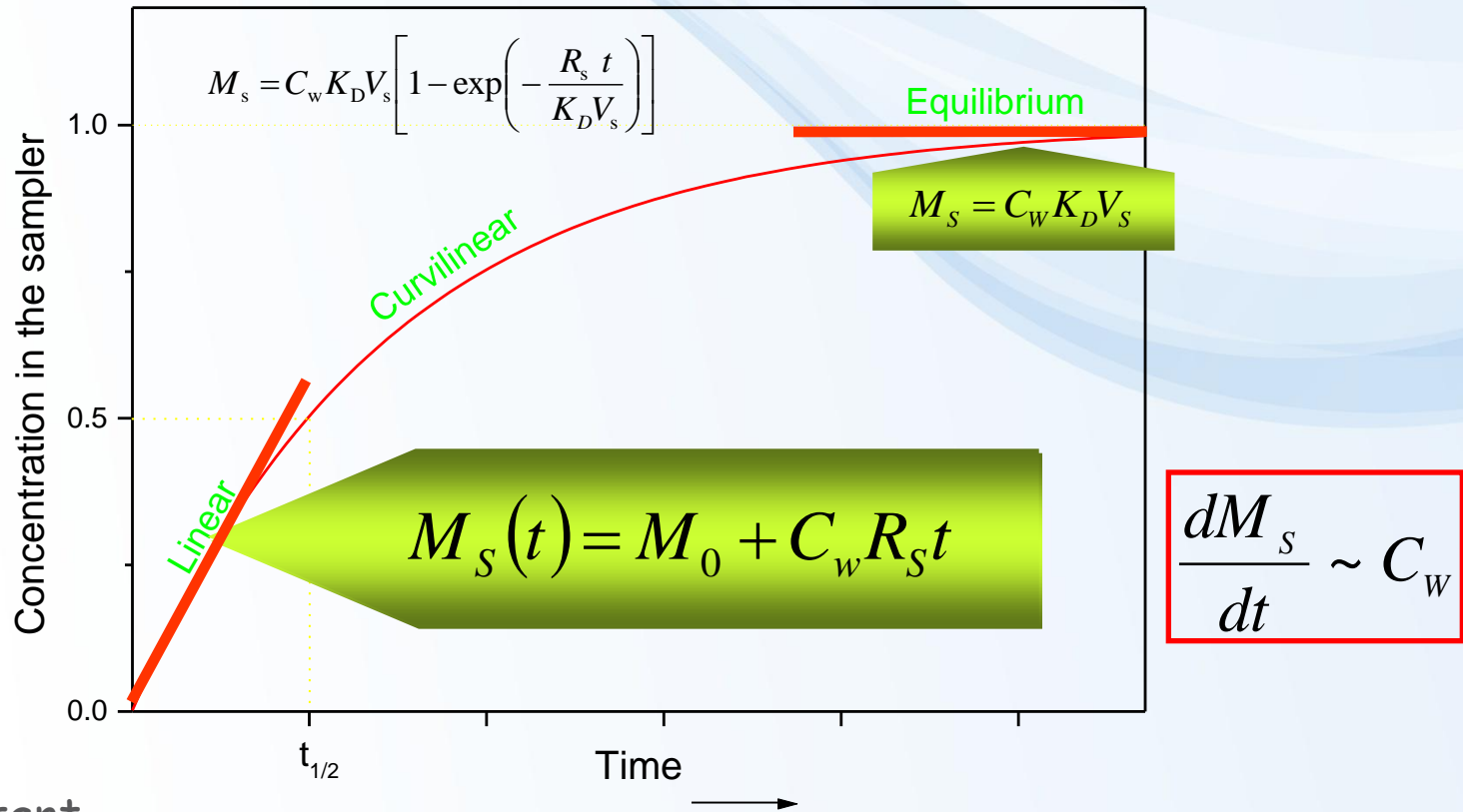
$$\frac{D_M K_{MW}}{\delta_w}$$

$$\frac{D_S K_D}{\delta_s}$$





# Uptake of a chemical by a passive sampler



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

## Measurement of TWA concentration

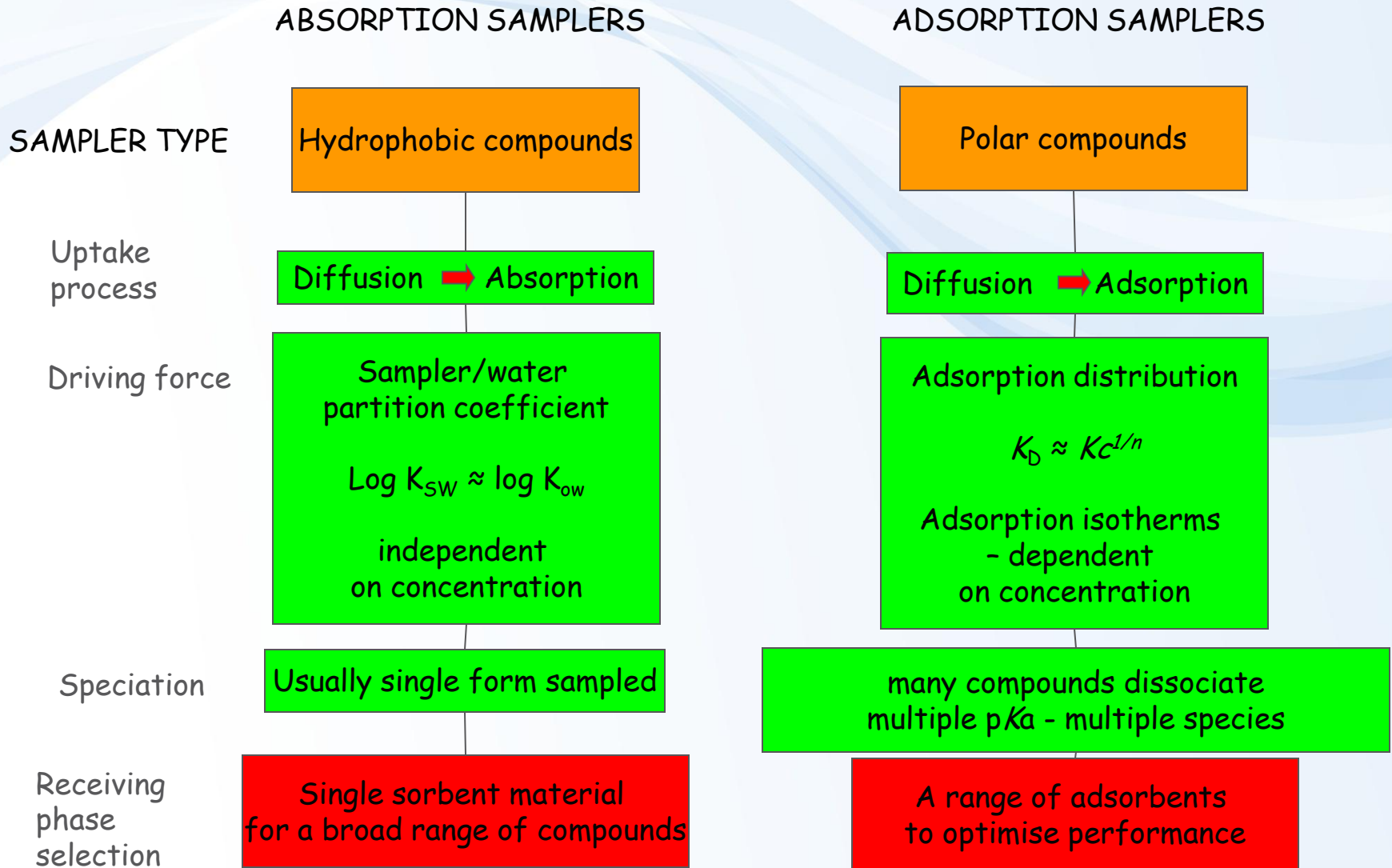
$$M_s = C_w K_D V_s \left[ 1 - \exp \left( - \frac{R_s t}{K_D V_s} \right) \right]$$

Sampling rate  $R_s$  [ $L d^{-1}$ ] - equivalent volume of water cleared of the target analyte per unit of time

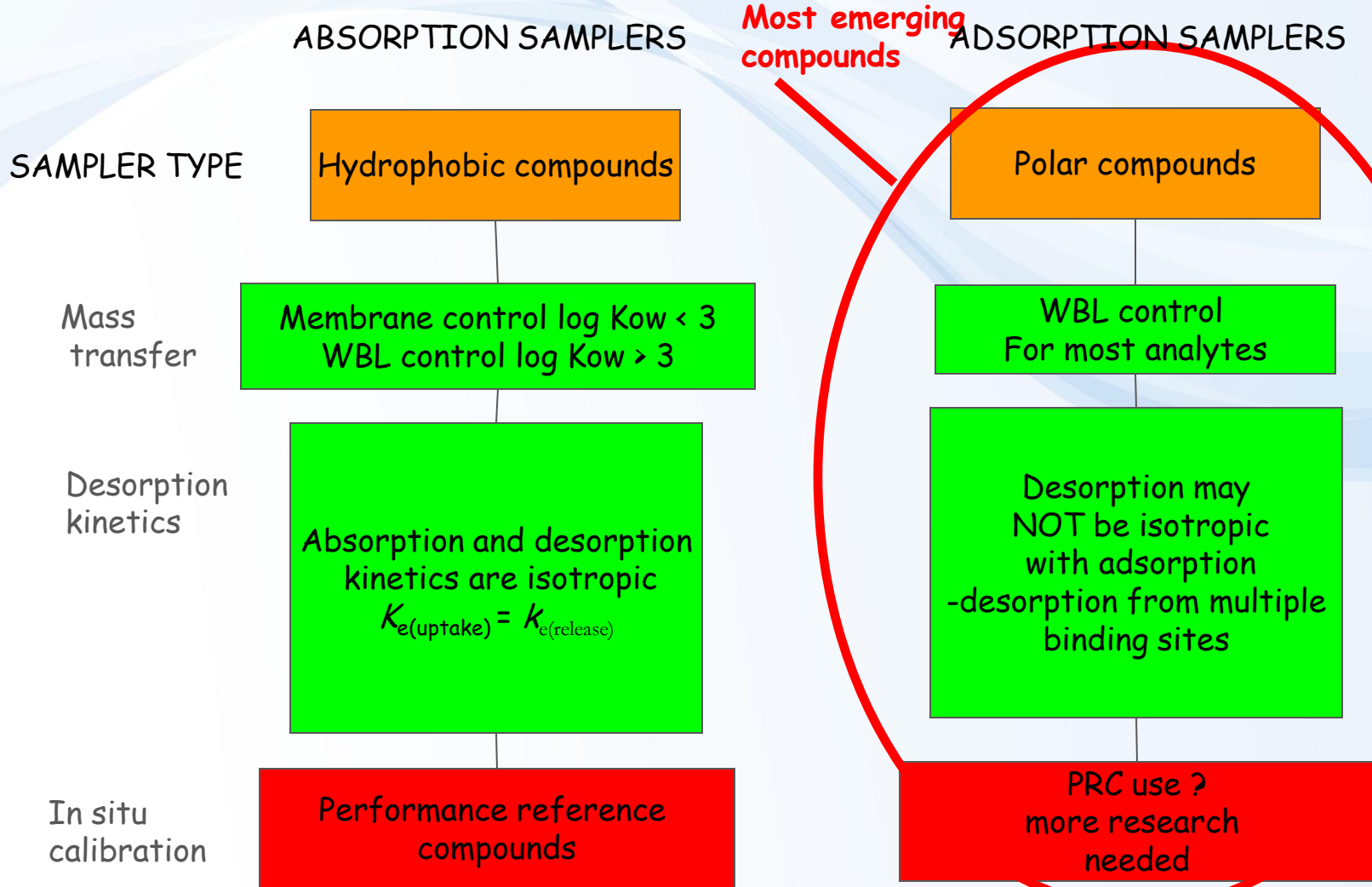
Sampler/water equilibrium distribution coefficient  $K_D$  [ $L/L$ ]

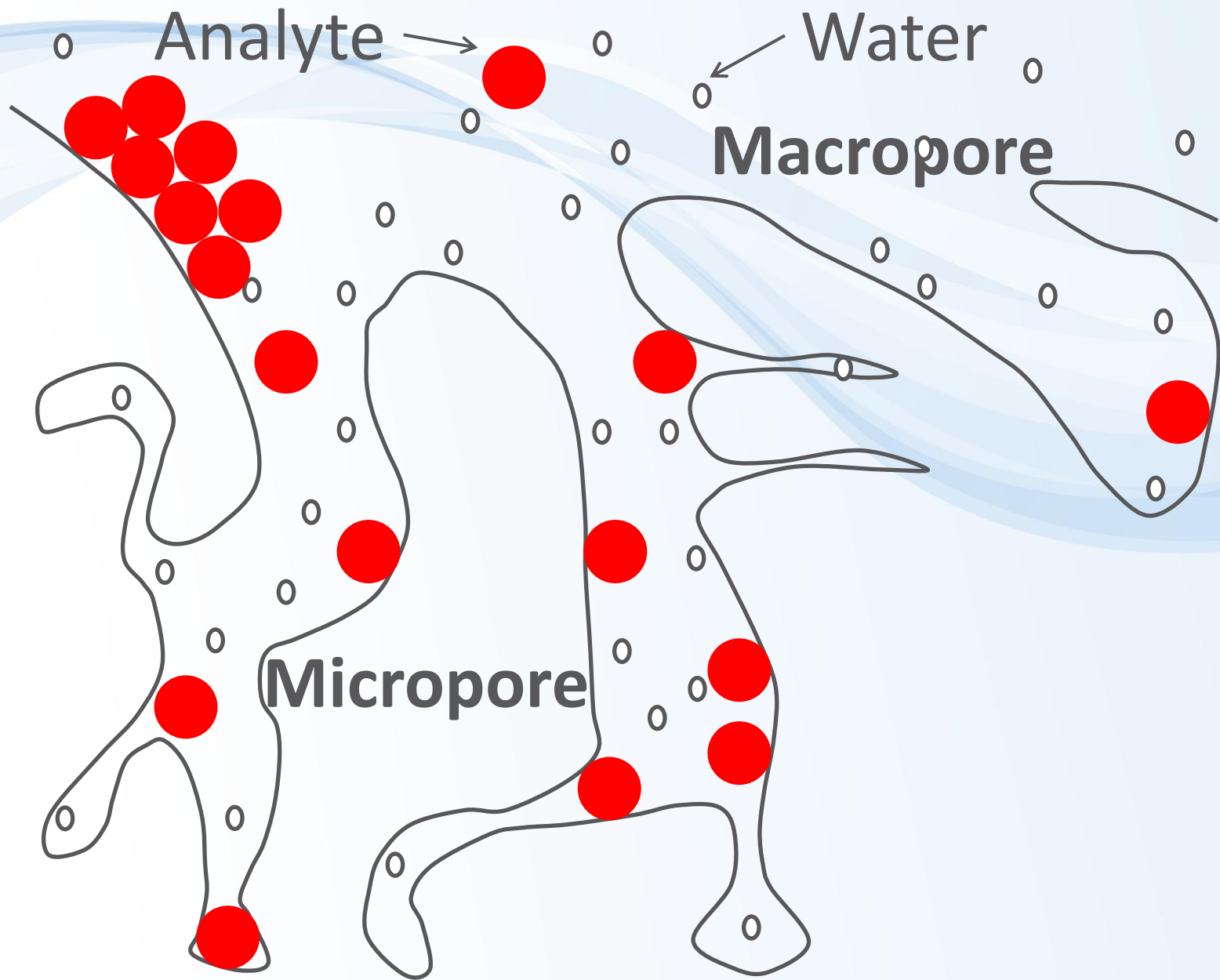


# Differences in sampling principles



# Differences in sampling principles





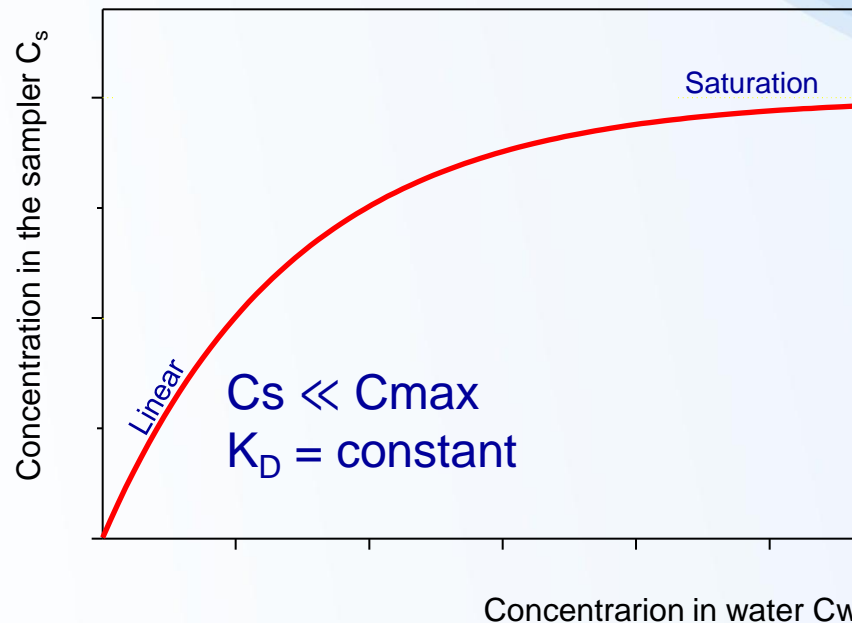
# Sorption models



Langmuir isotherm:

$$C_S = \frac{K_L C_{\max} C_w}{1 + K_L C_w}$$

$$K_D = \frac{C_S}{C_w}$$



$$K_D = K_L C_{\max}$$

# Langmuir sorption isotherms

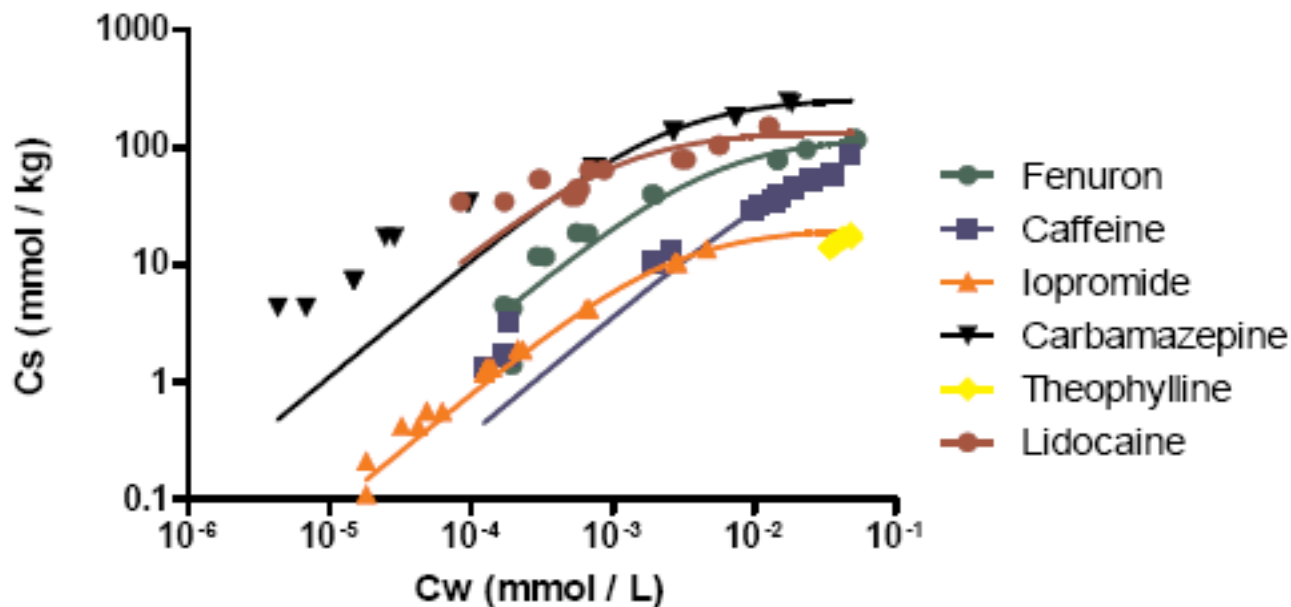
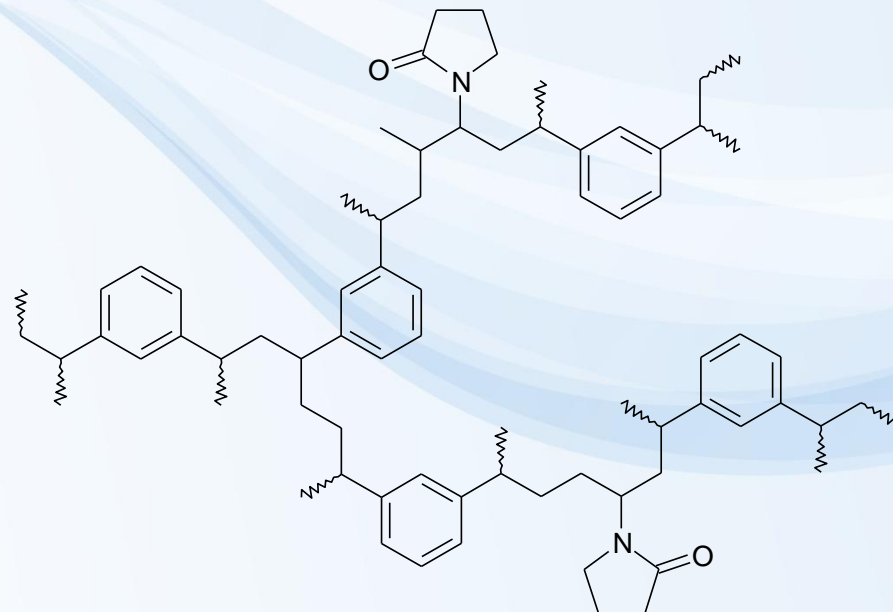
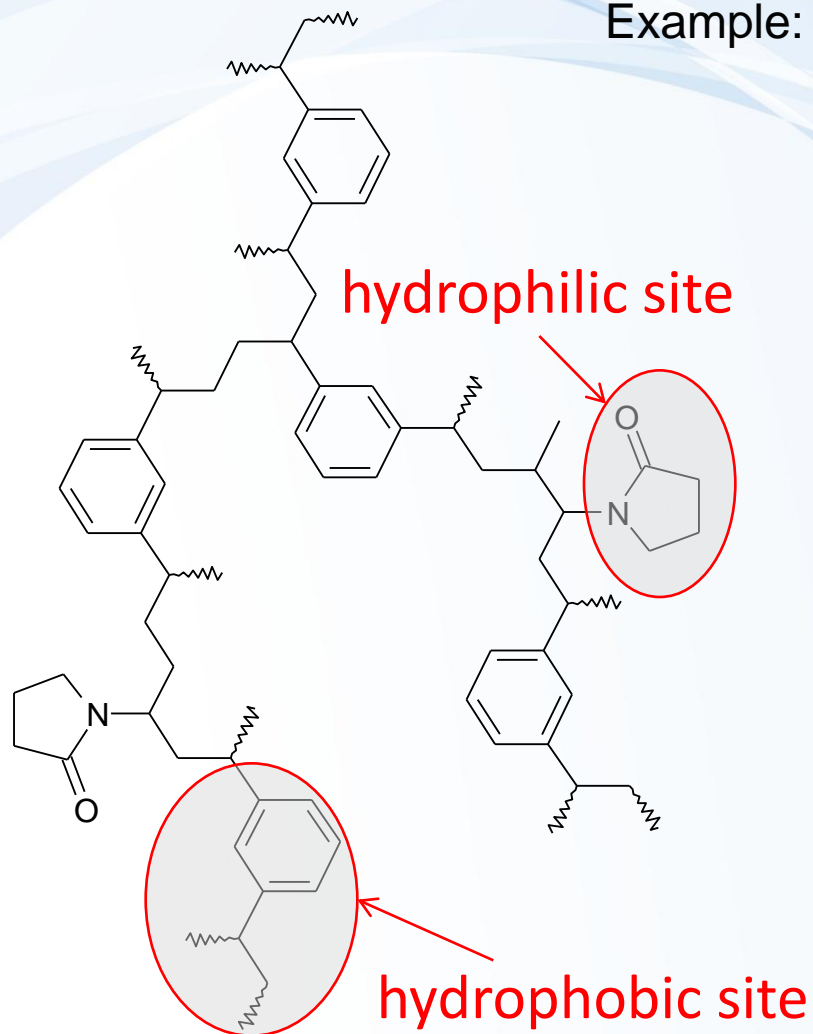


Figure S2: Isotherms for the OASIS HLB experiments



## Multiple binding sites Example: Oasis HLB



Solute – sorbent interactions:

- van der Waals
- Coulomb
- $\pi$ - $\pi$  interaction
- hydrogen bonding

# Multiple binding sites: combination of isotherms

$$C_s = \frac{K_{L1} \cdot C_{\max 1} \cdot C_w}{1 + K_{L1} \cdot C_w} + \frac{K_{L2} \cdot C_{\max 2} \cdot C_w}{1 + K_{L2} \cdot C_w}$$

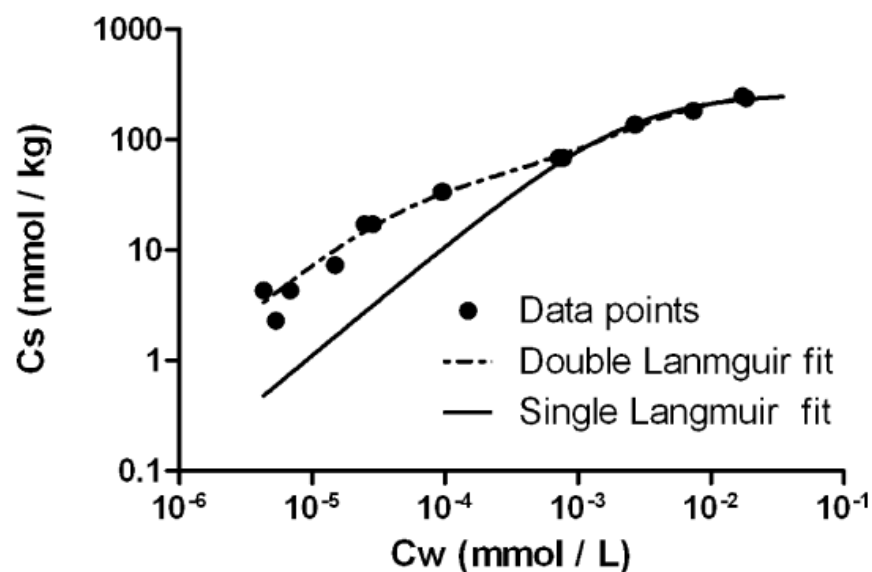


Figure 1. Single and double Langmuir fit for carbamazepine on HLB.

# Comparison of samplers

Chemcatcher



POCIS



Sorbent

SDB-XC

OASIS - HLB

Membrane

PES

PES

Surface area 17.5 cm<sup>2</sup> (one sided)

46 cm<sup>2</sup> (two sides)

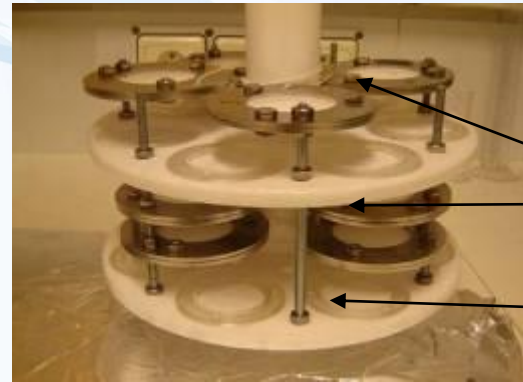
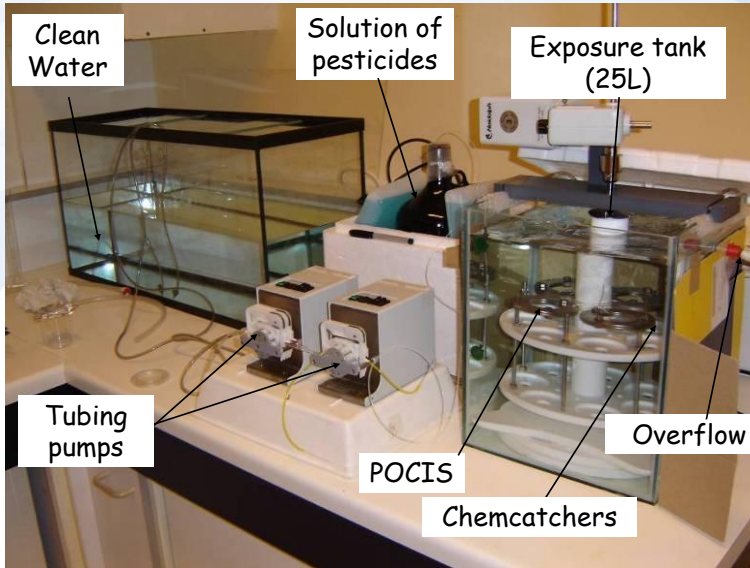
Geometry

flat disk

flat disk

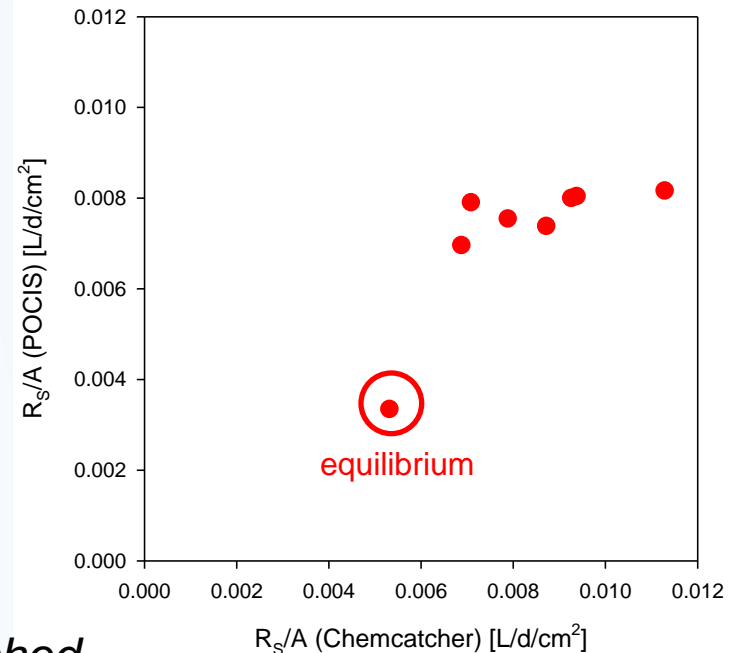
- samplers differed in surface area, type and mass of adsorbent material applied
- the same type of membrane and similar sampler geometry - similar mass transfer was expected

# Comparison of samplers: triazine pesticides



$$M_s(t) = C_w R_s t$$

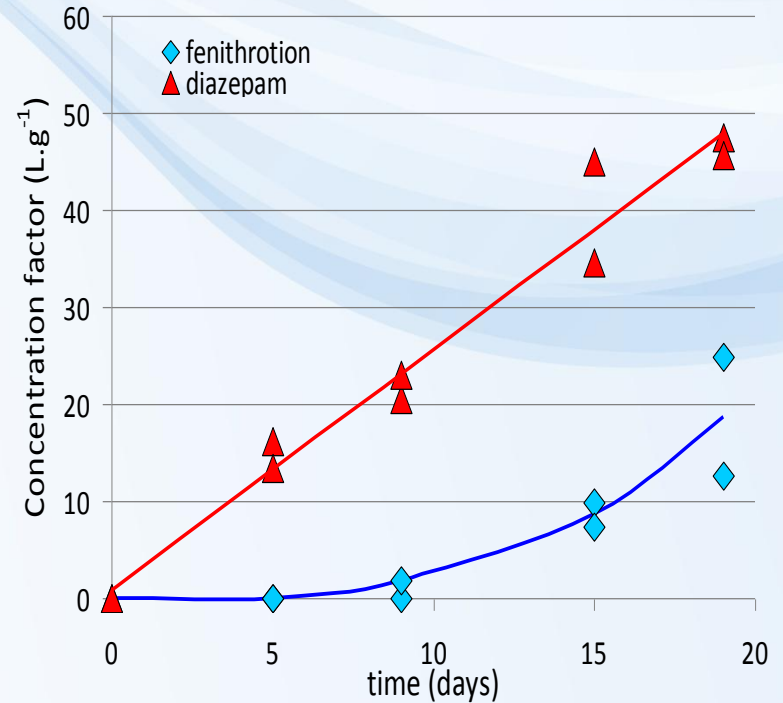
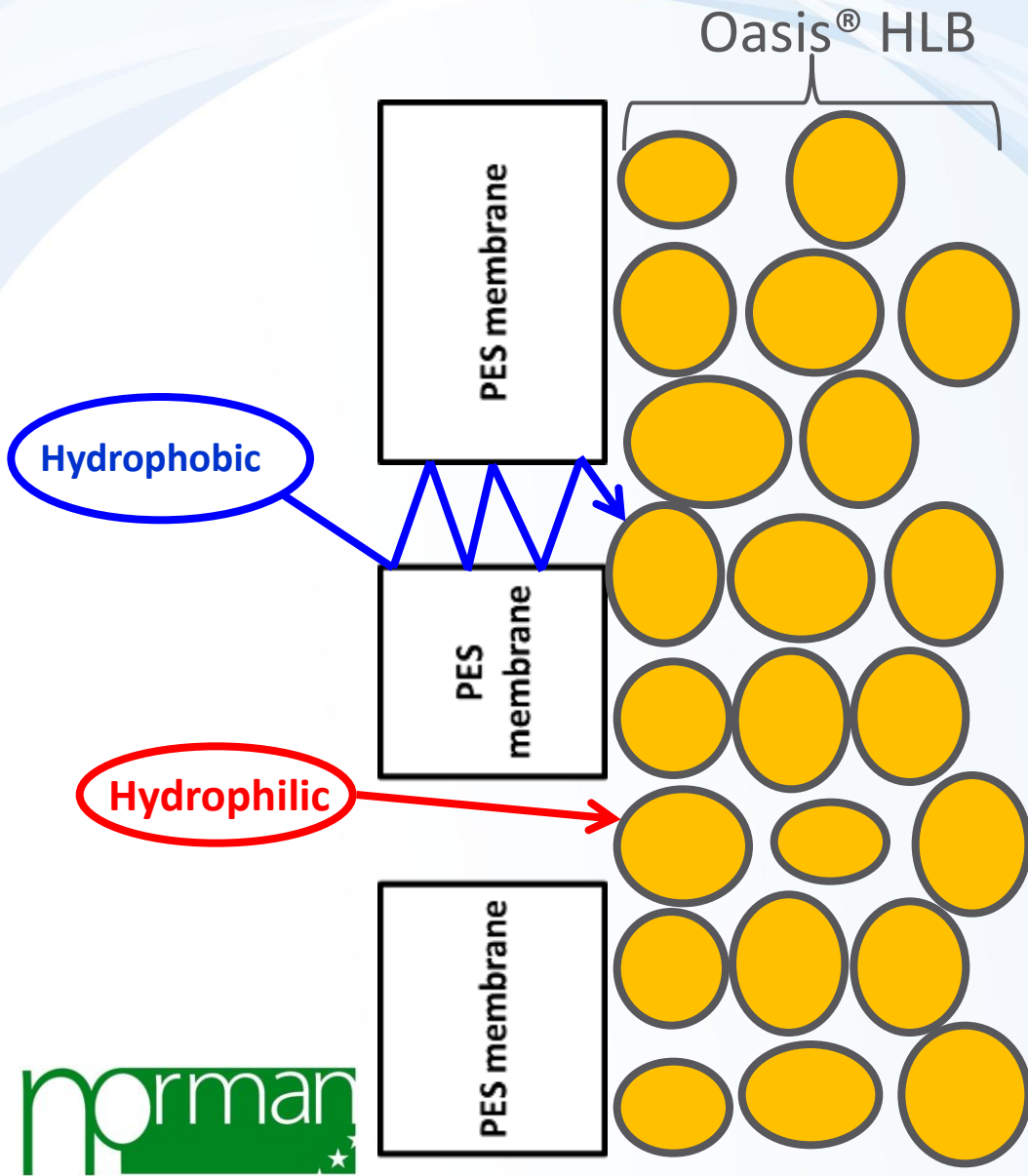
|                | $R_s$<br>Chemcatcher<br>$L \cdot d^{-1}$ | $R_s$<br>POCIS<br>$L \cdot d^{-1}$ |
|----------------|--|------------------------------------|
| Simazine       | 0.12                                     | 0.31                               |
| Atrazine       | 0.15                                     | 0.33                               |
| Cyromazine     | -  | 0.00                               |
| Propazine      | 0.16                                     | 0.36                               |
| Terbuthylazine | 0.19                                     | 0.37                               |
| Promethryn     | 0.16                                     | 0.36                               |
| Terbuthryn     | 0.13                                     | 0.34                               |
| Cyanazine      | 0.09                                     | 0.15                               |
| Irgarol        | 0.12                                     | 0.36                               |



## Comparison of samplers

- for most compounds uptake capacity was high and confirmed by integrative uptake over the 2 weeks of exposure
- thus mass of analyte found on sampler depended solely on the **sampling rate** and not on the sampler uptake capacity
- similar mass transfer coefficient [ $L/d/cm^2$ ] in two different samplers was observed
- **selection adsorbent material matters only close to equilibrium**

# Diffusion through the membrane

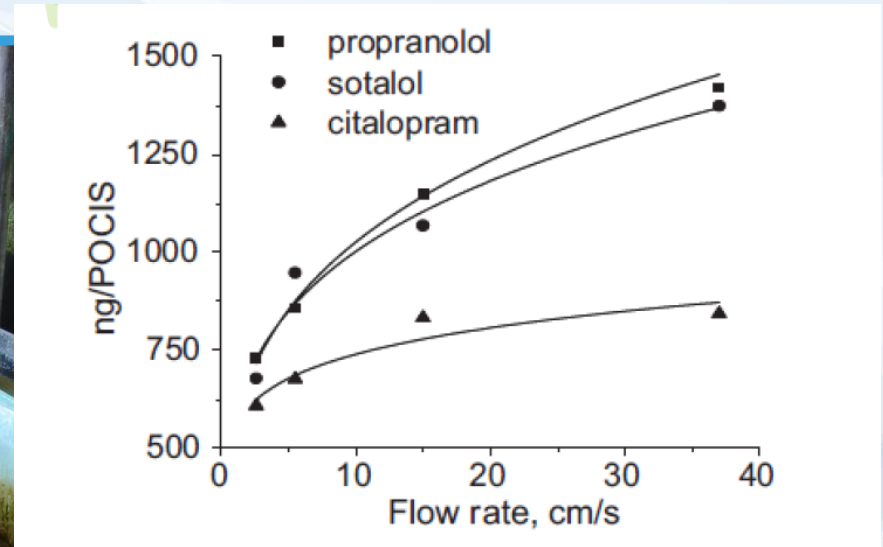
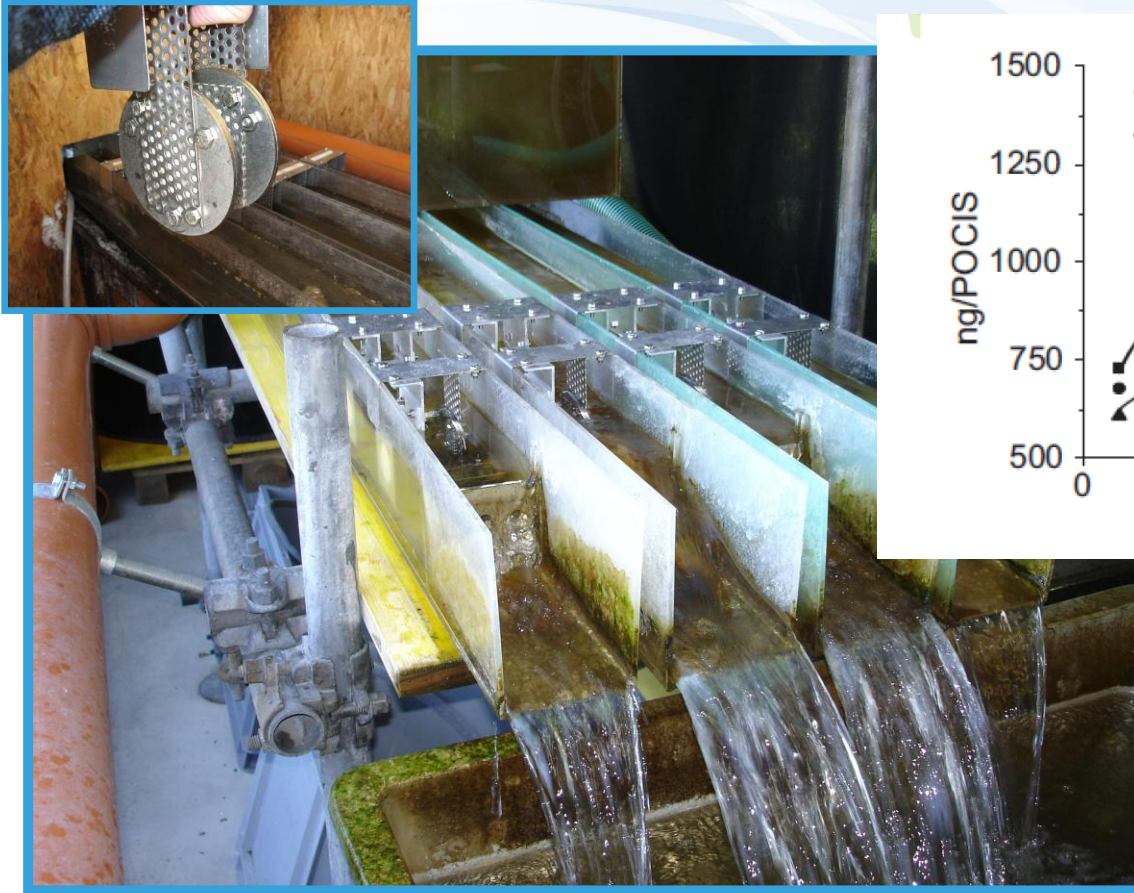


Fenithroton log Kow = 3.3

Diazepam log Kow = 2.9



# Effect of flow velocity on uptake

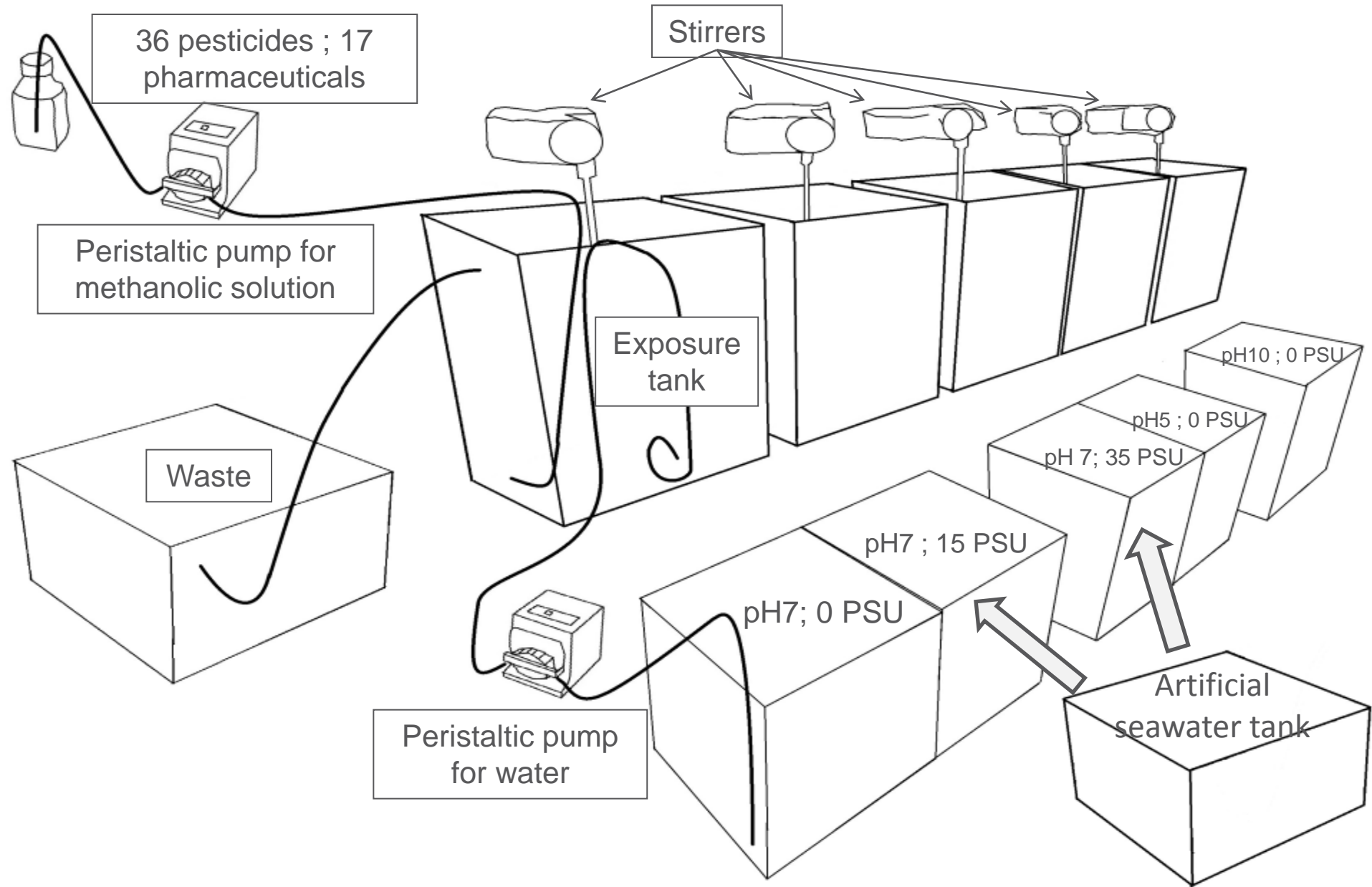


Li, H., Vermeirssen, E. L., Helm, P. A., & Metcalfe, C. D. (2010). Controlled field evaluation of water flow rate effects on sampling polar organic compounds using polar organic chemical integrative samplers. *ET&C* 29, 2461-2469



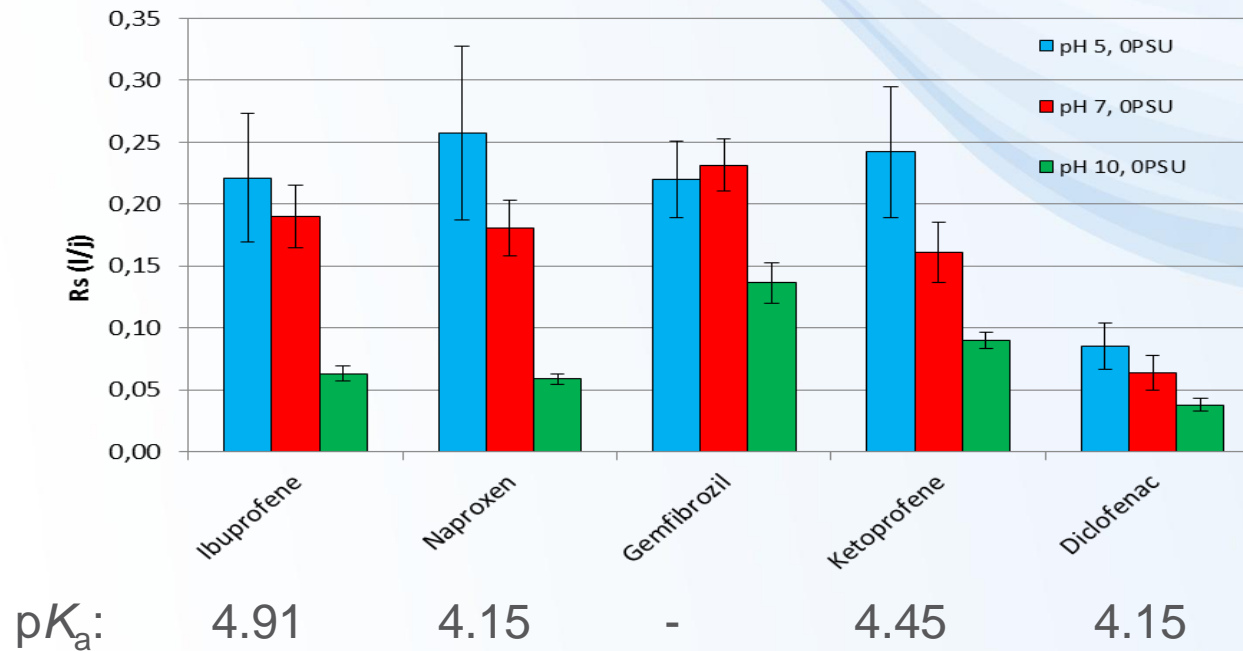
# Effect of pH and salinity on POCIS performance

Sampler calibration in a flow-through system:



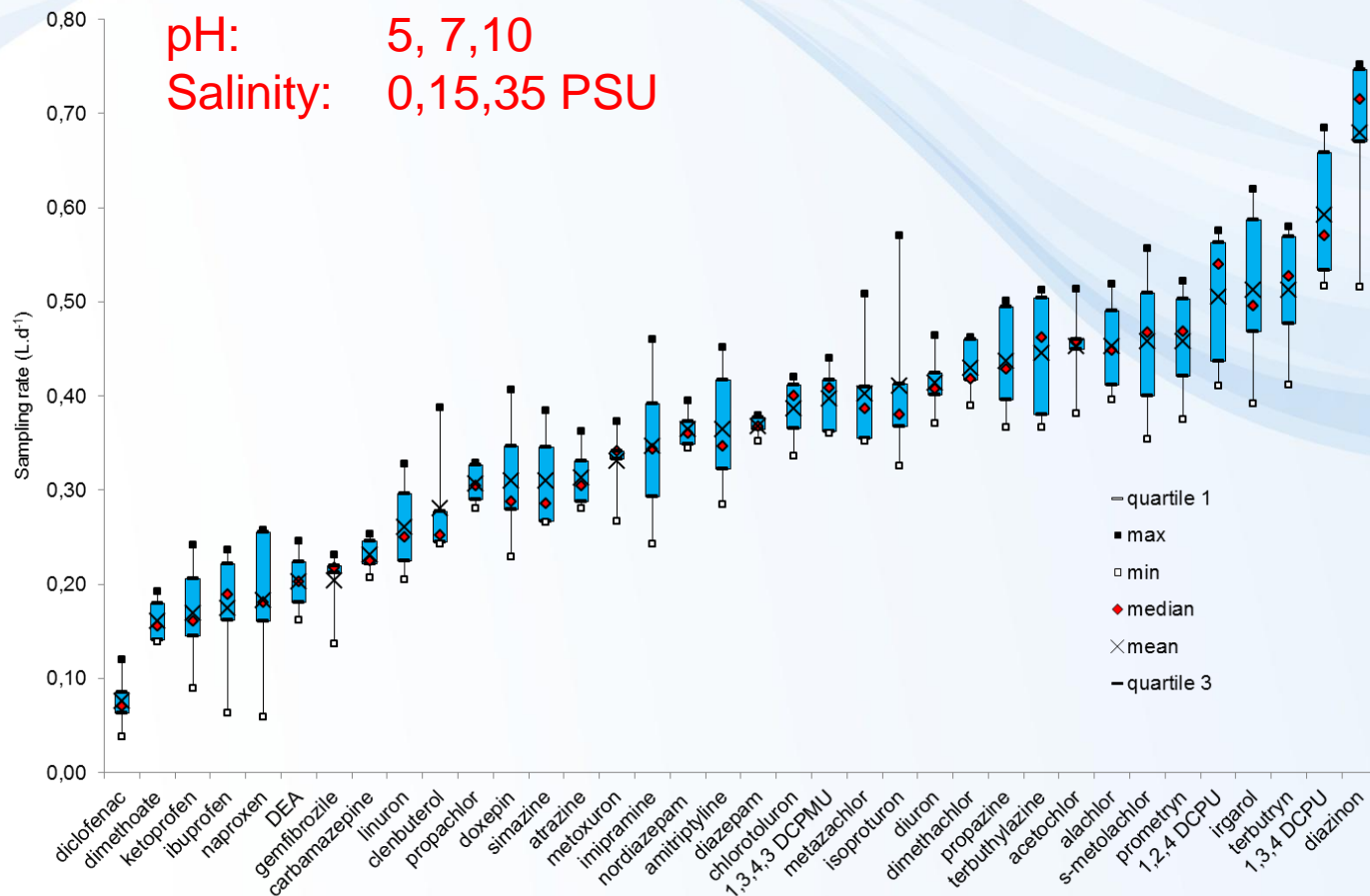
# Effect of pH on analyte uptake

Example: Dissociating acidic compounds



$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

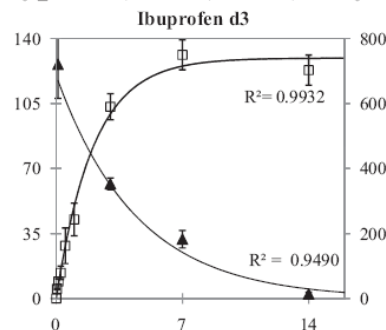
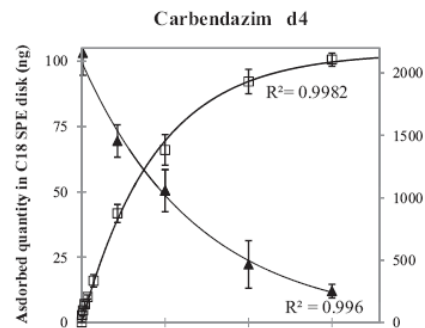
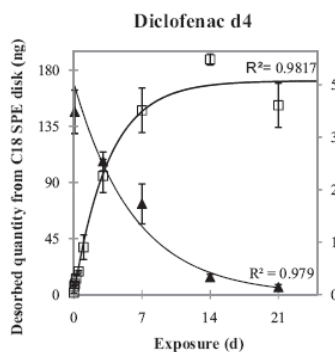
# Sampling rates



*Belles et al., in preparation*

# Does the PRC approach work?

- strong bonding means that the sampler effectively releases no substances to the water phase
- sorption may be non-linear
- significant dissipation observed only for highly polar compounds ( $\log K_{ow} < 1$ )
- PRC approach works for certain compounds and exposure scenarios, these may not necessarily be applied to all compounds and all exposures.
- in practice, sampling rates are used that were measured in the laboratory



Determination of the uptake and release rates of multifamilies of endocrine disruptor compounds on the polar C18 Chemcatcher. Three potential performance reference compounds to monitor polar pollutants in surface water by integrative sampling

[Camilleri, J.; Morin, N.; Miege, C.; Coquery, M.; Cren-Olive, C.](#)

*Journal of Chromatography A*, Volume 1237, Issue (May 11, 2012), p. 37-45.  
ISSN: 0021-9673 DOI: 10.1016/j.chroma.2012.03.025  
Elsevier Science

Evaluation of the Use of Performance Reference Compounds in an Oasis-HLB Adsorbent Based Passive Sampler for Improving Water Concentration Estimates of Polar Herbicides in Freshwater

[Mazzella, Nicolas; Lissalde, Sophie; Moreira, Sylvia; Delmas, François; Mazellier, Patrick; Huckins, James N.](#)

*Environmental Science & Technology*, Volume 44, issue 5 (March 1, 2010), p. 1713-1719.  
ISSN: 0013-936X DOI: 10.1021/es902256m  
American Chemical Society

# NORMAN POSITION PAPER



## NORMAN

Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives  
Position Paper

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This document has been written as a follow-up to the expert group meeting organised by the NORMAN association on 27<sup>th</sup> May 2009 in Prague. It reflects the position of the NORMAN association experts and invited speakers on the topic of passive sampling and its application in the monitoring of emerging pollutants in aquatic environment.

**Table 1. List of most discussed emerging pollutants in the aquatic environment and the established or expected/potential performance of passive samplers of these compounds.**

| Category / class      | Sub-class  | Individual substances                 | Potential of non-polar samplers <sup>a</sup> | Potential of polar samplers <sup>b</sup> | Stage of development <sup>c</sup> | Sampler calibration data <sup>d</sup> |         |
|-----------------------|--|---------------------------------------|--|--|-----------------------------------|---------------------------------------|---------|
| Natural products      | Cyanotoxins                                      | Microcystins                          | -  | +  | <b>d</b>                          | [125]                                 |         |
| Antioxidants          | Antioxidants                                     | 2,6-Di-tert-butylphenol               | -  | +  |                                   |                                       |         |
|                       |  | 4-tert-Butylphenol                    | -  | +  |                                   |                                       |         |
|                       |  | BHA                                   | -  | +  |                                   |                                       |         |
|                       |  | BHQ                                   | -  | +  |                                   |                                       |         |
|                       |  | BHT                                   | -  | +  |                                   |                                       |         |
| Antifouling compounds | Antifouling compounds                            | Irgarol                               | -  | +  | <b>d</b>                          | [9,99]                                |         |
|                       |  |                                       |  |  |                                   |                                       |         |
|                       | Organotin compounds                              | Organotin compounds                   | Dibutyltin ion                               | -  | +                                 | <b>d</b>                              | [38,39] |
|                       |  |                                       | Monobutyltin ion                             | -  | +                                 | <b>d</b>                              | [38,39] |
|                       |  |                                       | Tetrabutyltin ion                            | -  | +                                 | <b>d</b>                              | [38,39] |
|                       |  |                                       | Diphenyltin ion                              | -  | +                                 | <b>d</b>                              | [38,39] |
|                       |  |                                       | Triphenyltin ion                             | -  | +                                 | <b>d</b>                              | [38,39] |
| Detergents            | Ethoxylates/ carboxylates of octyl/nonyl phenols | 4-Nonylphenol di-ethoxylate (NPE2O)   | -  | +  | <b>d</b>                          | [25,126,127]                          |         |
|                       |  | 4-Nonylphenol mono-ethoxylate (NPE1O) | -  | +  | <b>d</b>                          | [25,126,127]                          |         |
|                       |  | 4-Nonylphenoxy acetic acid (NPE1C)    |  |  |                                   |                                       |         |

# Conclusions

- A lot of calibration data is available in the literature
- Most of the work has concentrated on making measurements rather than trying to understand the mechanisms involved
- Little is known about the link between the sampling rate, uptake capacity and compound properties
- More research is needed into in-situ calibration and conversion to concentrations in the water phase
- Although environmental variables affect uptake into samplers, sampling rates are not dramatically affected by environmental variables (flow, salinity, pH) over the range of conditions typically found in the environment
- Time integrative sampling offers great advantage that balances the uncertainty of adsorption samplers – discontinuous spot samples can give even more uncertain result





**Thank you for your attention!**



## Adsorption samplers

### Polar Organic Chemical Integrative Sampler (POCIS)

Adsorbent + PES membrane



### Chemcatcher

Empore disk +/- PES membrane

