Interest of integrative samplers for the measurement of micro-pollutants in complex matrixes

Validity of DGTs, SPMDs and POCIS in urban waters

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The AMPERES project

AMPERES : Analysis of prioritary and emerging micro-polluants in wastewater and freshwaters

Main objective : Evaluate the efficiency of wastewater treatment processes for priority and emerging substances removal

Coordination : Marina Coquery, Cemagref

Partners :

- ✓ CIRSEE (Suez-Environnement)
- ✓ Cemagref (Lyon, Antony)
- ✓ LPTC-ISM, Bordeaux-1 University
- ✓ Rhône - Méditerranée - Corse Water Agency
- ✓ Cereve (LEESU)
- ✓ UT2A

- Support : ANR PRECODD (2006-2009) + AXELERA (Rhodanos)

The AMPERES project : objectives

- Measure the micropollutant concentrations and fluxes in domestic wastewater treatment plants outputs (water and sludge)
  - Analytical developments
    - **Interest of integrative passive samplers in waters with high contamination variations**
- Evaluate the efficiency of conventional treatment processes for priority and emerging contaminants removal (water, sludge)
- Evaluate the efficiency of innovative processes.
- Assess the impact of micropollutants discharges on water uses: aquatic receiving ecosystems; water reuse; drinking water production

Passive sampler principles

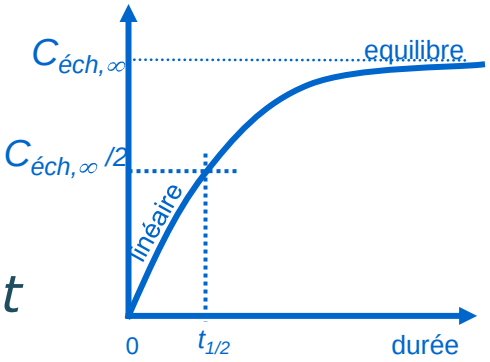
Immerged during a long period of time

- Few hours, few days, few months

Diffusion of a substance towards a membrane

- Accumulation in a receiving phase
  - Preconcentration for some devices
- Partitioning of substances between the accumulation phase of the sampler and the medium

$$\frac{dC_{éch.}}{dt} = \frac{R_S}{V_{éch.}} C_{eau} - k_e C_{éch.}$$



Some specific cases :

Sampling rate

- The accumulator is "linear" $M_{éch} = C_{éch} V_{éch} = R_S C_{eau} t$

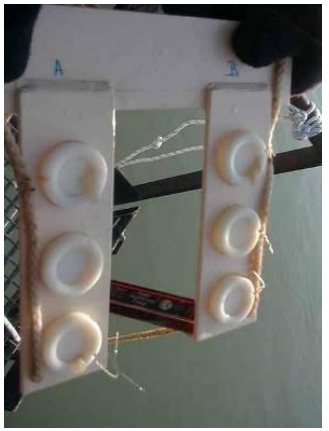
- The exposure is constant with time $M_{éch} = \frac{R_S}{k_e} C_{eau} (1 - e^{-k_e t})$ $t_{1/2} = \ln 2 / k_e$.

To evaluate a time-weighted average concentration in water from accumulated amounts, one needs R_s (and k_e) for each subtance

- Experimental data
  - *Not available for all substances*
- Influence of exposure conditions for some samplers
  - *Use of Performance Reference Compounds to control in situ exchanges*

Metals

DGT Chelex resin and a diffusion hydrogel (Davison and Wang, 1994)



In situ sampler

pre-concentration, sampling less prone to contamination

Measurement in the resin eluate, no matrix effect

Quantitative integrative sampler

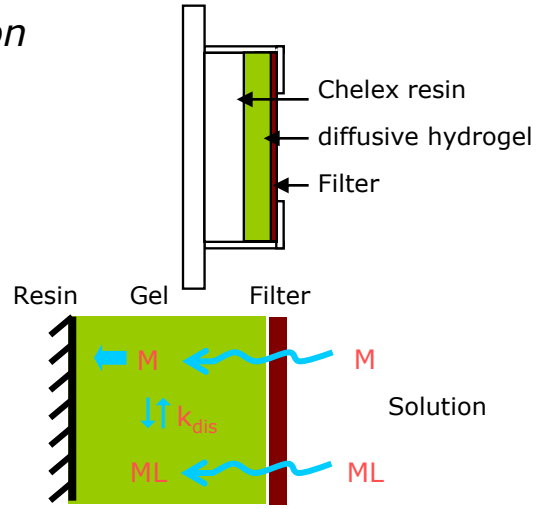
Integrative sampling (no metal removal from the resin)

Accumulation kinetic is controlled by the diffusion in the hydrogel

Calculation of a time-weight average concentration

$$C_{labile} = \frac{e}{AD}\frac{M_{resin}}{t}$$

M accumulated metal in the resin
e : gel thickness
A exposition surface
D Diffusion coefficient of the metal
t Exposition time

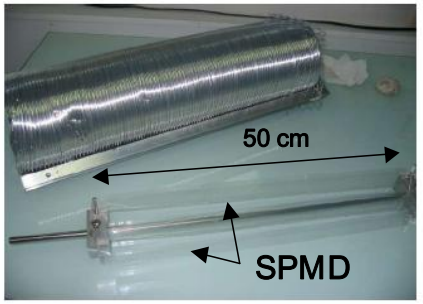


Selective sampling of labile metals

inorganic metal + small and weak complexes

Hydrophobic organic compounds

SPMD Semiperpeable membrane device: polyethylene tube filled with triolein (Huckins et al, 1993)



membranes

Polymeric membranes: polyethylene, silicone, polyamide… (Booij et al, 2002)

Passive diffusion of non polar hydrophobic compounds

Accumulation in the membrane and in the triolein

Membrane porosity ≈ 10 Å (1 000 Da)

Only truly dissolved compounds are available for sampling

Estimation of a time-weighted average concentration in water

$$\overline{C}_{labile} = \frac{C_{sampler}}{K_{sampler}\left(1 - e^{-k_e t}\right)}$$

$K_{sampler}$: sampler/water partitioning constant

➔ depends on the sampler and the substance

$k_e = R_S / (K_{sampler}, V_{sampler})$

k_e : exchange rate

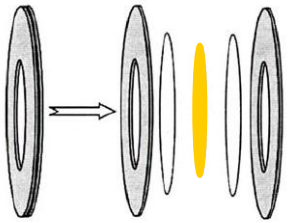
➔ depends on the sampler, the substance and the environment.

- Experimental data corrected with in situ use of PRC

Hydrophilic organic compounds

POCIS Polar Organic Compound Integrative Sampler (Alvarez et al, 2004)

HLB (Divinylbenzene – N-vinylpyrrolidone) phase sandwiched between two polyethersulfone membranes (0.1 µm) maintained by metallic disks



- Selective diffusion of dissolved substances according to their affinity with the receiving phase.
  - Sampling of hydrophilic substances
  - Screening (selection, pre-concentration)

Linear accumulation

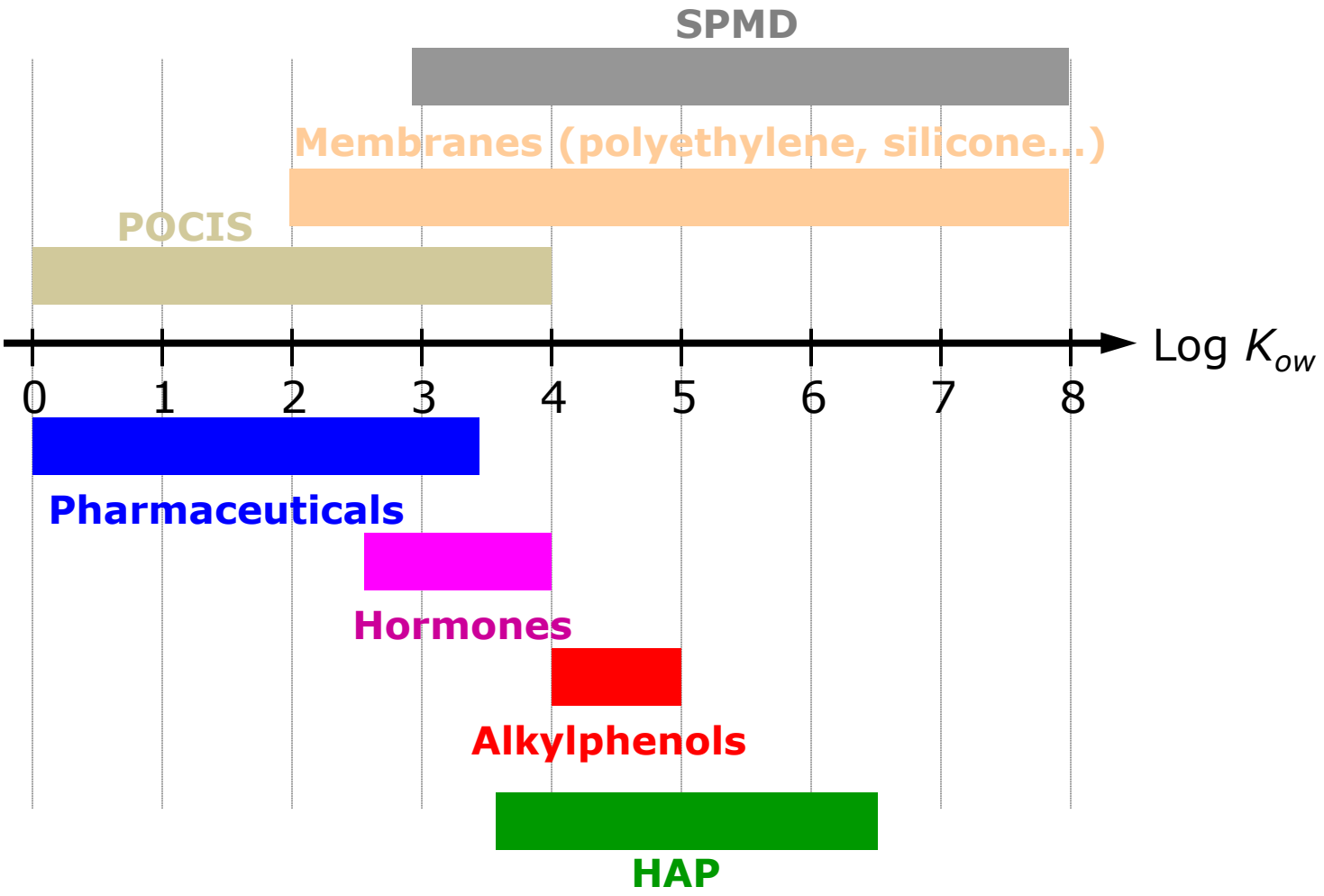
- Time-weighted averaging

$$C_{water} = \frac{C_{POCIS} . M_{POCIS}}{R_S . t}$$

The sampling rates R_S are evaluated in the laboratory and applied to POCIS exposed in situ

- *the R_S database is ongoing*
- *the quantification of a concentration in water is being validated*

Which samplers for which substances of the AMPERES project ?



Passive sampling issues in the AMPERES project

Applicability of passive sampling tools for the substances and the matrices of interest

- a wide variety of metallic and organic contaminants
- wastewaters, drinking waters, water ressources…

For metals and hydrophobic compounds

DGTs and SPMDs were already validated in aquatic media.

- validity of the measurement in highly loaded water ?
  - mechanical resistance of the samplers in wastewaters ?
  - Quantification? characterization of the labile fraction ?

Other substances (pharmaceuticals, alkyphenols…)

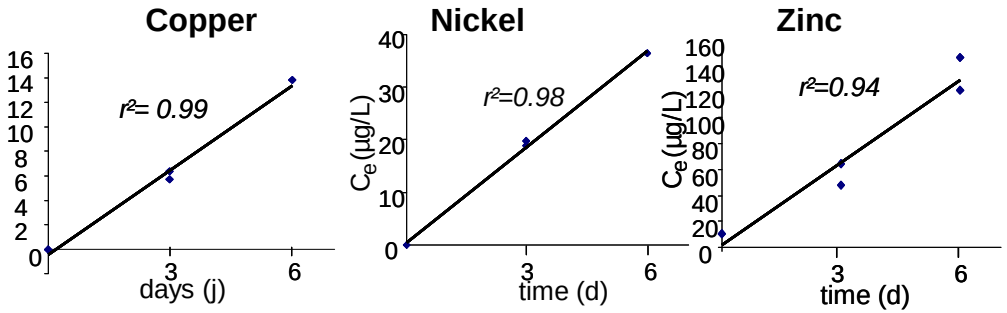
Little information on the sampling by integrative sampling devices

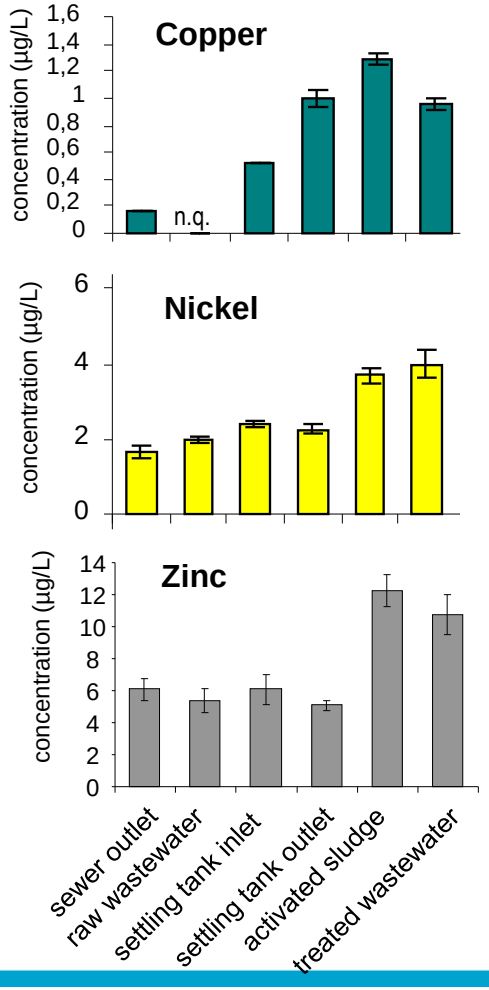
- efficiency of the samplers
  - matrix effects, concentrations factors, repeatability
  - accumulation linearity, sampling rates
- comparison of several devices for moderately hydrophobic compounds
- Applicability in situ

Metal sampling in wastewater using DGTs

sampling in the "SE2" plant at different stages of the treatment. DGTs were deployed for 6 days.

Metal concentration in resin eluate of DGTs deployed in an activated sludge reactor





- **The sampling is repeatable**
- **The accumulation in linear**

Gourlay-Francé et al, 2011, Wat. Sci. Technol.

Metal sampling in wastewater using DGTs

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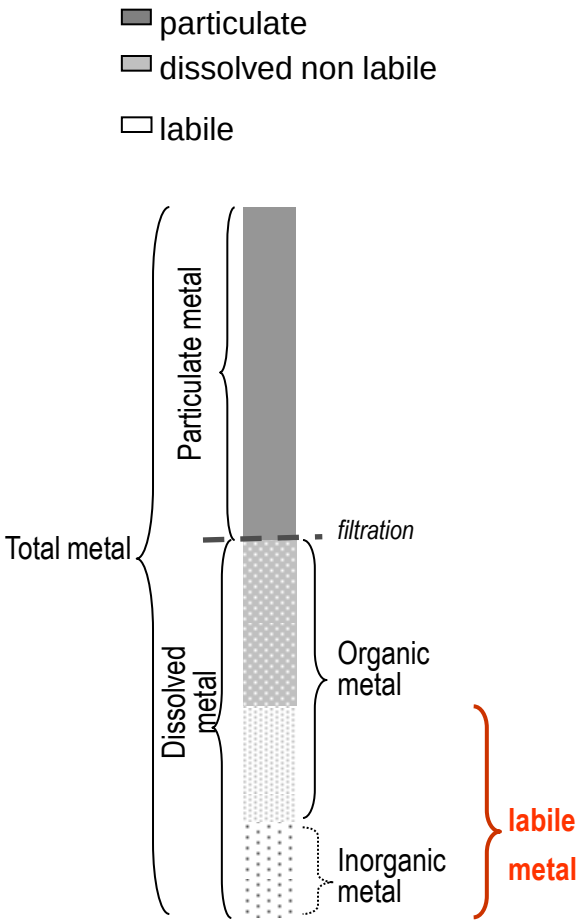
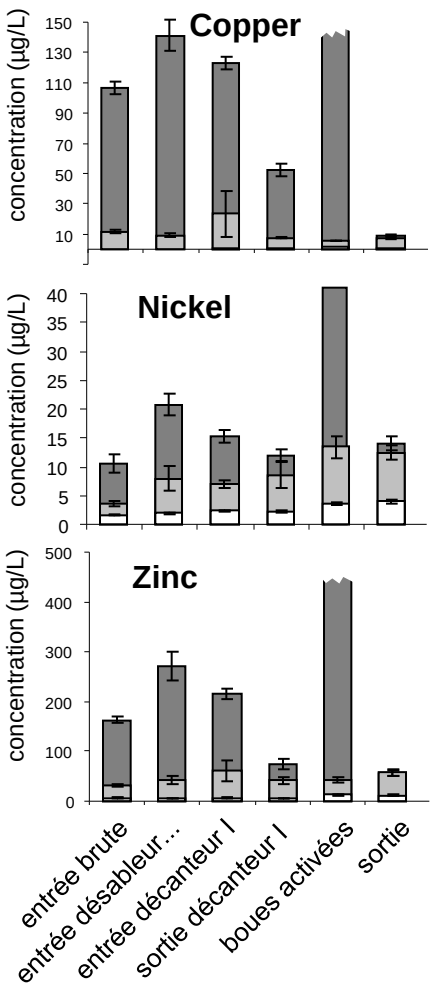
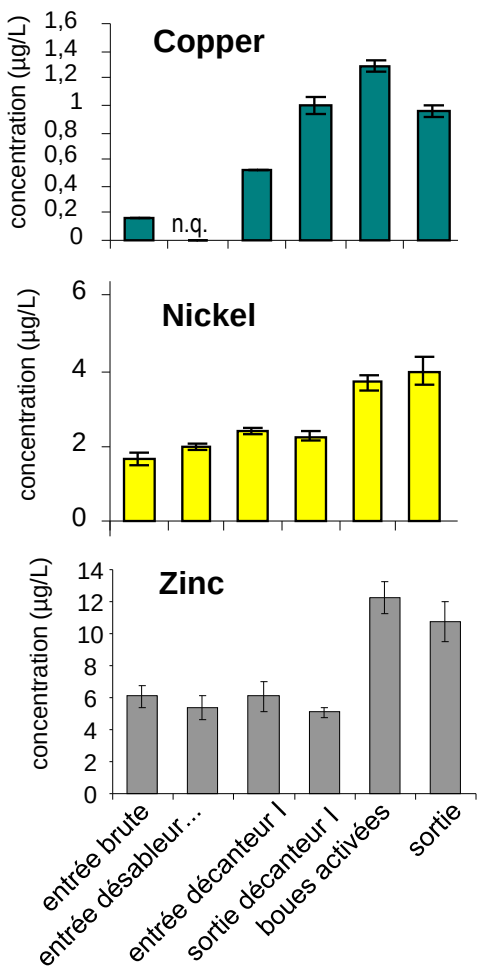
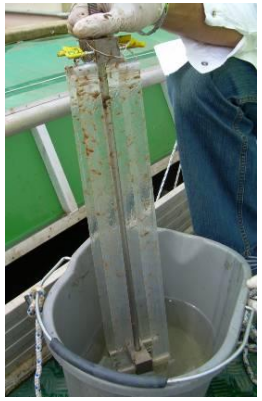


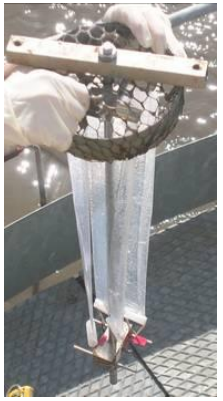


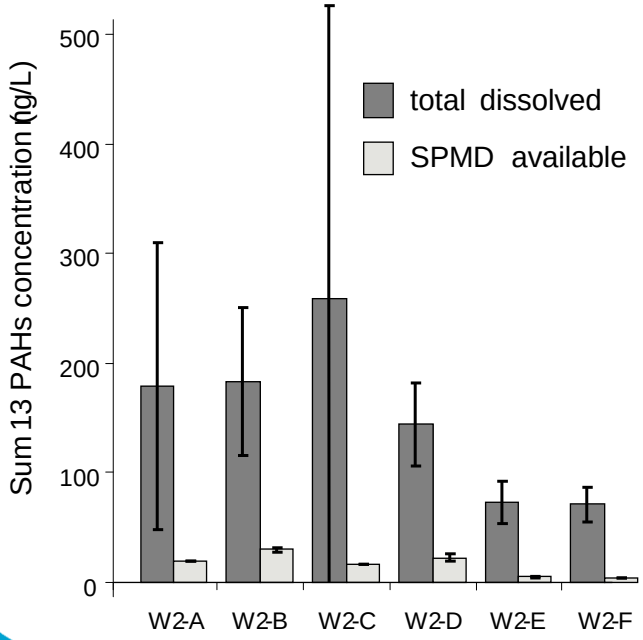


PAH sampling in wastewater using SPMDs

- "normal" functioning
  - good resistance to deployment
  - good consistency of PRC removal
  - Optimization of the SPMD extraction procedure
- Fast SPMD/water exchanges
  - high accumulation capacity







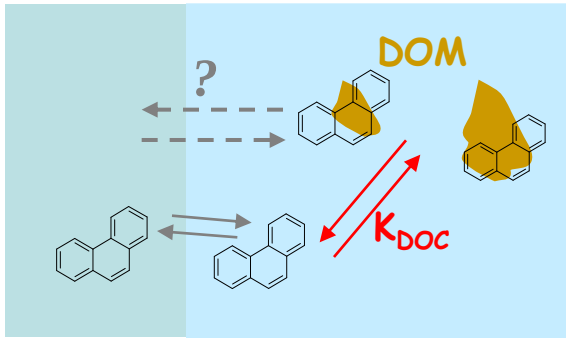
Quantification < ng/L with a good reproducibility

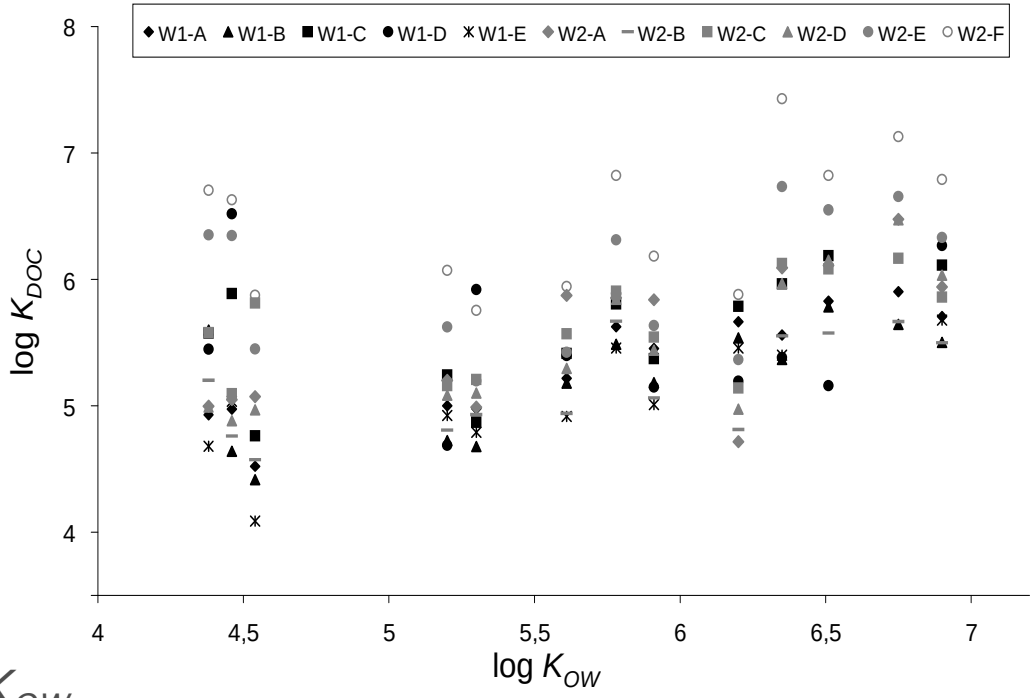
Labile PAH concentrations: 6 – 36 % of total dissolved PAHs

Gourlay-Francé et al, Chemosphere, 2008

PAH sampling in wastewater using SPMDs

$$K_{DOC} = \frac{C_{TD-W} - C_{SPMD-W}}{C_{SPMD-W}[DOC]}$$





- *In situ* K_{DOC} related with K_{OW}
  - Surprisingly high K_{DOC} for low K_{OW} compounds
- *In situ* K_{DOC} are close to experimental values
  - SPMD-available compounds are mostly truly dissolved

Gourlay-Francé et al, Chemosphere, 2008