Passive sampling: an innovative tool in the design of monitoring programmes

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Current monitoring practice

- Currently the method used for measuring chemical pollutants in water is spot (*bottle/grab*) sampling and laboratory analysis
- Has disadvantages:
  - Costly (manpower/transport)
  - Provides only a ‘snapshot’ of pollution at the instant of sampling
  - May not be representative where levels of pollutants fluctuate

- Alternative monitoring methods needed to overcome these problems

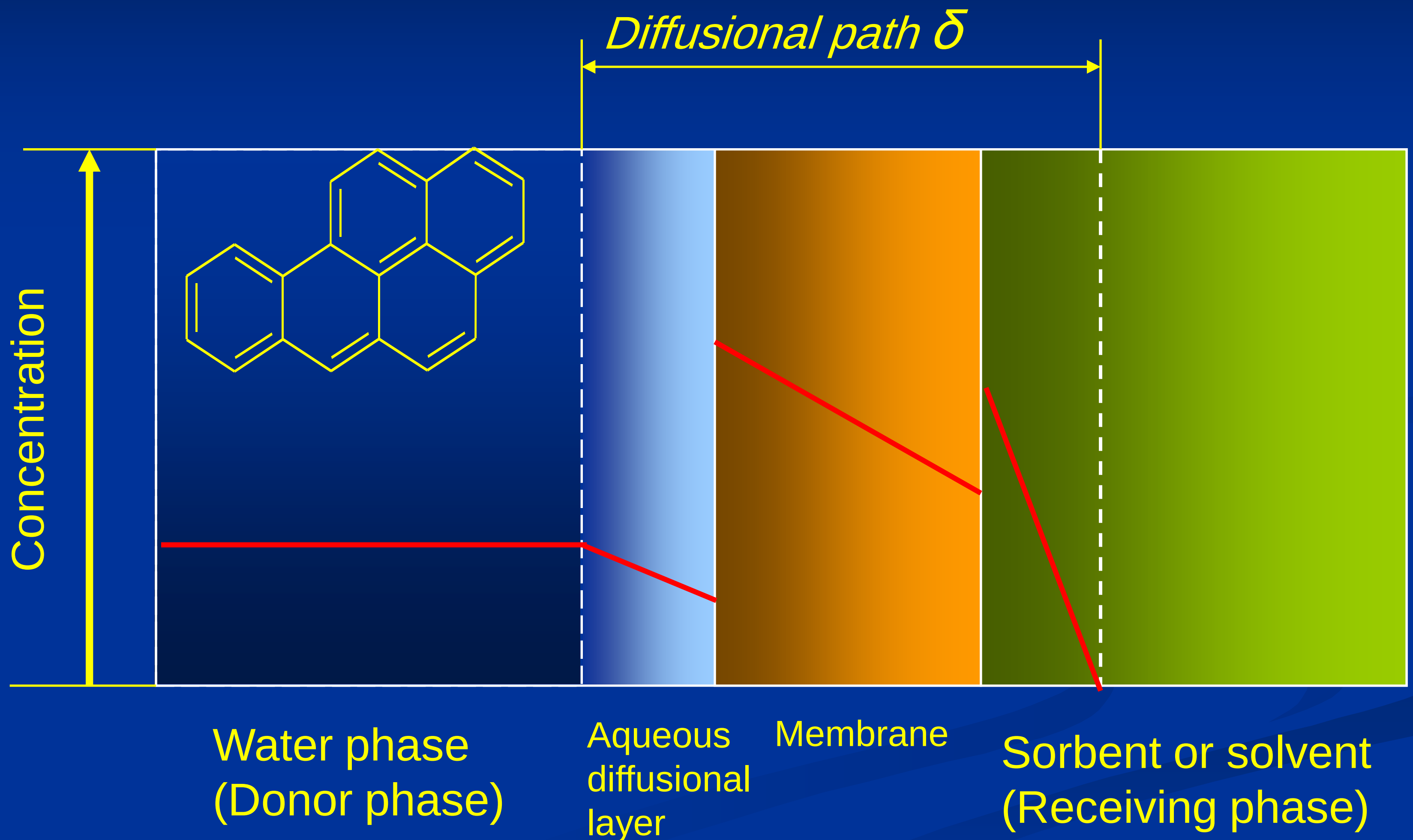
Representative methods for monitoring

- Frequent sampling
- Automatic sequential sampling to provide composite samples over a period of time (usually 24 hours)
- Continuous, on-line monitoring systems (e.g. the SAMOS system, some sensors, biological early warning systems)
- Biomonitoring (sentinel organisms)
- Passive samplers

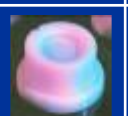
Passive samplers

- Used extensively in monitoring air quality for many years
- Provide time-weighted average (TWA) concentrations over the deployment time, rather than a snap shot at one moment
- Are non-mechanical; are easy to deploy and require no maintenance
- Can be deployed in a range of environments; at sites that have limited security; are remote with little/no infrastructure
- Are not dependent on a power or other energy supply
- Used for short (days) or long term (months) monitoring

Principle of a passive sampler



Available samplers

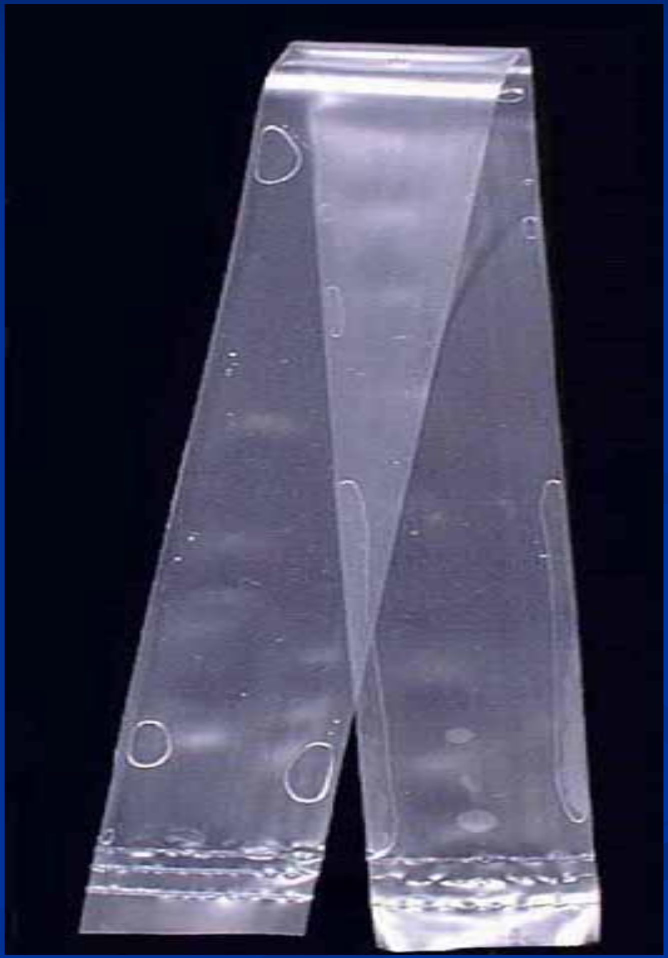
SAMPLER	CONSTRUCTION	ANALYTES
SPMD 	Semi-permeable membrane devices; flat tube of LDPE filled with triolein	Hydrophobic semivolatile organic compoundswith $K_{ow} > 3$
POCIS 	Solid sorbent material enclosed in a polyethersulphone membrane	Polar pesticides and Pharmaceuticals with log $K_{ow} < 3$
MESCO 	PDMS rod enclosed in a membrane made of regenerated cellulose or LDPE	Hydrophobic semivolatile organic compounds with log $K_{ow} > 3$
Ceramic Dosimeter 	Ceramic tube filled with a solid-phase sorbent material, closed with PTFE lids	Groundwater contaminants with a broad range of physico-chemical properties
DGT 	Two layers of acrylamide gel mounted in a holder device	Metals, phosphates, sulphides
Chemcatcher 	A housing made of inert plastic, containing a disk of solid sorbent and a disk of diffusion membrane.	Many taylor-made versions; polar and nonpolar organics, metals, organometallic compounds, mercury
TWA SPME 	A fibre coated with a liquid (polymer), a solid (sorbent), or a combination of both	Broad range of organic compounds

Application of passive samplers

- screening for the presence and absence of pollutants
- investigating temporal trends in levels of contaminants
- monitoring spatial contaminant distribution
- tracing point and diffusive pollution sources
- speciation of contaminants
- assessing pollutant fate and distribution between environmental compartments
- measuring TWA concentrations of pollutants
- biomimetic sampling to estimate organism exposure
- assessing toxicity of bioavailable pollutants in extracts from passive samplers

Semipermeable membrane device - SPMD

- Lipid-filled low density polyethylene sheet
- Integrative sampling up to one month
- Application range: semivolatile hydrophobic organic compounds

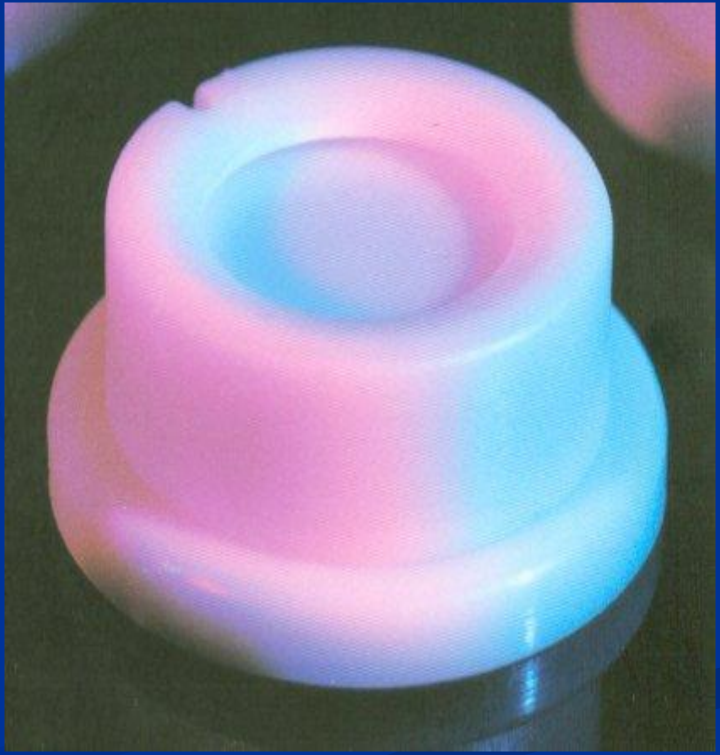


Polar Organic Chemical Integrative Sampler (POCIS)

- Sorbent receiving phase
- Polyethersulphone membrane
- Integrative sampling up to several weeks
- Application range: polar organic compounds

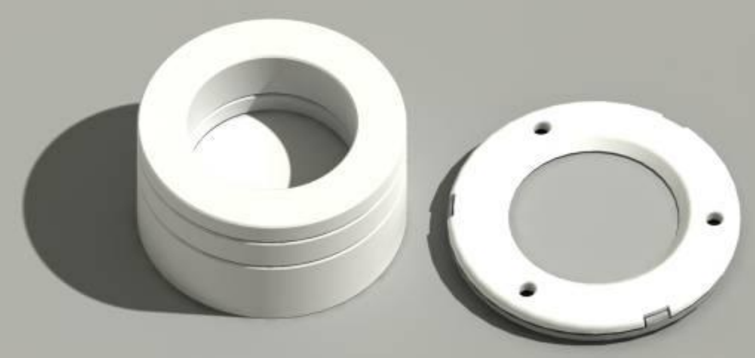
Diffusive gradients in thin films (DGT)

- A layer of binding agent impregnated in hydrogel to accumulate the solutes (a resin)
- A diffusive layer of hydrogel and a filter
- Application: metals, phosphate, sulphide, radionuclides
- If diffusion coefficients are known, no need for calibration



CHEMCATCHER

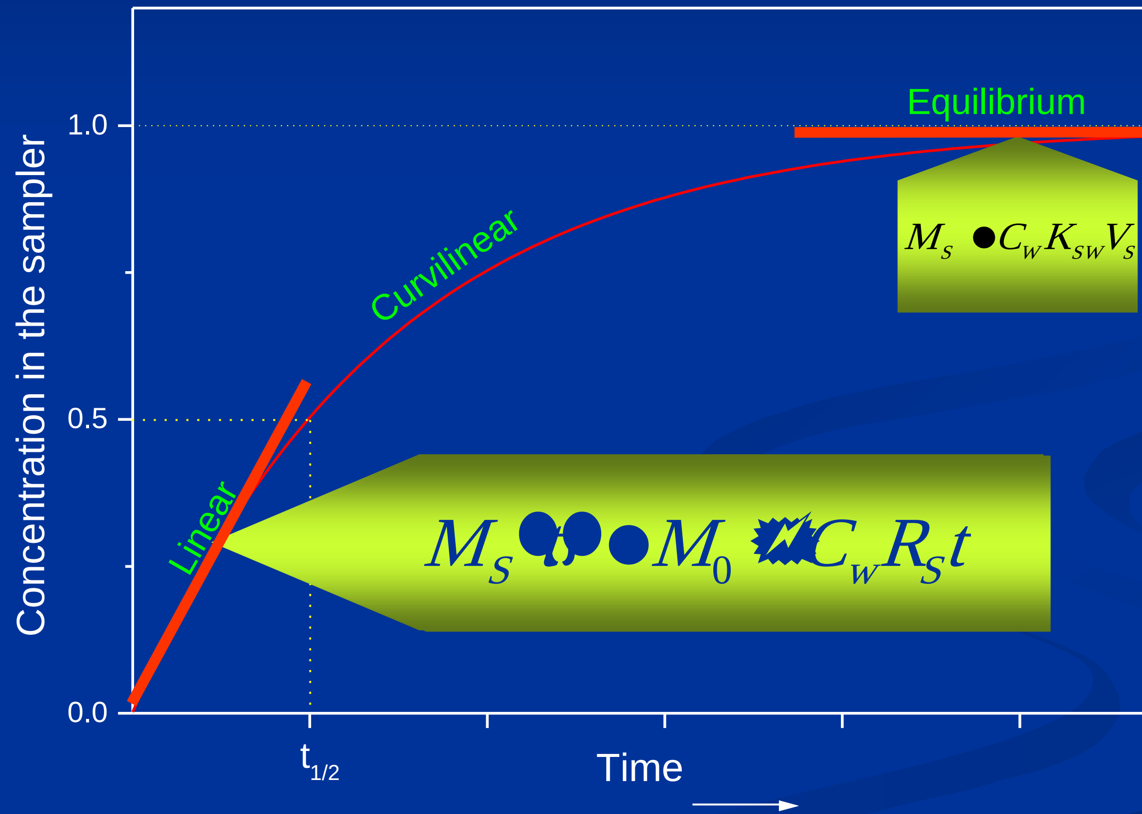
- The sampler consists of
  - Sampler body
  - Sorbent disk
  - Diffusion membrane
- Many particular sampler configurations
  - Non-polar organic
  - Polar organic
  - Metal
  - Organometallic
  - Mercury
- Two prototypes
  - 1st generation – reusable
  - 2nd genration – disposable



1st generation design

2nd generation design

Integrative sampling



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

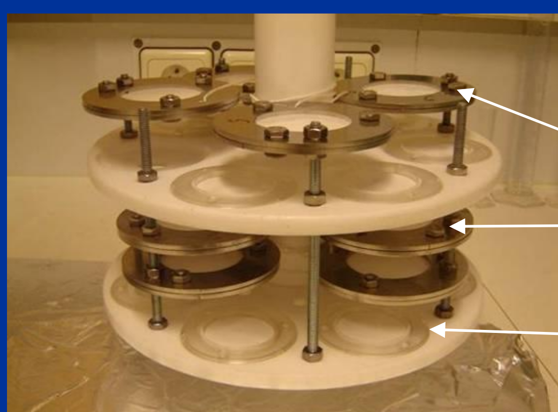
C_W = constant **R_S = substance specific sampling rate [L d^{-1}]**

Measurement of TWA concentration

$$C_w = \frac{M_S}{R_S t}$$

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

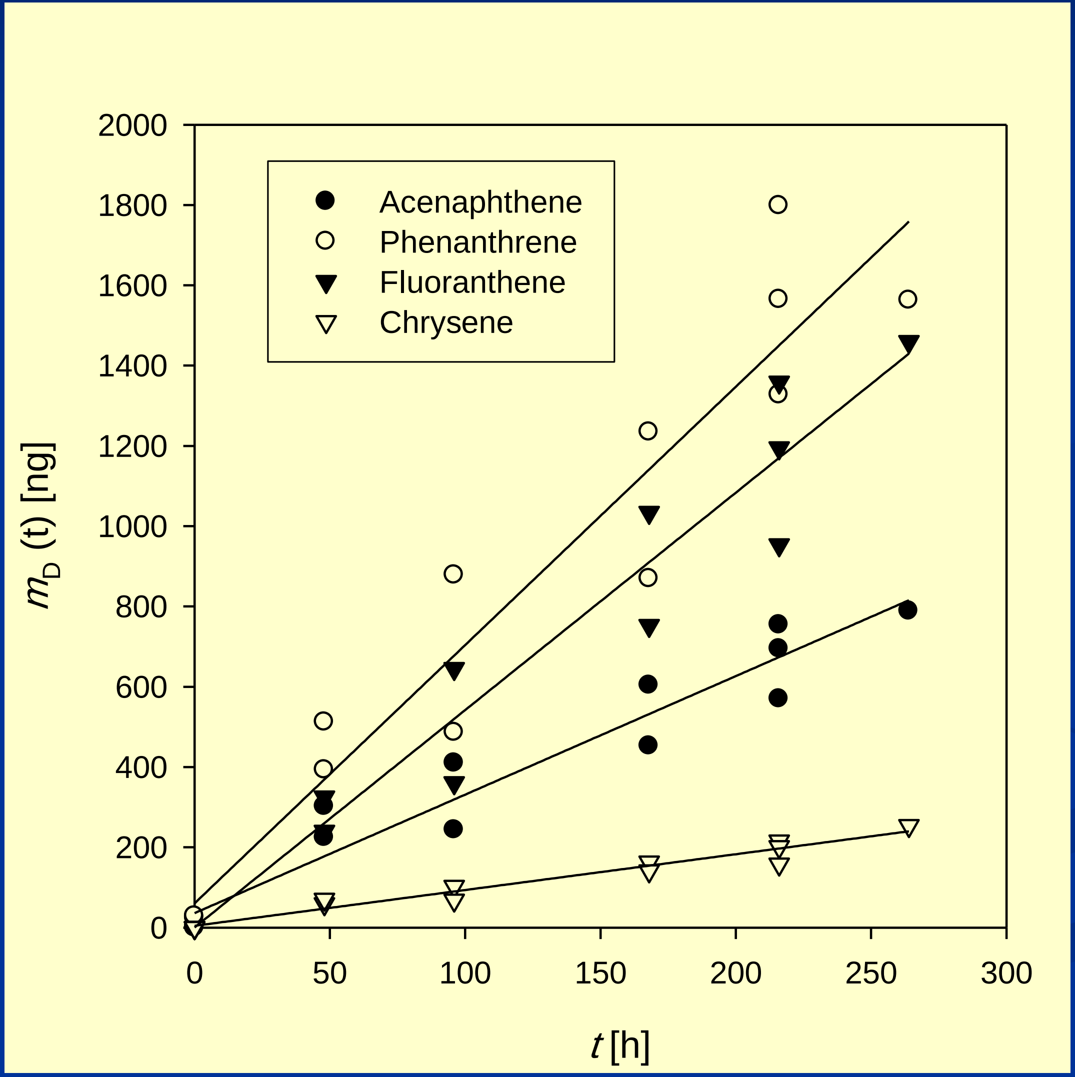
Calibration of samplers in a flow-through system



POCIS

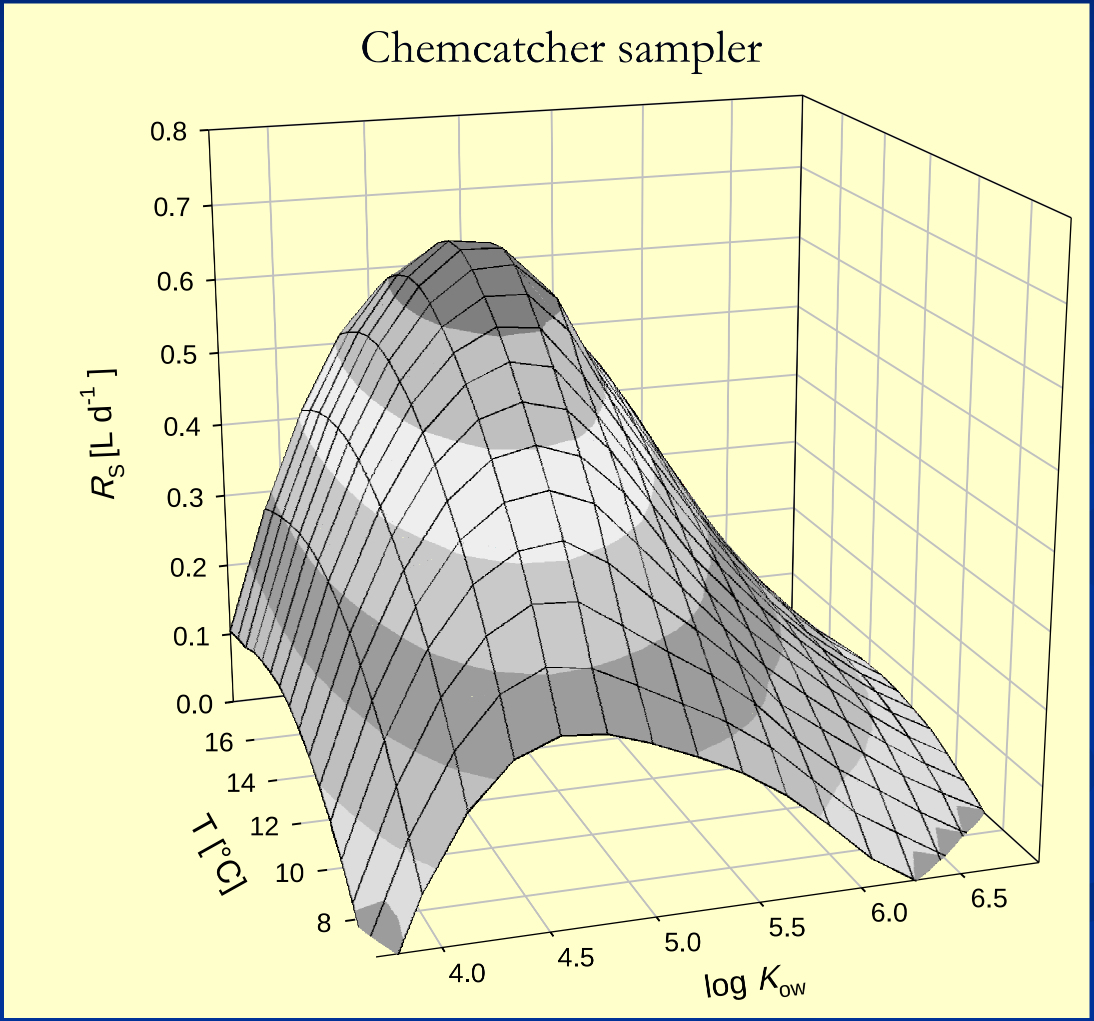
Chemcatcher

Uptake kinetics
Nonpolar CHEMCATCHER



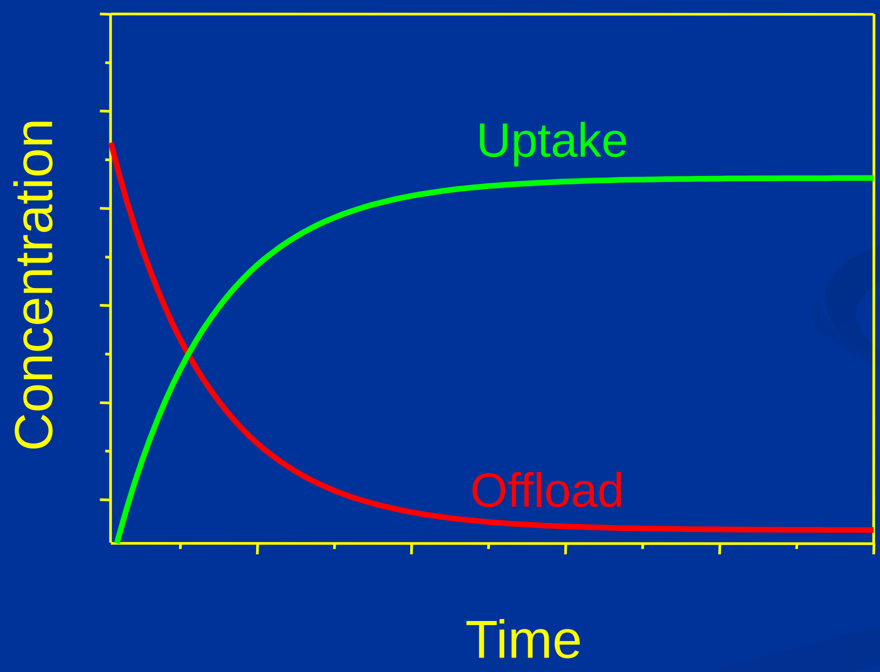
C_w = 100 ng L^{-1}
T = 11°C
Rotation speed 40 rpm

Effect of temperature and hydrophobicity on sampling rate



Correlation between uptake and offload – PRC concept

Both uptake and offload are governed by the same mass transfer law – isotropic exchange kinetics.

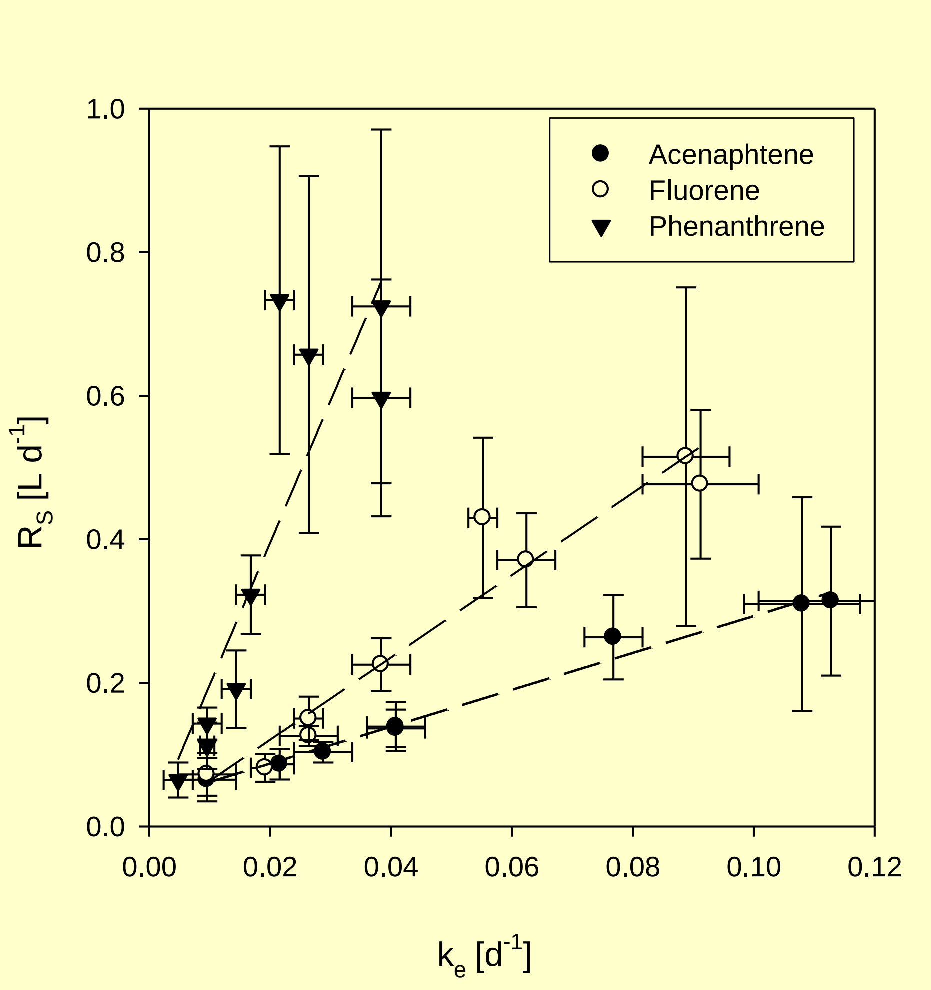


$M_S(0) = 0$ C_w= const.

$M_S(0) \neq 0$ $C_w = 0$

In situ calibration using isotropic exchange kinetics: uptake vs. offload

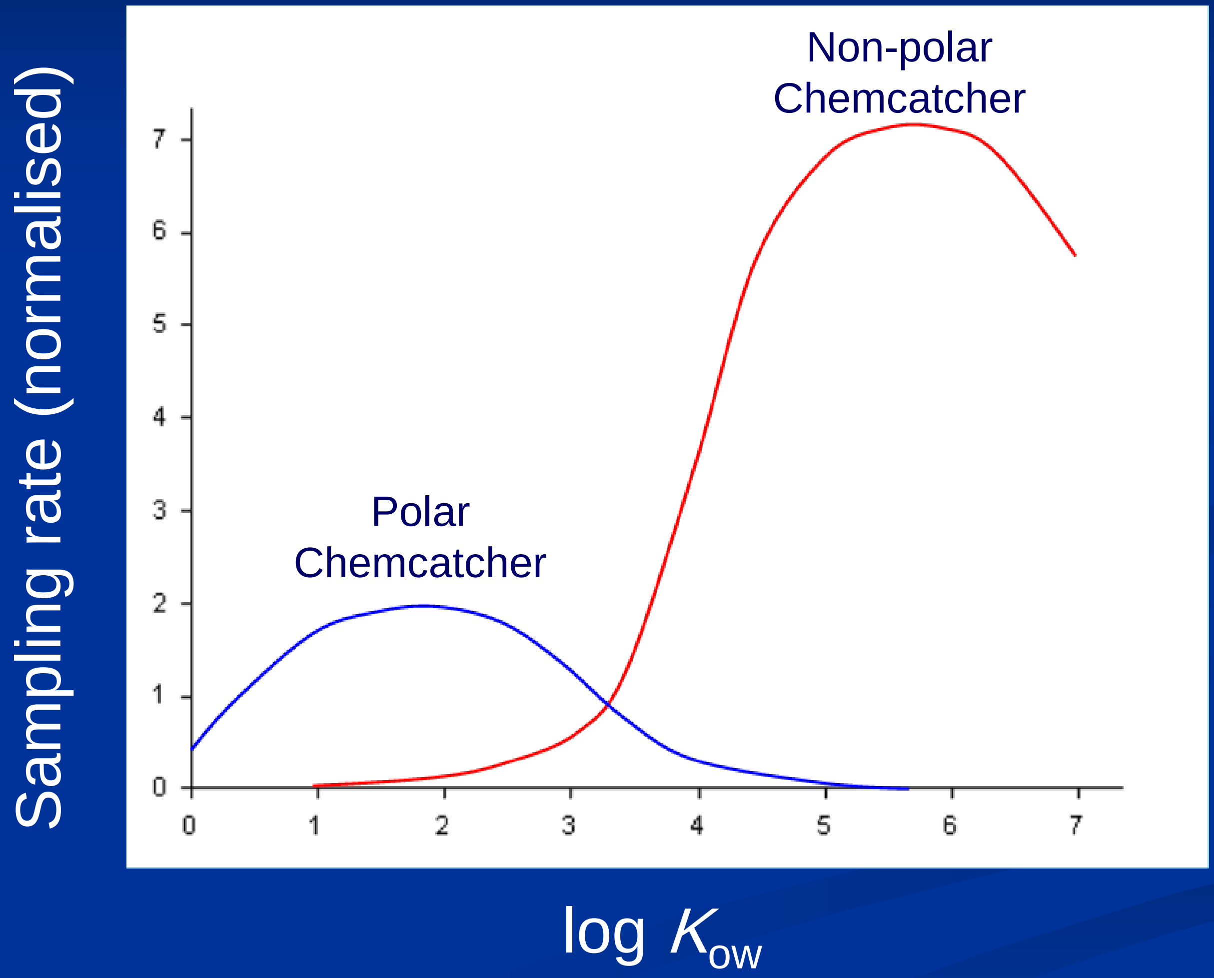
Analyte uptake rate



PRC offload rate

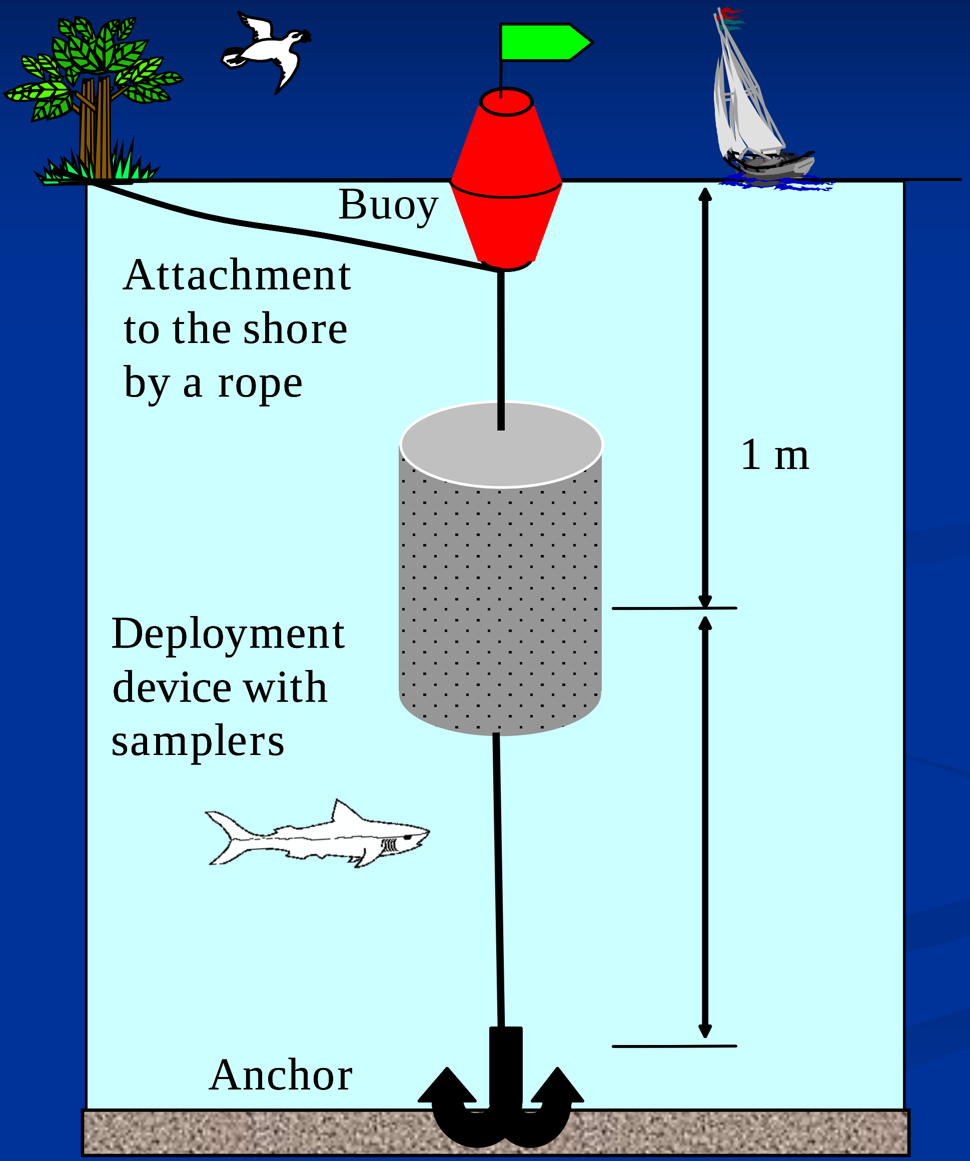
Temperature: 4 – 18°C
Turbulence: 0 – 70 rpm

Sampler selectivity



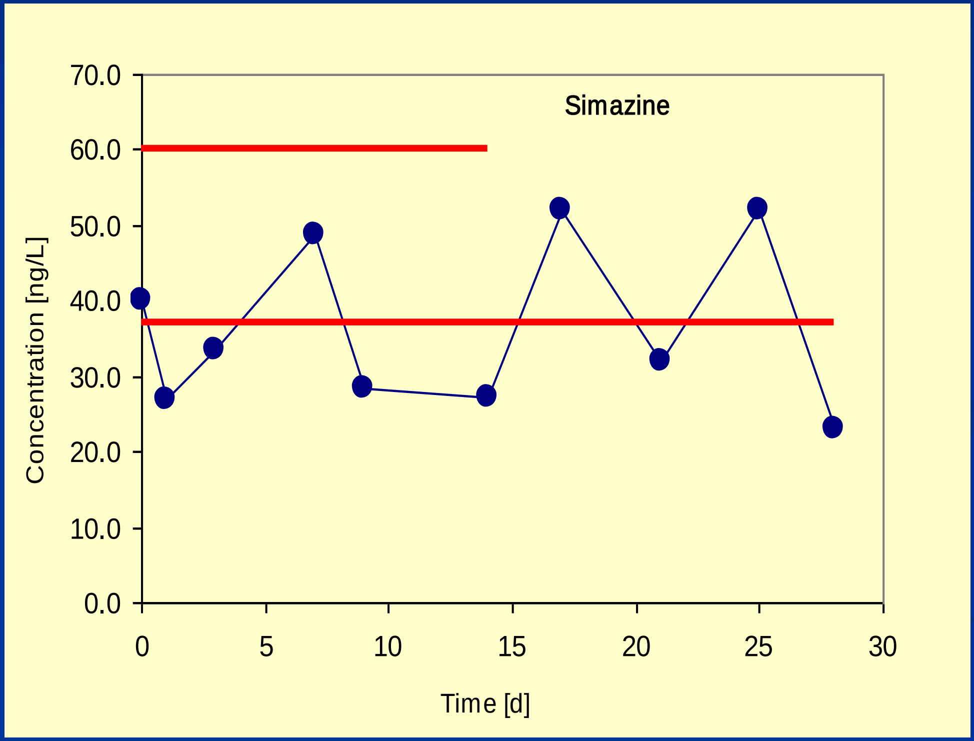
Sampler deployment

Sampler deployment



Biofouling and deposition of suspended material

Comparison of passive sampler and spot sample data Polar CHEMCATCHER



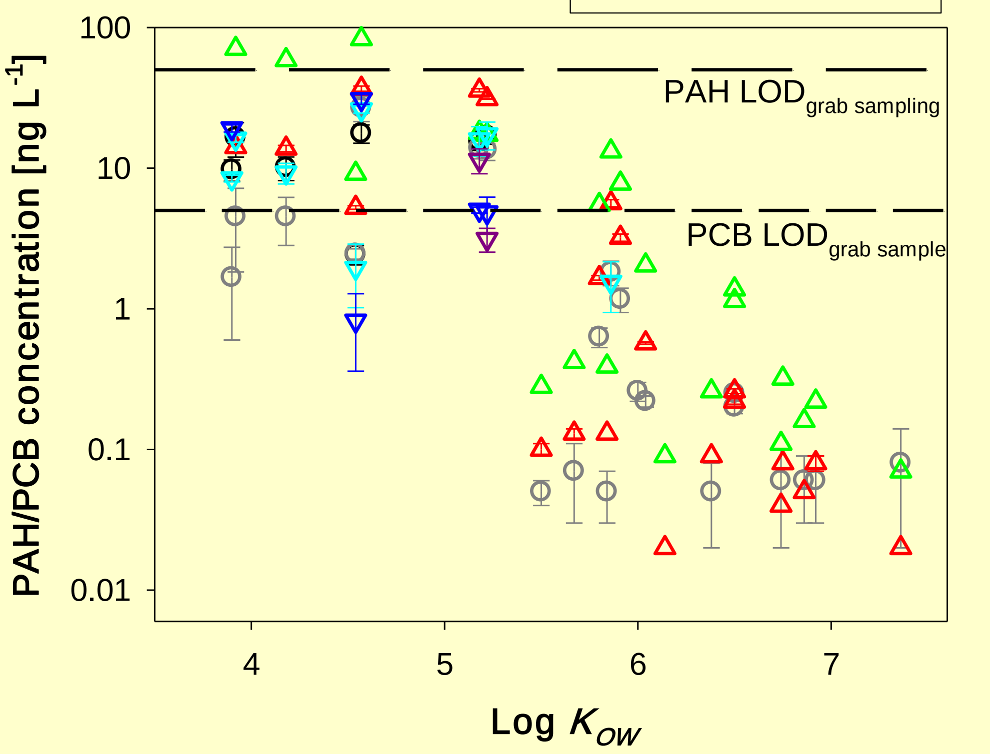
Meuse River

Spring 2004

Mean of 10 filtered spot samples collected in 3 day intervals vs. an estimate from triplicate sampler exposed for 14 and 28 days

TWA concentrations measured by 7 various samplers

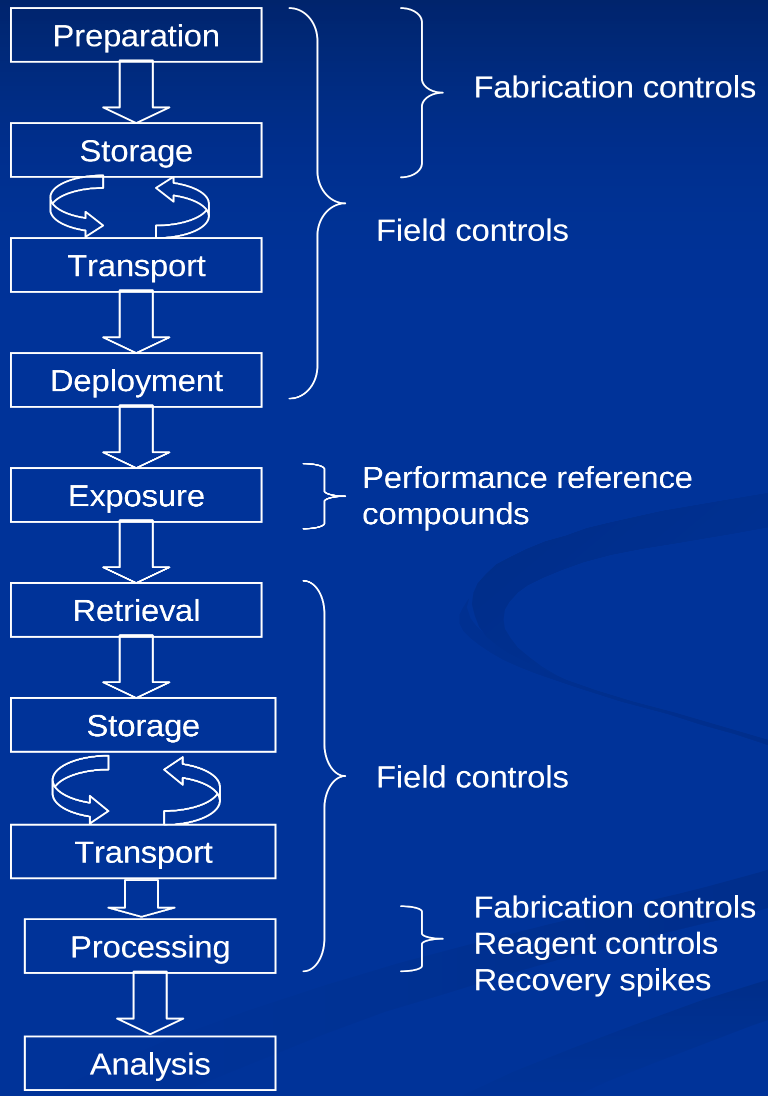
Meuse River (Eijsden, The Netherlands) 2005



Exposure: 7 days

I. Allan, K. Booij, A. Paschke, B. Vrana, G. A. Mills and R. Greenwood, Monitoring of hydrophobic substances in surface waters with a range of passive sampling devices, in preparation

Quality control



BSI PAS 61

Conclusions

Passive samplers show a great potential in:

- identification of emerging polluants (e.g. in combination with a bioassays directed chemical analysis)
- assessment of bioavailability
- assessment of bioaccumulation (biomimetic devices)
- *in situ* measurement of time-weighted average (TWA) concentrations over extended periods

Problems to be solved: a challenge for future research

- Further development of samplers for hydrophilic compounds (e.g. POCIS) – PRC concept not applicable
- Validation of the technology - lack of robust calibration data for many compounds, especially for emerging pollutants
- Most samplers measure the dissolved fraction of contaminants present in water, whereas present EQS for organic compounds in surface waters in Europe are based on “total” concentrations.
- development of passive sampling linked with toxicity bioassays for the design of improved monitoring programmes and toxicological assessments.

NORMAN
Joint Programme of Activities
for 2009

Harmonise work in the area of passive sampling, and bring together the disparate research groups to develop sound validation procedures for all aspects of the use of passive sampling devices, including

- handling
- laboratory calibration
- field deployment
- chemical and toxicological analysis
- data interpretation

NORMAN Actions for 2009 and beyond

- Science note in the **Scientific Watch Bulletin**
- Expert group meeting
- Interlaboratory exercises (2010 – 2011)

Expert group meeting

Passive sampling of emerging pollutants: state of the art and perspectives

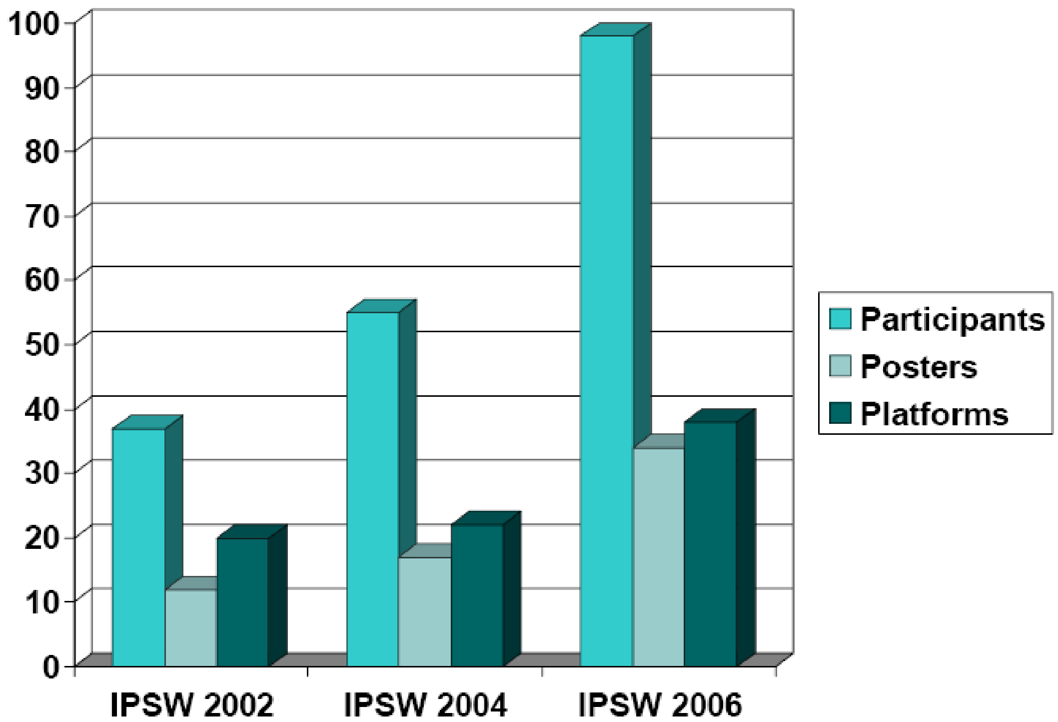
27th May 2009 in Prague, associated with a conference dedicated to passive sampling - IPSW

- Capabilities and limitations – for emerging pollutants
- Translation of lab. calibrations to field deployments
- Consensus approach to QA/QC, normation
- Utility of the technology within regulatory context
- Use in ecotoxicological assessment
- Agreement on interlaboratory exercises for 2010-2011

3rd International Passive Sampling Workshop and Symposium

May 28-29, 2008, Prague, Czech Republic

Development of IPSW



www.animaracio.com/ipsw2009

An overview of passive sampling techniques

R. Greenwood, G. A. Mills and B. Vrana

Comprehensive Analytical Chemistry, *Volume 48*

Passive Sampling Techniques in Environmental Monitoring

Elsevier, Amsterdam, *2007*

Thank you for your attention!